

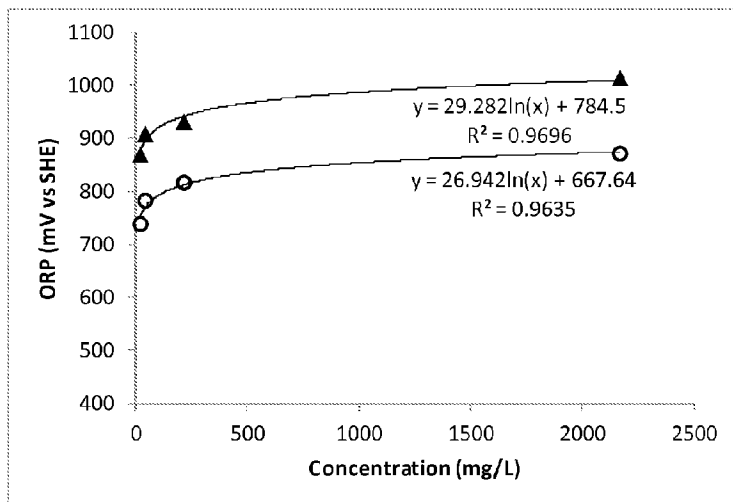


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(54) Title: SYSTEMS AND METHODS FOR GENERATION OF REACTIVE OXYGEN SPECIES AND APPLICATIONS THEREOF



(57) Abrégé/Abstract:

Reactive oxygen species formulations as well as methods for making and using such formulations. Reactive oxygen species formulations comprising one or more parent oxidants, such as peroxides, or peroxyacids, and one or more reactive oxygen species. (ROS). The formulations optionally contain in addition one or more reactive species other than ROS. The reactive oxygen species and other reactive species when present provide chemical reactivity, oxidative activity and/or antimicrobial activity not provided otherwise by the parent oxidant.

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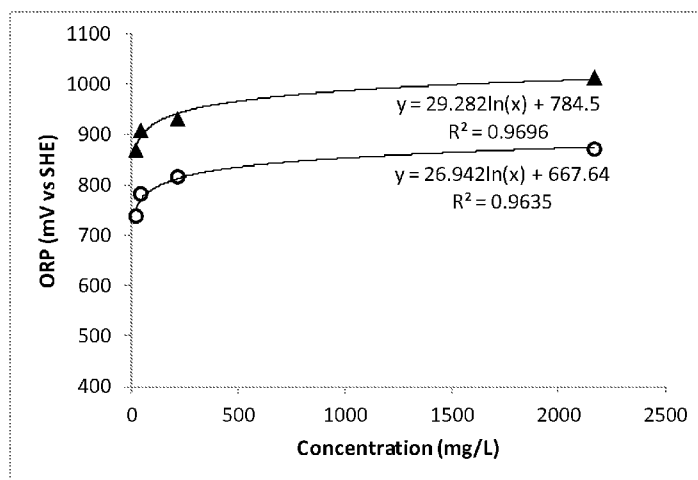
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(54) Title: SYSTEMS AND METHODS FOR GENERATION OF REACTIVE OXYGEN SPECIES AND APPLICATIONS
THEREOF**FIG. 22**

(57) **Abstract:** Reactive oxygen species formulations as well as methods for making and using such formulations. Reactive oxygen species formulations comprising one or more parent oxidants, such as peroxides, or peroxyacids, and one or more reactive oxygen species (ROS). The formulations optionally contain in addition one or more reactive species other than ROS. The reactive oxygen species and other reactive species when present provide chemical reactivity, oxidative activity and/or antimicrobial activity not provided otherwise by the parent oxidant.

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SYSTEMS AND METHODS FOR GENERATION OF REACTIVE OXYGEN SPECIES AND APPLICATIONS THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. provisional application 61/698,550 filed September 7, 2012.

BACKGROUND

[0002] It is well known that a combination of reactive oxidant species can be beneficial to water treatment, cleaning, decontamination and remediation applications as they will combat a variety of substrate types which may be present and react with a variety of oxidation byproducts during their breakdown.

[0003] Several common issues arise with the use of conventional reactive oxygen species formulations including, for example, limited shelf life, low mobility of oxidants and/or catalysts; highly acidic or alkaline oxidants which cause significant changes in the natural soil or groundwater pH; limited options for oxidant types available from a single product or system; and logistic, cost, regulatory (e.g., permitting requirements), or safety issues associated with bringing large quantities of strong oxidizers and hazardous chemicals on site. Additionally, the use of conventional iron—based hydrogen peroxide Fenton catalysts and sodium persulfate activators, such as iron (II) sulfate, require an acidic pH of less than 4 to be active, but as the pH increases toward neutral pH, the precipitation of iron oxides and oxyhydroxides occurs. Precipitated iron can cause pore plugging in soils, fouling and staining of equipment and can promote population blooms of iron bacteria which cause biofouling of soils, and accelerated microbial corrosion of steel well casings, pipes and equipment.

[0004] This invention relates to methods and systems for generating reactive oxidant species, as well as to formulations contain such reactive oxidant species and particularly to formulations containing mixtures of different reactive oxidant species. The formulation of the invention provide for improved activity and overcome problems associated with the use of such formulation.

[0005] The invention further provides methods of use of the inventive formulation, particularly in which the improved activity of the formulations is employed. The invention in particular provides methods water treatment.

[0006] Reactive Oxygen Species are discussed in the following.

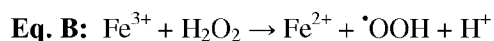
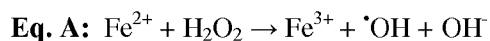
Hydroxyl Radicals

[0007] Of the common oxidants used in water treatment and remediation, the hydroxyl radical has the most positive standard oxidation potential of 2.80 V and is very effective at oxidizing a wide variety of substances. Hydroxyl radicals react very rapidly with a wide variety of oxidizable substrates. However, the hydroxyl radical lifetime is very short in aqueous media, merely several nanoseconds, and therefore must be produced within several tens of angstroms of a target substrate due to minimal diffusion path length. Hydroxyl radicals can further be quenched by undesirable reactions including reactions with radical quenchers, precursor oxidants and other hydroxyl radicals. For example, carbonate and bicarbonate ions present in natural waters are effective radical quenchers. Further, hydrogen peroxide and ozone can react with hydroxyl radicals; therefore when generating hydroxyl radicals from hydrogen peroxide and/or ozone precursors in water, the precursor is traditionally kept below 10 g/mL to avoid excessive consumption of hydroxyl radicals by the parent oxidant.

[0008] One issue with using hydroxyl radicals in water treatment is their ability to oxidize halide salts with much lower standard potentials and even to oxidize sulfate dianion to the persulfate radical anion. A single electron oxidation of halide by a hydroxyl radical will produce hypochlorous acid, hypobromous acid and their hypohalite forms depending on the pH. However, an excess of hydroxyl radicals in the presence of hypohalites will further oxidize the hypohalites in subsequent steps to chlorate, which is toxic, and bromate, which is carcinogenic.

Fenton Catalyst Activation

[0009] Fenton catalyst activation of hydrogen peroxide occurs when a reduced iron species, Fe^{2+} , is oxidized by hydrogen peroxide thereby producing hydroxyl radical ($\cdot\text{OH}$), and an oxidized iron species, Fe^{3+} . The catalytic cycle is completed when hydrogen peroxide reduces Fe^{3+} back to Fe^{2+} thereby producing hydroperoxyl radical ($\text{HOO}\cdot$), which is in equilibrium with superoxide. The Fenton process is summarized in Equations A and B:

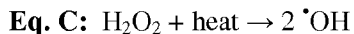


Similar Fenton-like chemistry occurs with other peroxides such as peroxyacetic acid. Iron sulfate is the most common Fenton catalyst and must be used at a pH near or below pH 4 to avoid excessive precipitation of Fe^{3+} oxides and oxyhydroxides. Other iron

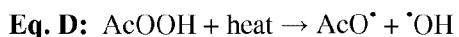
catalyst forms such as iron minerals (e.g., magnetite) and chelated iron compounds have stability at higher pH.

Ultrasound Activation

[0010] Ultrasound activation of hydrogen peroxide in aqueous solution occurs when ultrasound waves induce cavitation of water forming bubbles, which leads to very high localized heating as cavitation bubbles collapse resulting in the thermal dissociation of hydrogen peroxide to hydroxyl radicals as in Equation C.



Similar thermal dissociation of peracids occurs to generate two different radical species as in Equation D.



Ultraviolet Activation

[0011] Ultraviolet light activation of hydrogen peroxide occurs by the absorption of ultraviolet light, typically in the wavelength range of 180 to 220 nanometers, which leads to dissociation of hydrogen peroxide forming hydroxyl radicals as summarized in Equation E.

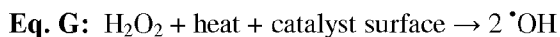


Similar ultraviolet activation and dissociation of peracids occurs to generate two different radical species as in Equation F.



Thermal Activation:

[0012] Thermal activation of hydrogen peroxide can be conducted, for example, by impinging a liquid, spray, mist, vapor, or steam containing hydrogen peroxide upon a hot surface coated with a catalyst (e.g., silver oxide, iron oxide, ruthenium oxide, glass, quartz, Mo glass, $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ spinels, Fe_2O_3 with Cu-ferrite, MgO and Al_2O_3 .) and heating to above 200 °C, to form hydroxyl radicals as in Equation G.



[0013] The initial peroxide activation step in Equation G is followed by a series of radical propagation steps in the gas phase where intermediate radical species form such as the hydroperoxyl radical.

Singlet oxygen

[0014] Singlet oxygen is molecular oxygen in an excited electronic state.

Singlet oxygen is most commonly produced in aqueous solutions by photolysis of dissolved oxygen directly by ultraviolet radiation or indirectly by energy transfer from a visible light photosensitizer dye to molecular oxygen. However, the use of photosensitizing dyes such as methylene blue, certain metalloporphyrins, semiconductors and other materials to generate singlet oxygen to degrade contaminants in water, disinfection and other uses are not practical for wastewater treatment due to degradation of dyes by singlet oxygen over time (i.e., photobleaching) and at elevated concentrations.

[0015] Another common method of singlet oxygen generation is by chemical reactions, where singlet oxygen is released as a byproduct, including, for example, the Haber-Weiss reaction (see eq. 4, below), the reaction between hydrogen peroxide and hypochlorite, the decomposition of 9,10-diphenylanthracene endoperoxide and the reaction between neutral and ionized forms of organic peroxyacids. However, these methods cause the rapid quenching of the singlet oxygen species by physical and chemical pathways. Chemical quenching reactions occur when singlet oxygen is consumed by a non-beneficial chemical reaction involving electron transfer. Physical quenching reactions occur by radiative or non-radiative relaxation of the excited state by physical contact with its surroundings without electron transfer. In these methods, excess hydrogen peroxide is a very effective quenching agent resulting in little or no oxidative activity from singlet oxygen generated in the presence of significant concentrations of hydrogen peroxide. When hydrogen peroxide is present in significant concentrations, as is the case for most commercially produced peroxyacetic acid, singlet oxygen is rapidly quenched by hydrogen peroxide, which reduces singlet oxygen concentration. Chlorine, azide, certain tertiary amines and beta-carotene are other known examples of singlet oxygen quenchers.

[0016] Peroxyacetic acid (i.e. AcOOH) is typically made by commercial producers by an equilibrium reaction between concentrated acetic acid (i.e. AcOH). The equilibrium reaction can be catalyzed by a mineral acid such as sulfuric acid at a pH <1 and occurs over a time period of several hours to several days depending on the concentration of hydrogen peroxide, acetic acid and acid catalyst. There is typically a significant concentration of residual hydrogen peroxide and acetic acid in peroxyacetic acid made by the equilibrium reaction. For example, the [peroxyacetic acid]/[H₂O]/[acetic acid]/[H₂O₂] concentration ratios are often between 1.8 and 2.5 for commercial grades

having between 5 and 30 wt% peroxyacetic acid. Peroxyacetic acid solutions are generally unstable at room temperature and pose a significant fire hazard. Therefore peroxyacetic acid is typically produced on site by the equilibrium process or shipped in vented containers from a producer. Peroxyacetic acid may be distilled under reduced pressure to obtain a pure form with low hydrogen peroxide residual, however, distillation is generally not practical and can create a severe explosion hazard.

Superoxide

[0017] Superoxide is the radical anion form of molecular oxygen ($\cdot\text{O}_2^-$) and is a mild reducing agent with a standard oxidation potential commonly reported as -0.33 V in aqueous environments. Superoxide can be produced in bulk as the anhydrous potassium salt, KO_2 , which rapidly reacts with water or carbon dioxide releasing molecular oxygen and potassium hydroxide or potassium carbonate, respectively. Superoxide can also be produced in situ by ultraviolet irradiation of oxygen containing solutions, including seawater, by enzymatic processes and by electrochemical reduction of oxygen. For large scale applications, superoxide is typically supplied as a bulk chemical or generated in situ from activated hydrogen peroxide reactions. Potassium superoxide is a water-sensitive hazardous material and combustion aid, which may be prohibitive barriers to its use in some locations. Also, potassium superoxide must be fed into a treatment process as a solid feed, which can be problematic due to water absorption, caking and clogging of solid feeders.

SUMMARY OF THE INVENTION

[0018] The invention provides reactive oxygen species formulations as well as methods for making and using such formulations.

[0019] The invention provides reactive oxygen formulations comprising one or more parent oxidants, such as peroxides, or peroxyacids, and one or more reactive oxygen species (ROS). The formulations can optionally contain in addition one or more reactive species other than ROS. In these formulations, the reactive oxygen species and other reactive species, if present, provide chemical reactivity, oxidative activity and/or antimicrobial activity not provided otherwise by the parent oxidant. The invention provides methods for making such formulation and applications of such formulations. In specific embodiments, ROS and other reactive species are generated in situ in the formulation by an activation event, such as a change in pH to an activation pH, a change

in temperature (e.g., heating), irradiation with electromagnetic radiation (e.g., UV or microwave, for example) or by the addition of one or more precursors or a combination of precursors. In an embodiment, peracid containing precursors are activated by adjusting the pH of the formulation to be within an activation pH range. In an embodiment. In an embodiment, additional ROS or other reactive species are generated in a formulation after a selected time delay.

[0020] Additional ROS or other reactive species can be generated in formulations by a variety of methods including, but not limited to, creation in-situ by secondary reactions of the singlet oxygen precursor(s); creation in-situ by catalyst-activated reactions; creation in-situ by ultraviolet light-activated reactions; and/or by addition of reactive oxygen species. Combination of different ROS in a formulation can function additively, synergistically or react in a manner to provide entirely different ROS imparting new characteristics to solutions. Formulations of the invention can be subjected to two or more activation events to generate one or more ROS and optionally to generated reactive species other than ROS.

[0021] In an embodiment, reactive oxygen species formulations are active for up to several hours, during which time the reactive species therein are consumed and degrade to oxygen, water, and simple, non-toxic and biodegradable organic acids and alcohols. In an embodiment, reactive oxygen species formulations optionally contain additives that can enhance a treatment, decontamination, cleaning or separation process.

[0022] In an embodiment, reactive oxygen species formulations include at least one peroxygen species (e.g., peroxy acid, and/or hydrogen peroxide) which may be present at least in part in ionic form, in various combinations with one or more of singlet oxygen, superoxide, or peroxy radicals. In an embodiment, certain formulations are formulated to create additional reactive oxygen species by reaction between singlet oxygen and superoxide and other radical species produced as decomposition byproducts of at least one peroxy acid in combination with singlet oxygen and/or superoxide.

[0023] The presence of ROS or other reactive species in the formulations herein may in some cases be directly detected and it may be possible to determine the concentrations of certain reactive species, e.g., using spectroscopic methods. However, in formulations herein the presence of reactive species may only be indirectly demonstrated by measurement of changing properties of the formulation, e.g., oxidative-reductive potential (ORP) measurements or pH change, by changes in concentration of precursors (e.g., rate of peroxyacetic acid concentration decline) or by changes in

reactivity of the formulation, e. g., the rate of oxidation of dyes (bleaching) rate or the rate or occurrence of oxidation of certain species, e.g., polysaccharide breakdown.

[0024] In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 550 mV vs SHE or higher. In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 600 mV vs SHE or higher. In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 650 mV vs SHE or higher and are improved for use as antimicrobials. In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 700 mV vs SHE or higher. In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 800 mV vs SHE or higher. In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 900 mV vs SHE or higher. In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 650 mV vs SHE or higher which is retained for 4 hours or longer (as measured in ORP measurements described herein) which are improved for use as antimicrobials. In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 700 mV vs SHE or higher which is retained for 4 hours or longer (as measured in ORP measurements described herein). In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 650 mV vs SHE or higher which is retained for 10 hours or longer and are improved for use as antimicrobials. In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 700 mV vs SHE or higher which is retained for 10 hours or longer. In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 650 mV vs SHE or higher which is retained for 20 hours or longer. In specific embodiments, reactive oxygen species formulations of this invention include those having pH of 6-8, and ORP of 650 mV vs SHE or higher which is retained for 10 hours or longer. In specific embodiments, reactive oxygen species formulations of this invention include those having pH 6-8 and ORP of 650 mV vs SHE or higher which is retained for 20 hours or longer. In specific embodiments, reactive oxygen species formulations of this invention include those having ORP of 700 mV vs SHE or higher which is retained for 20 hours or longer. In specific embodiments, reactive oxygen species formulations of this invention include those having pH of 6-8, and ORP of 700 mV vs SHE or higher which is retained for 10 hours or longer. In

specific embodiments, reactive oxygen species formulations of this invention include those having pH 6-8 and ORP of 700 mV vs SHE or higher which is retained for 20 hours or longer.

[0025] In specific embodiments, the formulations are prepared and used as liquid formulations. In related embodiments, the formulations are in the form of an ice, foam, emulsion, microemulsion or an aerosol as desired for a selected oxidation application and for a selected method of dispensing or applying the formulation. The formulations are typically prepared in aqueous solution and may contain one or more co-solvents. The formulations optionally comprise one or more additives or stabilizers as defined herein below. The formulations can have a selected pH (or range of pH), selected relative concentrations or molar or weight ratios of components (or range of such ratios), and/or selected ionic strength. Formulations are described herein as generated to form ROS and optional other reactive species, but it will be appreciated that the formulations contain reactive species, some of which may be very reactive and short-lived, thus the concentrations of formulation components and other formulation characteristics (e.g., pH) will change after the formulation is generated or activated. It will also be appreciated, particularly in view of examples herein, that initially generated reactive species in a formulation may react to generate secondary reactive species, such that the components and concentrations thereof in the compositions and other characteristics of the formulations will change with time as well as with conditions such as temperature. In an embodiment, the ROS and other reactive species are generated in the formulations by one or more activation events (activations). Multiple activation events may be separated in time. Activation events include any physical or chemical change that generates the desired reactive species and can include, for example, the mixing of one or more precursors, the adjustment of pH to an activation pH, adjustment of relative concentrations of one or more precursors, addition or presence of a catalyst or other activating material, electromagnetic irradiation (e.g., UV radiation with e.g., exposure for a selected time), a change in temperature, ultrasonic treatment or the like. Secondary reactive species may simply be generated with the passage of sufficient time to allow for the reaction of primary reactive species to generate the secondary reactive species. In certain embodiments, ROS or ROS precursors are generated electrochemically.

[0026] In an embodiment, the reactive oxygen formulations comprise the ROS, singlet oxygen. In another embodiment, the reactive oxygen formulations

comprise the ROS, superoxide. In another embodiment the reactive oxygen formulations comprise a combination of superoxide and singlet oxygen. In other embodiments, formulations herein can comprise one or more of singlet oxygen, superoxide, hydroxyl radical, hydroperoxy radical, or hydrogen trioxide. In additional embodiments, formulation herein can comprise one or more ROS in combination with other reactive species which can include, for example, one or more organic radicals, such as organoperoxy radicals, acyl radicals, hydrocarbon radicals (e.g., methyl or other alkyl radicals), or carboxyl radicals. In additional embodiments, formulation herein can comprise one or more ROS in combination with other reactive species, such as radicals or trioxorganoacids, such as trioxyacetic acid.

[0027] In an embodiment, reactive oxygen formulations comprise a parent oxidant that is peroxyacid, such as peroxyacetic acid, or a mixture thereof with hydrogen peroxide and the ROS, singlet oxygen. In an embodiment, singlet oxygen is generated by reaction of parent oxygen species, particular when the pH of the precursor formulation is within the activation pH range. In a preferred embodiment, minimal or no hydrogen peroxide is present in the formulation to avoid quenching of singlet oxygen. In another, embodiment, a selected amount of hydrogen peroxide is present in the formulation to control activity of singlet oxygen. A preferred method of generating peroxyacetic acids with minimal hydrogen peroxide is by a non-equilibrium chemical reaction between an acetyl donor molecule and alkaline hydrogen peroxide, as described herein. Formulations containing peroxyacid in combination with singlet oxygen is found to be more active than peroxy acid. Such formulations can function as biocides and are capable of oxidizing unsaturated hydrocarbons, certain aromatic hydrocarbons, dyes and can breakdown polysaccharides, such as guar gum. These formulations are also reactive with polyamines, nitrile rubber, and EDTA, but are compatible with salinity, scaling minerals, saturated hydrocarbons, phosphonic acids, several polymers, stainless steel and aluminum.

[0028] In an embodiment, the invention provides a method for generating a reactive oxygen species formulation comprising (1) generating an alkaline hydrogen peroxide solution from the combination of an alkali and a hydrogen peroxide concentrate; (2) mixing the alkaline hydrogen peroxide solution with an acyl or acetyl donor such that a peracid concentrate is produced, wherein the peracid concentrate has minimal hydrogen peroxide residual; and (3) adjusting the peracid pH level to the activated pH range for generating the reactive oxygen species. The reactive oxygen

species formulation can be a singlet oxygen precursor formulation. In an embodiment, the hydrogen peroxide solution is generated using a molar ratio of H_2O_2 to alkali in the range of 1:1.2 to 1:2.5. The molar ratio of H_2O_2 to alkali can be 1:1.2 to 1:1.4, 1.4 to 1:2.0 or 1:2.0 to 1:2.5. In an embodiment, the peracid concentrate is produced by mixing the alkaline hydrogen peroxide solution with the acyl or acetyl donor such that the molar ratio of hydrogen peroxide to acyl or acetyl donor ranges from 1:1.25 to 1:4. The molar ratio of hydrogen peroxide to acyl or acetyl donor can be 1:1.25 to 1:1.5, 1:1.5 to 1:2, or 1:2 to 1:4. In an embodiment, the activated pH range is in the range of pH 6.5 to 12.5. The activated pH range can be 6.5 to 9.5 or 9.5 to 12.5. In an embodiment, the method further comprises entraining byproducts of the reaction between the alkaline hydrogen peroxide solution and the acyl or acetyl donor. In an embodiment, the method further comprises diluting the peracid concentrate. In an embodiment, the method further comprises mixing the peracid solution with an additives concentrate. In an embodiment, the method comprises storing the alkaline hydrogen peroxide in a holding tank for immediate or future use. In an embodiment, mixing the alkaline hydrogen peroxide solution with an acyl or acetyl donor produces a concentrated peracid solution.

[0029] In an embodiment, the invention provides a method for generating a reactive oxygen species formulation wherein an alkaline hydrogen peroxide concentrate is electrochemically generating, the electrochemically generated alkaline hydrogen peroxide concentrate is combined with an acyl or acetyl donor to produce a peracid concentrate, wherein the peracid concentrate has minimal hydrogen peroxide residual and the peracid solution is combined with an acid concentrate to produce the reactive oxygen species formulation having a pH level in the activated pH range. In an embodiment, the electrochemically generated alkaline hydrogen peroxide concentrate has a pH in the range of 12.0 to 13.0, and a percent weight of hydrogen peroxide in the range of 0.1 to 3 wt%. In an embodiment, the acid concentrate is co-generated during electrochemically generating the alkaline hydrogen peroxide concentrate. The co-generated acid concentrate can have 0.1 wt% to 20 wt% acid. In an embodiment, the peracid concentrate is produced by mixing the electrochemically generated alkaline hydrogen peroxide solution with the acyl or acetyl donor such that the molar ratio of hydrogen peroxide to acyl or acetyl donor is in the range of 1:1.25 to 1:4. The molar ratio of hydrogen peroxide to acyl or acetyl donor can be 1:1.25 to 1:1.5, 1:1.5 to 1:2, or 1:2 to 1:4. In an embodiment, the activated pH range is in the range of pH 6.5 to 12.5. The activated pH range can be 6.5 to 9.5 or 9.5 to 12.5. In an embodiment, the method further

comprises entraining byproducts of the reaction between the alkaline hydrogen peroxide solution and the acyl or acetyl donor. In an embodiment, the method further comprises diluting the peracid concentrate. In an embodiment, the method further comprises mixing the peracid solution with an additives concentrate. In an embodiment, the method comprises storing the alkaline hydrogen peroxide in a holding tank for immediate or future use. In an embodiment, mixing the alkaline hydrogen peroxide solution with an acyl or acetyl donor produces a concentrated peracid solution.

[0030] In an embodiment, the invention provides a method for generating a superoxide reactive oxygen species formulation comprising electrochemically co-generating a solution containing hydrogen peroxide and superoxide. In an embodiment, the formulation containing co-generated hydrogen peroxide and superoxide has a pH of 8-13. In an embodiment, the molar ratio of superoxide to hydrogen peroxide co-generated ranges from 0.01:1 to 10:1. In an embodiment, the pH of the superoxide solution is adjusted by addition of an acid concentrate. In an embodiment, the acid concentrate is co-generated during the step of electrochemically generating the superoxide solution. In an embodiment, the superoxide solution is combined with an additives concentrate. In an embodiment, the superoxide solution is diluted. More specifically, the superoxide solution is diluted to a near point of use concentration. In an embodiment, co-generation of hydrogen peroxide and superoxide produces at least one radical species which can among others be a hydroperoxyl radical and/or a hydroxyl radical.

[0031] In related embodiments, the methods for generating reactive oxygen formulations further comprise further activating the reactive oxygen species using activation chosen from the group a Fenton or Fenton-like catalyst, ultrasound, ultraviolet radiation and thermal activation. More specifically activation produces radical species, which can be the hydroxyl radical.

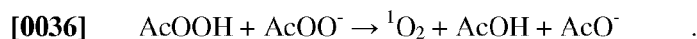
[0032] In an embodiment, a reactive oxygen formulation produced by the methods herein is distributed to its point of use. The form in which the reactive oxygen formulation is distributed can as a liquid, an ice, a foam, an emulsion, a microemulsion or an aerosol. The invention also provides reactive oxygen formulations for point of use applications which are appropriately formulated for application by injection, flooding, spraying, and/or circulation.

[0033] In specific embodiments, in the methods herein the reactive oxygen species is singlet oxygen. The invention also provides formulations containing reactive

oxygen species, particularly those prepared by the methods of the invention. In specific embodiments, the reactive oxygen species formulations are singlet oxygen formulations. Such formulations can be concentrated or can be diluted. Diluted formulation can be prepared by addition of water.

[0034] In specific embodiments, the invention provides a reactive oxygen species precursor comprising a peracid concentrate comprising a mixture of alkaline hydrogen peroxide and an acyl or acetyl donor. The reactive oxygen species precursor can be a diluted singlet oxygen precursor. More specifically, the diluted singlet oxygen precursor has a pH in the range 6.5 to 12.5, in the range 6.5 to 9.5 or in the range 9.5 to 12.5. The reactive oxygen species precursor can be a concentrated singlet oxygen precursor. More specifically, the concentrated singlet oxygen precursor has a pH in the range 6.5 to 12.5, in the range 6.5 to 9.5 or in the range 9.5 to 12.5.

[0035] In an embodiment, the invention provides a peracid formulation capable of generating singlet oxygen, particularly where the singlet oxygen is generated by the reaction of alkaline hydrogen peroxide and an acyl or acetyl donor. The invention also provides a method for making such peracid formulations. Preferably the peracid formulation has minimal hydrogen peroxide residual to minimize quenching of the singlet oxygen. In an embodiment, the peracid formulation has a pH in the activated pH range. In a specific embodiment, in the peracid formulation, the ratio of alkaline hydrogen peroxide to acyl or acetyl donor reactive groups is in the range 1:1.25 to 1:2 to 1:4. More specifically, the ratio of alkaline hydrogen peroxide to acyl or acetyl donor reactive groups is 1:1.25 to 1:1.5, 1:1.5 to 1:2, or 1:2 to 1:4. The peracid formulation can have pH in the range 6.5 to 12.5, 6.5 to 9.5 or 9.5 to 12.5. In a specific embodiment, the peracid formulation is further reacted with an acid concentration resulting in both peracetic acid and peracetic acid anion, wherein the reaction of the peracid formulation and acid concentrate comprises the reaction:

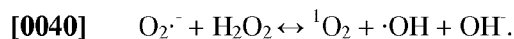


[0037] Peracid formulation of the invention can be distributed in any suitable form and can be distributed in the form of a liquid, an ice, a foam, an emulsion, a microemulsion or an aerosol. The peracid formulations of the invention can be applied to a point of use by an application chosen from injection, flooding, spraying, and circulation. The peracid formulations of the invention can be used for clean-in-place applications in food, dairy, beverage and biopharma; hard surface cleaning; decontamination; remediation of soil and groundwater; cleaning of membrane filtration

systems; flushing of well casings and water distribution pipes; and in-situ chemical oxidation, among others.

[0038] In an embodiment, the invention provides an electrochemically generated, reactive oxygen species solution comprising superoxide formulation co-generated with a hydrogen peroxide solution. More specifically, the superoxide/hydrogen peroxide solutions are generated such that the ratio of superoxide to hydrogen peroxide is 0.01:1 to 10:1. More specifically, the superoxide to hydrogen peroxide solutions are generated such that the ratio of superoxide to hydrogen peroxide ranges from 0.01:1 to 0.5:1, from 0.5:1 to 1.5:1, from 1.5:1 to 3:1, from 3:1 to 5:1, or from 5:1 to 10:1. In an embodiment, the electrochemically generated, reactive oxygen species solution has initial pH of 8-13, or 8-9, or 9-12, or 12-13.

[0039] In an embodiment, the invention provides a formulation containing an electrochemically generated hydroperoxyl radical. In an embodiment, the radical is created by the reaction of electrochemically generated superoxide formulation co-generated with hydrogen peroxide formulation by the reaction:



[0041] The invention provides methods of oxidation which employ reactive oxygen species formulations as described herein. The oxidation method includes application of one or more selected reactive oxygen species formulations to an environment, a substrate in an environment or to a substrate that is to be subjected to oxidization. The term substrate is used herein broadly to refer to a place, a material, a chemical and/or a biological species that is to be subject to at least partial oxidation. In an embodiment, the place or substrate are containers, tanks, pools, equipment or pipes that are subjected to oxidative cleaning. In an embodiment, the environment is water and the substrate is one or more organic or inorganic chemical species that are to be oxidized and/or the substrate is microorganism that are to be killed. In an embodiment, the environment or substrate is a soil sample or a contaminated soil environment from which contaminants are to be removed at least in part by oxidation. In an embodiment, the environment or substrate is water containing undesirable chemical or biological species that are to be at least in part removed by oxidative treatment. In an embodiment, water to be treated is waste water, greywater, raw water, ground water, or a tailing pond. In an embodiment, the substrate is paper, pulp or textiles and the formulations function for bleaching of the substrate. In an embodiment, the environment or substrate is

contaminated with higher than desirable levels of microorganisms wherein the environment or substrate is to be disinfected.

[0042] In an embodiment, the invention provides a method for treating water

[0043] In an embodiment, the invention provides a method for treating waste water employing formulations of the invention containing reactive oxygen species. In a specific embodiment, the method includes electrochemically co-generating a cathode output solution comprising superoxide and hydrogen peroxide; mixing the cathode output solution into a waste water source; and adjusting the pH of the mixture. In an embodiment, pH is adjusted after the step of mixing the cathode output solution into the waste water source.

[0044] In applications of the reactive oxygen species formulations of this invention, the formulation is brought into contact with the environment and/or substrate to be oxidized or treated. The environment and/or substrate can be contacted with an activated liquid formulation containing reactive oxygen species. Alternatively, the environment and/or substrate can be contacted with a liquid precursor formulation that will generate reactive oxygen species on activation and the formulation is activated as or after it comes into contact with the environment or substrate. For example, the environment or substrate may itself provide for activation, such as a pH adjustment to the activation pH. One or more additional steps of activation to form additional reactive species can occur after the formulation or precursor formulation contact the environment and/or substrate. For example, steps of pH adjustment may occur after contact. Contact with the environment or substrate may be controlled addition of a selected volume or concentration of formulation or its precursor to the environment or in contact with the substrate. Alternatively, contact can occur by addition of the substrate to the formulation or a precursor thereof.

[0045] Other embodiments of the invention will be become apparent on review of the following drawings and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0046] FIG. 1 shows one exemplary system 100 for generation of a diluted reactive oxygen species 116 where in one embodiment bulk chemical feedstock constituents are used.

[0047] FIG. 2 shows an exemplary method 200 for generating reactive oxygen species output 116 using system 100 of FIG. 1.

[0048] FIG. 3 shows one exemplary system 300 for generation of a concentrated reactive oxygen species output 314 using bulk chemical precursor constituents, in one embodiment.

[0049] FIG. 4 shows an exemplary method 400 for generating reactive oxygen species output 314 using system 300 of FIG. 3.

[0050] FIG. 5 shows an exemplary system 500 for generating chemicals using an electrochemical reactor 514 to produce a diluted reactive oxygen species output.

[0051] FIGs. 6A/6B depict a cross-sectional view of the general configuration and components of an exemplary electrochemical reactor 600 for use in system 500 of FIG. 5. More details of this and similar configurations and electrochemical reactors are found in published International application W02012166997.

[0052] FIG. 7 depicts an embodiment of a reactor system 700 that has a reactor system fluid process flow, also known as a flow pathway, that enables gas recirculation within reactor system 700.

[0053] FIG. 8 shows an exemplary method 800 for generating a diluted reactive oxygen species output 522 using system 500 of FIG. 5.

[0054] FIG. 9 shows an exemplary system 900 for generating chemicals using an electrochemical reactor 914 and mixing the reactor's 914 outputs together and optionally with other materials to produce a concentrated reactive oxygen species output 922.

[0055] FIG. 10 shows an exemplary method 1000 for generating a concentrated reactive oxygen species output 922 using system 900 of FIG. 9.

[0056] FIG. 11 shows an exemplary system 1100 for generating chemicals using an electrochemical reactor 1114 to produce a superoxide reactive oxygen species output.

[0057] FIG. 12 shows an exemplary method 1200 for generating a concentrated superoxide reactive oxygen species output 1122 using system 1100 of FIG. 11, in one embodiment.

[0058] FIG. 13 shows exemplary results of the percent color removal of 50 mg/L MB (Methylene blue) solutions observed over time starting with different initial peroxyacetic acid concentrations.

[0059] FIG. 14A shows graph 1400 that shows the full spectra of samples diluted to 100 +/- 4 mg/L hydrogen peroxide and adjusted to pH 12.00 +/- 0.04.

[0060] FIG. 14B shows the spectra of FIG. 14A with hydrogen peroxide absorbance subtracted off.

[0061] FIGs. 15A/B show graphs 1500, 1550 that show the evolution of the UV absorbance spectrum over five hours for the co-generated hydrogen peroxide and superoxide output produced at 8 amps in Example 11 diluted to 100 +/- 4 mg/L hydrogen peroxide, adjusted to pH 12.00 +/- 0.04 and analyzed over time.

[0062] FIGs. 16A/B show graphs 1600, 1650 that shows the evolution of the UV absorbance spectrum over five hours for the co-generated hydrogen peroxide and superoxide output produced at 8 amps in Example 11 diluted to 100 +/- 8 mg/L hydrogen peroxide, adjusted to pH 11.04 +/- 0.04 and analyzed over time.

[0063] FIG. 17 shows an exemplary system and flow process for electrochemically generating a CIP cleanser, in one embodiment.

[0064] FIG. 18 shows one exemplary system used in Example 17 to show an exemplar of producing a superoxide precursor formulation using an electrochemical generator used in a water treatment application, in one embodiment.

[0065] FIG. 19 is a graph illustrating oxidative-reductive potential (ORP, mV vs SHE, see Example 18) as a function of PH for several formulations of Example 18. Solid Squares = 28.5 mM PAA + approximately 129 mM Superoxide; Open Squares = 28.5 mM PAA

[0066] Solid Circles = 28.5 mM PAA + 29.4 mM HP; Open Diamonds = 29.4 mM HP + approximately 133 mM Superoxide.

[0067] FIG. 20 is a graph illustrating the effect on oxidative-reductive potential (ORP, mV vs SHE, see Example 18) for a S-PM solution (containing PAA and superoxide) diluted in distilled water (solid squares) or tap water (solid diamonds).

[0068] FIG. 21 is a graph illustrating the change over time of oxidative-reductive potential (ORP, mV vs SHE, see Example 18) for solution 3 at pH 7 (solid triangles) or 9 (open circles).

[0069] FIG. 22 is a graph illustrating the effect on oxidative-reductive potential (ORP, mV vs SHE, see Example 18) for solution 3 of Example 18.

[0070] FIGs. 23A and B are graphs illustrating the change in oxidative-reductive potential (ORP, mV vs SHE, see Example 18) as a function of time in various PAA + superoxide containing formulations as a function of the molar ratio of PAA to superoxide. FIG. 23A extends over the period of 500 minutes. FIG. 23B extends over the period of over 40 hours.

[0071] FIGs. 24A and B are graphs illustrating the rate of methylene blue oxidation by certain reactive oxygen species formulations of this invention. FIG. 24A compares the rate of methylene blue oxidation for a PM formulation (solid circles) to a S-PM formulation (solid squares) and FIG. 24B compares the rate of methylene blue oxidation for the S-PM formulation (solid squares) to an analogous S-PM-B formulation (solid triangles).

[0072] FIG. 25 is a flow chart illustrating an exemplary water treatment process (2500) employing reactive oxygen species formulation of this invention in one or more process steps.

DETAILED DESCRIPTION

Reactive Oxygen Species From Bulk Chemicals:

[0073] In the following embodiments, systems and methods are shown to generate reactive oxygen species. More specifically, reactive oxygen species can be formed in situ from a mixture of bulk chemical feedstocks in close proximity to various substrates that are to be treated. The term substrate is used very broadly herein for materials, compounds, atoms or ions (organic or inorganic) to be oxidized or microorganisms to be denatured or killed.

[0074] In the following embodiments, exemplary systems and methods are shown, for example, that describe alternatives to the use of hydroxyl radical oxidation chemistry that are more compatible with saline or highly contaminated waters and that minimize chlorate and bromate formation by having lower standard oxidation potentials than chloride, bromide or their hypohalite forms while possessing high chemical reactivity toward a variety of substrates.

[0075] In another embodiment, an exemplary system and method is shown for enabling the production of larger quantities and higher concentrations of singlet oxygen from chemical precursor formulations not containing singlet oxygen quenching agents.

[0076] In yet another embodiment, an exemplary method and system is shown for singlet oxygen production to occur for extended periods of time while the amount and rate of singlet oxygen evolved can be controlled by the more readily measurable precursor formulation and concentration.

[0077] FIG. 1 shows one exemplary system 100 for generation of a diluted reactive oxygen species 116 using bulk chemical feedstock constituents, in an embodiment. In an embodiment, diluted reactive oxygen species output 116 is used in

applications where a fluid is conveyed to a surface or material including clean in place, hard surface cleaning, decontamination, remediation and in situ chemical oxidation applications. System 100 includes hydrogen peroxide (H_2O_2) concentrate 102, alkali concentrate 104, acetyl donor 106, makeup water 108, additives concentrate 110, acid concentrate 112, peracid holding tank 114, reactive oxygen species output 116, pumps 118, and mixing chambers 120. In one embodiment, reactive oxygen species output 116 is diluted singlet oxygen precursor solution. The system of FIG. 1 is illustrated for use of an acetyl donor, as discussed herein more generally acyl donors (both oxygen-acyl and nitrogen-acyl donors) can be employed in preparation of formulations herein. Choice of acyl donor or mixture of donors employed determines the peracid or mixture of peracids in a given formulation.

[0078] Hydrogen Peroxide Concentrate 102 is typically an aqueous hydrogen peroxide solution, for example. However, in alternative embodiments, hydrogen peroxide concentrate 102 may include other chemical forms of peroxide chosen from the group including: calcium peroxide, potassium peroxide, sodium peroxide, lithium peroxide, percarbonates, and perborates.

[0079] In one embodiment, alkali concentrate 104 is an aqueous sodium hydroxide solution. In an alternative embodiment, Alkali concentrate 104 is potassium hydroxide. Acyl or acetyl donor 106 or mixture of donors may be in liquid or solid form, or dissolved in a solvent when reacted with a solution of hydrogen peroxide.

[0080] Acid concentrate 112, for example, includes at least one pH buffer chosen from the group including: weak acid electrolytes including acetate, citrate, propionate, phosphate and sulfate.

[0081] In an embodiment, reactive oxygen species output 116 is a peroxyacetic acid in the absence of hydrogen peroxide and includes at least one chemical precursor species capable of releasing singlet oxygen. In alternative embodiments, reactive oxygen species output 116 includes two chemical precursor species may be used to release singlet oxygen. In yet another embodiment, reactive oxygen species output 116 includes more than two chemical precursor species to release singlet oxygen.

[0082] FIG. 2 shows an exemplary method 200 for generating reactive oxygen species output 116 using system 100 of FIG. 1. FIG. 2 is illustrated for use of an acetyl donor, but as discussed more generically an acyl donor can be employed. In an embodiment, the reactive oxygen species output 116 generated by method 200 is singlet oxygen. In step 202, an alkaline hydrogen peroxide anion solution 122 is created by

mixing H₂O₂ concentrate 102 with alkali concentrate 104 in mixing tank 120(1). For example, molar ratios of H₂O₂ concentrate 102 to alkali in alkali concentrate 104 may range from 1:1.2 to 1:2.5. In an embodiment, the preferred molar ratio range is 1:1.4 to 1:2, for example. The preferred molar ratio range is determined by the preferred pH range of the alkaline hydrogen peroxide solution of pH 12.0 to 12.6, which promotes the reaction between hydrogen peroxide and the acetyl or acyl donor. In one embodiment, hydrogen peroxide concentrate 102 is a weak acid with a pKa of 11.6 and therefore its combination with alkali converts it in an acid-base equilibrium to the hydrogen peroxide anion form as in Equation 1 below:



In some embodiments, raising the pH of a hydrogen peroxide solution enough to put a significant proportion of hydrogen peroxide into the anion form requires an excess of alkali 104 over hydrogen peroxide 102. In one embodiment, the molar excess of alkali 104 over H₂O₂ 102 may range from 20% to 100% greater alkali 104. For example, a preferred molar excess range is 20% to 40% greater alkali 104. The equilibrium reaction in Equation 1 consumes alkali in a 1:1 molar ratio, therefore an excess of alkali over hydrogen peroxide is required to raise the pH of the alkaline hydrogen peroxide solution to the preferred pH range.

[0083] In step 204, the resulting alkaline hydrogen peroxide 122 is combined with an acyl or acetyl donor 106 in mixing tank 120(2) to create a resulting alkaline peracid concentrate 122'. In one embodiment, alkaline peracid concentrate 122' may be a peroxyacetic acid solution. In one embodiment, the acyl or acetyl donor is added in proportion to the hydrogen peroxide. In an alternative embodiment, the molar ratio of H₂O₂ 122 to acyl or acetyl donor 106 reactive group equivalents can range from 1:1.25 to 1:4. For example, a preferred molar ratio range is 1:1.5 to 1:2. If the ratio is too low a high hydrogen peroxide residual will remain in the peracid concentrate where it will significantly quench singlet oxygen. If the ratio is higher than needed to achieve a low hydrogen peroxide residual that does not significantly quench singlet oxygen then excess acyl or acetyl donor remains unused. In one embodiment, the acyl or acetyl donor is an oxygen-acyl or oxygen-acetyl donor shown in Equation 2a below:



Where Ac is acyl [-C(O)R'] or acetyl [-C(O)CH₃] and R and R' are hydrocarbon-based substituents and more specifically are alkyl or aryl groups. In an alternative

embodiment, the acyl or acetyl donor is a nitrogen-acyl or nitrogen-acetyl donor as shown in Equation 2b below:



Where Ac is acyl [-C(O)R'] or acetyl [-C(O)CH₃] and R and R' are hydrocarbon-based substituents and more specifically are alkyl or aryl groups.

[0084] In Equations 2a/2b above, the reaction between an acyl or acetyl donor 106 and hydrogen peroxide 122 occurs at alkaline pH by nucleophilic attack of the acyl carbonyl carbon atom by the hydrogen peroxide anion, which displaces the donor molecule fragment as an alcohol or amine in a manner analogous to saponification. In some embodiments, the non-equilibrium reactions generalized in Equations 2a/2b are conducted between pH 10 and pH 13.

[0085] The use of non-equilibrium reaction in Equations 2a/2b produces alkaline peracid concentrate 122' with concentrations of less than approximately 10 wt% peroxyacetic acid and/or other organic peracids that are produced efficiently and rapidly. Alkaline peracid concentrate can be produced with concentrations of less than approximately 5 wt% peroxyacetic acid and/or other organic peracids. Using the non-equilibrium reaction allows the hydrogen peroxide residual to be minimized if necessary. Minimizing the hydrogen peroxide residual, for example, significantly increases the concentration of the singlet oxygen available to oxidize target substrates. In one embodiment, for example, the [peroxyacetic acid]/[water]/[hydrogen peroxide] concentration ratios are from 10, 100, or 1000 depending on the ratio of hydrogen peroxide to acyl or acetyl donor ratio in Equations 2a/2b. Hydrogen peroxide is preferably minimized in alkaline peracid concentrate. Hydrogen peroxide is preferably less than 3% the mass concentration of peroxyacetic acid or other peracid, and more preferably less than 0.5% the mass concentration of peroxyacetic acid or other peracid. Concentrates having only trace or no detectable levels of hydrogen peroxide are preferred. In one embodiment, at least one molar equivalent of acyl or acetyl donor 106 reactive groups is added for each equivalent of hydrogen peroxide in alkaline hydrogen peroxide anion solution 122 used in Equations 2a/2b to consume all of the hydrogen peroxide. In alternative embodiments, excess acyl or acetyl donor 106 reactive groups is necessary to minimize the hydrogen peroxide residual due to the competing conversion of acyl or acetyl donor 106 reactive groups to the corresponding carboxylic acid by the alkali concentrate 104 used to raise the pH of the H₂O₂ concentrate 102. In one embodiment, the molar excess of acyl or acetyl donor 106 reactive groups over H₂O₂

solution 122 may range from 25% to 300% greater acyl or acetyl donor 106. For example, a preferred molar excess range is 50% to 100% greater acyl or acetyl donor 106 reactive groups.

[0086] In optional step 206, as indicated by the dashed lines, method 200 entrains byproducts 124 produced by the reactions of Equations 2a/2b. For example, byproducts 124 are entrained in solution with the alkaline peracid concentrate 204. In one embodiment, byproducts 124 are useful as co-solvents, pH buffers, chelating agents or stabilizers and carbon substrates for microbial processes after a chemical oxidation process. For example, the byproduct 124 of acetyl donors 106 of monacetin, diacetin and triacetin is glycerol, a potential co-solvent and favorable carbon source for microbes. In another embodiment, byproduct 124 of acetyl donor 106 of TAED, diacetylenediamine, acts as a chelating agent for transition metal ions and potentially serves as a peroxide stabilizer. In yet another embodiment, byproduct 124 is the carboxylic acid produced after alkaline peracid concentrate 122' reacts with a material or decomposes. Alternatively, acetic acid, a byproduct 124 of peroxyacetic acid, serves as a co-solvent, a pH buffer, a chelating agent, and a biological substrate.

[0087] In step 208, method 200 dilutes the resulting alkaline peracid concentrate 122' to nearly point of use concentration by adding makeup water 108. The amount of dilution is dependent on the concentration of alkaline peracid concentrate 122' and the desired point of use concentration of reactive oxygen species output 116. For example, the alkaline peracid concentration 122' may be 19 wt% to 21 wt% using 50 wt% hydrogen peroxide concentrate 102, 50 wt% sodium hydroxide as the alkali concentrate 104 and triacetin as the acetyl donor 106. In another example, the alkaline peroxyacetic acid concentration can be 17 wt% to 19 wt% using 30 wt% hydrogen peroxide concentrate 102, 50 wt% sodium hydroxide as the alkali concentrate 104 and triacetin as the acetyl donor 106.

[0088] In step 212, method 200 then stores the resulting combination in peracid holding tank 114. In optional step 210, as indicated by a dashed outline, method 200 adds additives concentrate 110 to the resulting diluted peracid from step 208, and then stores the combination in peracid holding tank 114 in step 212. In one embodiment, the alkaline peracid stored in peracid holding tank 114 contains all constituents for formulation of reactive oxygen species output 116 except for the final activating pH adjustment. This allows for the diluted alkaline peracid 122" to have a modest lifetime prior to use and be stored in peracid holding tank 114 for several minutes to a few hours,

depending on the concentration determined in step 208, and any additives added in step 210. In an alternative embodiment, optional step 210 may be performed by adding an additive concentration 110 of peroxide stabilizer before, during, or after combination of the acyl or acetyl donor 106 in step 204.

[0089] In step 214, method 200 adjusts the diluted peracid's 122" pH to the activated pH level for producing reactive oxygen species output 116 by adding acid concentrate 112 and mixing in mixing chamber 120(3). The resulting reactive oxygen species output 116 is then distributed to its point of use in liquid form. The reactive oxygen species output 116 may then be used in the form of a liquid, an ice, a foam, an emulsion, a micro-emulsion or an aerosol applied by means such as injection, flooding, spraying, circulation or any other means of conveying a fluid. In one embodiment, the diluted peracid's 122" pH does not require the addition of acid concentrate 112 and is ready for immediate distribution 214 to its point of use.

[0090] In one embodiment, during step 214, an acid concentration 112 is combined with diluted peracid 122" such that there is a population of both peracetic acid and peracetic acid anion which react together to generate singlet oxygen according to Equation 3 below:



Wherein the reaction rate for Equation 3 above follows a second order kinetics and is maximized when the ratio of the two forms of peroxyacetic acid is equivalent at its pKa of 8.3. The evolution and release of singlet oxygen occurs over time ranging from minutes to several hours depending on the rate of reaction in Equation 3 above. In one embodiment, the evolution of singlet oxygen from peroxyacetic acid, or other organic peracid having a similar pKa, the pH is between 6 and 11 or between 6.5 and 9.5. In another embodiment the evolution of singlet oxygen from peroxyacetic acid, or other organic peracid having a similar pKa, may be substantially retarded between about pH 9.5 and 12.5. For example, as pH becomes more alkaline the peracetic acid anion dominates the composition leaving very little peracetic acid to react with by the reaction in Equation 3. Retardation of singlet oxygen production extends the lifetime of the peroxyacetic acid or peracid solution and also allows for singlet oxygen use at elevated pH relevant to certain applications which use alkaline oxidants or cleansers up to pH 12 to 12.5.

[0091] In optional step 216, as shown by the dashed outline, method 200 further activates the reactive oxygen species output 116 by means of a Fenton or Fenton-

like catalyst, ultrasound, ultraviolet radiation or thermal activation (not shown in FIG. 1) to produce other reactive species.

[0092] FIG. 3 shows one exemplary system 300 for generation of a concentrated reactive oxygen species output 314 using bulk chemical precursor constituents, in one embodiment. FIG. 3 is illustrated with use of an acetyl donor, but as discussed herein can more generally use an acyl donor. In one embodiment, concentrated reactive oxygen species output 314 is used in applications where a concentrate is dosed into a liquid stream, including, but not limited to water and wastewater treatment; cooling tower water treatment and cooling tower system cleaning; desulfurization and deodorization of gases; water treatment in forestry operations, pulp and paper making processes; oil and gas produced water and hydraulic fracturing flowback water treatment. System 300 includes hydrogen peroxide (H_2O_2) concentrate 302, alkali concentrate 304, acyl or acetyl donor 306, acid concentrate 308, additives concentrate 310, alkaline hydrogen peroxide holding tank 312, reactive oxygen species output 314, pumps 316 and mixing chambers 318. In one embodiment, reactive oxygen species output 316 is concentrated singlet oxygen precursor solution.

[0093] In one embodiment, alkali concentrate 304 is an aqueous sodium hydroxide solution. In another embodiment, alkali concentrate is an aqueous potassium hydroxide solution. Acyl or acetyl donor 306 or mixture of donors may be in liquid or solid form, or dissolved in a solvent when reacted with a solution of hydrogen peroxide.

[0094] Acid concentrate 308, for example, includes at least one pH buffer chosen from the group including: weak acid electrolytes including acetate, citrate, propionate, phosphate and sulfate. Additives concentrate 310, for example, includes at least one of the following additives chosen from the group including: salts, surfactants, co-solvents, stabilizers, and emulsifiers.

[0095] In an embodiment, reactive oxygen species output 314 is a peroxyacetic acid in the absence of hydrogen peroxide and includes at least one chemical precursor species capable of releasing singlet oxygen. In alternative embodiments, reactive oxygen species output 316 includes two chemical precursor species may be used to release singlet oxygen. In yet another embodiment, reactive oxygen species output 316 includes more than two chemical precursor species to release singlet oxygen.

[0096] FIG. 4 shows an exemplary method 400 for generating reactive oxygen species output 314 using system 300 of FIG. 3. FIG. 4 is illustrated with use of an acetyl donor, but as discussed herein can more generally use an acyl donor. In an

embodiment, reactive oxygen species output 316 generated by method 400 is concentrated singlet oxygen precursor solution. In step 402, an alkaline hydrogen peroxide anion solution 320 is created by mixing H_2O_2 concentrate 302 with alkali concentrate 304. For example, molar ratios of H_2O_2 concentrate 302 to alkali 304 may range from 1:1.2 to 1:2.5. In one embodiment, a preferred molar ratio range is 1:1.4 to 1:2. In one embodiment, hydrogen peroxide is a weak acid with a pK_a of 11.6 and therefore its combination with alkali converts it in an acid-base equilibrium to the hydrogen peroxide anion form as in Equation 1 above. In some embodiments, raising the pH of a hydrogen peroxide solution enough to put a significant proportion of hydrogen peroxide into the anion form requires an excess of alkali over hydrogen peroxide. For example, the molar excess of alkali 304 over H_2O_2 concentrate 302 may range from 20% to 100% greater alkali 304. In one embodiment, a preferred molar excess range is 20% to 40% greater alkali 304.

[0097] In step 404, the resulting alkaline hydrogen peroxide 320 is stored in alkaline hydrogen peroxide holding tank 312 for immediate or later use. Alkaline hydrogen peroxide 320 has a longer lifetime prior to use which allows the alkaline hydrogen peroxide 320 to be stored for several minutes to a few hours in alkaline hydrogen peroxide holding tank 312 without as much decomposition as a peracid at a similar concentration.

[0098] In step 406, the alkaline hydrogen peroxide 320 is combined with an acyl or acetyl donor 306 in mixing tank 318(1) to create a resulting alkaline peracid concentrate 320'. . In one embodiment, the acetyl donor 30 is added in proportion to the alkaline hydrogen peroxide 320. In one embodiment, the molar ratio of H_2O_2 320 to acyl or acetyl donor 304 reactive groups may range from 1:1.25 to 1:4. For example, a preferred molar ratio range is 1:1.5 to 1:2. In one embodiment, the acyl or acetyl donor is an oxygen–acyl or oxygen–acetyl donor shown in Equation 2a above, where Ac is acyl [$-\text{C}(\text{O})\text{R}'$] or acetyl [$-\text{C}(\text{O})\text{CH}_3$] and R and R' are hydrocarbon-based substituents, and more specifically are alkyl or aryl groups. In an alternative embodiment, the acyl or acetyl donor is a nitrogen–acyl or nitrogen–acetyl donor as shown in Equation 2b above, where Ac is acyl [$-\text{C}(\text{O})\text{R}'$] or acetyl [$-\text{C}(\text{O})\text{CH}_3$] and R and R' are hydrocarbon-based substituents, or more specifically are alkyl or aryl groups.

[0099] In Equations 2a/2b above, the reaction between an acyl or acetyl donor 306 and alkaline hydrogen peroxide 320 occurs at alkaline pH by nucleophilic attack of the acyl carbonyl carbon atom by the hydrogen peroxide anion, which displaces

the donor molecule fragment as an alcohol or amine in a manner analogous to saponification. In some embodiments, the non-equilibrium reactions generalized in Equations 2a/2b are conducted between pH 10 and pH 13.

[00100] The use of non-equilibrium reaction in Equations 2a/2b provides, for example, alkaline peracid concentrates 320' with concentrations of less than approximately 10 wt% peroxyacetic acid or less than 5wt% peroxyacetic acid and other organic peracids are produced efficiently and rapidly. Using the non-equilibrium reaction allows the hydrogen peroxide residual to be minimized, if necessary. In one embodiment, for example, the peroxyacetic acid water/peroxide concentration ratios can be 10, 100, or 1000 depending on the ratio of hydrogen peroxide to acyl or acetyl donor ratio in Equations 2a/2b. Hydrogen peroxide is preferably minimized in alkaline peracid concentrate. Hydrogen peroxide is preferably less than 3% the mass concentration of peroxyacetic acid or other peracid, and more preferably less than 0.5% the mass concentration of peroxyacetic acid or other peracid. Concentrates having only trace or no detectible levels of hydrogen peroxide are preferred. In one embodiment, at least one molar equivalent of acyl donor 106 is added for each equivalent of hydrogen peroxide in alkaline hydrogen peroxide anion 320 used in Equations 2a/2b to consume all of the hydrogen peroxide. In alternative embodiments, excess acyl donor 306 reactive groups is necessary to minimize the hydrogen peroxide residual due to the competing conversion of acyl donor 306 reactive groups to the corresponding carboxylic acid by the alkali concentrate 304 used to raise the pH of the H₂O₂ concentrate 302. The molar ratio of hydroxide to hydrogen peroxide affects the preferred ratio of acyl or acetyl donor reactive groups to hydrogen peroxide. For example, in an embodiment, for example, for bulk chemical mixing illustrated in Figure 3, the preferred molar ratio of sodium hydroxide to hydrogen peroxide is 1:1 resulting in a preferred ratio of acyl donor reactive groups to hydrogen peroxide of about 2:1. This will provide preferred low relative amounts of hydrogen to peracid. In another embodiment, for example, for alkaline hydrogen peroxide produced by an electrochemical reactor in cathode output, as illustrated in Fig 5, the molar ratio of sodium hydroxide to hydrogen peroxide is about 2:1, with the ratio increasing as current efficiency for hydrogen peroxide production decreases, resulting in a preferred ratio of acyl donor reactive groups to hydrogen peroxide of at least 2:1 and preferably about 2.3:1. In another embodiment, alkaline hydroperoxide and superoxide produced by in the cathode output of an electrochemical reactor, as illustrated in Fig 11, the molar ratio of sodium hydroxide to hydrogen

peroxide is about 4.5:1, with the ratio increasing as current efficiency for hydrogen peroxide and superoxide production decreases, resulting in a preferred ratio of acyl donor reactive groups to hydrogen peroxide of at least 3:1. In the above examples the ratio of acyl donor reactive groups to hydrogen peroxide can be increased by 2-fold or more without significant detriment to performance.

[00101] In optional step 408, as indicated by the dashed lines, method 400 entrains byproducts 320 produced by the reactions of Equations 2a/2b occurring in step 406. For example, byproducts 322 are entrained in solution with the alkaline peracid concentrate 320'. In one embodiment, byproducts 322 are useful as co-solvents, pH buffers, chelating agents or stabilizers and carbon substrates for microbial processes after a chemical oxidation process. For example, the byproduct 322 of acetyl donors 306 of monacetin, diacetin and triacetin is glycerol, a potential co-solvent and favorable carbon source for microbes. In another embodiment, byproduct 322 of acetyl donor 106 of TAED, diacetylenediamine, acts as a chelating agent for transition metal ions and potentially serves as a peroxide stabilizer. In yet another embodiment, byproduct 322 is the carboxylic acid produced after an alkaline peracid concentrate 320' reacts with a material or decomposes. Alternatively, acetic acid, a byproduct 322 of peroxyacetic acid, serves as a co-solvent, a pH buffer, a chelating agent, and a biological substrate.

[00102] In step 410, method 400 adjusts the alkaline peracid concentrate 320' pH to the activated pH level for producing reactive oxygen species output 314 by adding acid concentrate 308 and mixing in mixing chamber 318(2). The resulting reactive oxygen species output 314 is then distributed to its point of use in liquid form. The reactive oxygen species output 314 may then be used in the form of a liquid, an ice, a foam, an emulsion, a micro-emulsion or an aerosol applied by means such as injection, flooding, spraying, circulation or any other means of conveying a fluid. In one embodiment, the alkaline peracid concentrate 320' pH does not require the addition of acid concentrate 308 and is ready for immediate distribution 410 to its point of use.

[00103] In one embodiment, during step 410, an acid concentration 308 is combined with alkaline peracid concentrate 320' such that there is a population of both peracetic acid and peracetic acid anion which react together to generate singlet oxygen according to Equation 3 above, wherein the reaction rate for Equation 3 above follows a second order kinetics and is maximized when the ratio of the two forms of peroxyacetic acid is equivalent at its pKa of 8.3. The evolution and release of singlet oxygen occurs over time ranging from minutes to several hours depending on the rate of reaction in

Equation 3 above. In one embodiment, the evolution of singlet oxygen from peroxyacetic acid, or other organic peracid having a similar pKa, the pH is between 6 and 11 or more specifically between 6.5 and 9.5.

[00104] In optional step 412, as indicated by a dashed outline, method 400 adds additives concentrate 310 to the resulting peracid from step 410, and then distributes the resulting solution for use.

[00105] In optional step 414, as shown by the dashed outline, method 400 further activates the reactive oxygen species output 314 by means of a Fenton or Fenton-like catalyst, ultrasound, ultraviolet radiation or thermal activation (not shown in FIG. 3) to produce radical species such as hydroxyl radicals.

Generation of Reactive Oxygen Species Using Electrochemical Generator

[00106] In the following embodiments, reactive oxygen species are generated by creating the necessary constituents and their mixing through the generation of all or a portion of these materials on site in a manner that minimizes the number of bulk chemical feedstocks and eliminates hazardous bulk chemical feedstocks. For example, the required components of hydrogen peroxide, alkali, and acid may be co-generated electrochemically from simple feedstocks including water, oxygen gas, and a salt or brine.

[00107] In the following embodiments, alternative methods are shown, for example, for delivering reactive oxygen compositions which can also generate hydroxyl radicals in cases where chlorate and bromate formation is not a primary issue.

[00108] FIG. 5 shows an exemplary system 500 for generating chemicals using an electrochemical reactor 514 and mixing the reactor's 514 outputs together and optionally with other materials to produce a diluted reactive oxygen species output 522. FIG. 5 is illustrated with use of an acetyl donor, but as discussed herein can more generally use an acyl donor. In one embodiment, diluted reactive oxygen species output 520 is used, but not limited to, in applications where a fluid is conveyed to a surface or material as the primary reactive oxygen species in addition to the parent oxidants at the point of use or in situ. In some embodiments, applications include, but are not limited to, in situ chemical oxidation for remediation of soil and groundwater; ex-situ chemical oxidation for remediation of soil, construction or demolition debris; hard surface cleaning and decontamination, clean-in place applications in food, dairy, beverage and biopharma production and processing; cleaning of membrane filtration systems; and flushing of well casings and water distribution pipes.

[00109] System 500 includes an electrochemical reactor 514 including inputs of a makeup water 502(1), brine 504, oxygen gas 506, and power source 508, an acyl or acetyl donor 510, an additives concentrate 512, pumps 516, holding tanks 518, mixing chambers 520, and reactive oxygen species output 522. In one embodiment, the electrochemical reactor 514 is that embodied by PCT Application No. PCT/US2012/040325 titled "Electrochemical Reactor and Process." This published PCT application includes description for reactor device configurations including cathodes and anodes which are useful in embodiments of this invention. The reference also includes descriptions of reactors useful for preparation of oxidants including hydrogen peroxide, superoxide, sodium hypochlorite, hypochlorites among others and for generation of alkali, and acids. An exemplary electrochemical reactor is shown in FIG. 6.

Exemplary Electrochemical Reactor

[00110] FIGs. 6A/6B depict an exemplary cross-sectional view of the general configuration and components of an exemplary electrochemical reactor 600 for use in system 500 of FIG. 5, in one embodiment. In one embodiment, electrochemical reactor 600 has a general tubular or annular configuration. The housing for electrochemical reactor 600 has three distinct parts an anode housing 620, a seat plate 634, and an end plate 636, each of which may be fabricated in quantity from structural thermoplastics (pure and filled) including, but not limited to, polyvinyl chloride (PVC), chlorinated polyvinylchloride (CPVC), polyvinylidene difluoride (PVDF), polyethylene, polytetrafluoroethylene (PTFE), ethylene tetrafluoroethylene (ETFE), acrylonitrile butadiene styrene (ABS) polymer blends, etc.

[00111] In an embodiment, anode housing 620 is an extruded tube, such as a standard schedule 80 pipe that is modified with tube fittings, feed-throughs, O-ring, or gasket sealing surfaces and threaded bolt holes. In an embodiment, anode housing 620 contains the anolyte solution within electrochemical reactor 600. In an embodiment, anode housing 620 contains the anolyte solution within an anolyte chamber 618. In an embodiment, anode housing 620 provides structural integrity to electrochemical reactor 600 and is what seat plate 634 and end plate 636 are fastened to, thereby holding

electrochemical reactor 600 and its contents together as a single unit. In some embodiments, anode housing 620 is made from PVC.

[00112] In an embodiment, seat plate 634 contains a central opening with a tapered surface on which a separator 614 is sealed. A cathode 612 extends through seat plate 634. A cathode current distributor and compression ferrule 630 contacts cathode 612 and anchors it in place while simultaneously compressing separator 614 to make a gas-tight seal between a cathode flow channel 610 and the anolyte chamber 618. Seat plate 634 also has gasket or O-ring sealing surfaces for making gas-tight seals with anode housing 620 and with cathode current distributor and compression ferrule assembly 630.

[00113] In an embodiment, cathode current distributor and compression ferrule 630 may be constructed of a rigid material that is conductive and non-corrosive such as stainless steel alloys, high nickel alloys, and high purity titanium, for example. In an embodiment, cathode current distributor and compression ferrule 630 is 316 stainless steel. In yet another embodiment, the surfaces of current distributor and compression ferrule 630 facing into cathode flow channel 610 and manifold are masked with a non-conductive material such as a thermoplastic, a polymer coating, or an elastomeric adhesive coating.

[00114] In an embodiment, end plate 636 provides a gas inlet 602 and catholyte fluid distribution manifolds which are accessed through the catholyte inlet or outlet 608. In an embodiment end plate 636 seals against the end of a gas distributor tube 606 creating a separate gas chamber 604 down the center axis of electrochemical reactor 600. End plate 636 contains gasket and O-ring sealing surfaces for making gas-tight seals with gas distributor tube 606 and cathode current distributor and compression ferrule assembly 630. In an embodiment, end plate 636 provides the compressive force to seal separator 614 to seat plate 634, seal seat plate 634 to anode housing 620, seal the faces of the cathode current distributor and compression ferrule assembly 630 to end plate 636 and seat plate 634, seal gas distributor tube 606 and fasten electrochemical reactor 600 together.

[00115] In an embodiment, end plate 636 holds the cathode electrical feed-through posts 632, which contact cathode current distributor and compression ferrule 630 and are connected by means of conductors to the negative pole (direct current, DC) or ground (alternating current, AC) of a power supply. In one embodiment, electrical feed-through posts 632 are made from a material that is conductive and non-corrosive such as

stainless steel alloys, high nickel alloys, and high purity titanium, for example. In an embodiment, cathode electrical feed-through posts 632 are 18-8 stainless steel.

[00116] In one embodiment, gas distribution tube 606 is a porous or microporous material that allows gas to permeate through its wall and resists water permeation. In an embodiment, gas distribution tube 606 is a non-conductive, hydrophobic material such as polyethylene, polypropylene, polytetrafluoroethylene, or polyvinylidene difluoride, for example. In an embodiment, gas distribution tube 606 may be a microporous ceramic such as alumina, zirconia, titania or other suitable material with a hydrophobic coating. Gas distribution tube 606 may be made by casting-sintering or extrusion production methods, for example. In an embodiment, gas distribution tube 606 contains pores having a diameter rating that is less than about 10 microns. In an embodiment, gas distribution tube 206 contains pores having a diameter rating that is less than about or equal to 5 microns. The pores of gas distribution tube 606 may be masked in part to bias the gas permeation through regions of gas distribution tube 606 for purposes including making the ends gas and liquid impermeable in the catholyte manifold and current collector regions, compensating for pressure gradients, gas loading in the catholyte, and/or modulating residence time in the cathode flow chamber.

[00117] In an embodiment, cathode flow channel 610 is defined by gas distribution tube 606 and separator 614. Cathode 612 resides within cathode flow channel 610 immersed in the catholyte liquid while gas is supplied from the back side of cathode 612 and the front side of cathode 612 faces the separator 614. Cathode 612 may be positioned anywhere within cathode flow channel 610, including having direct contact with the separator 614 and/or gas distribution tube 606.

[00118] In one embodiment, separator 614 separates the catholyte and anolyte fluids from one another, thereby keeping the respective reactants and products from mixing in an uncontrolled manner, providing control of two-phase fluid dynamics (flow distribution, mixing, electrode contact, partial pressures of gases), preventing undesirable side reactions, preventing electrode shorting or shunt losses, and allowing for precise control of process conditions at each electrode. In an embodiment separator 614 may be a porous, microporous or nanoporous separator composed of materials including polypropylene, polyethylene, polytetrafluoroethylene, polyvinylidene difluoride, polysulfone, polyethersulfone or a ceramic material (e.g., alumina, zirconia, rare earth oxide, nitride). In an embodiment, separator 614 may be an ion exchange including

cation exchange membranes (e.g., perfluorosulfonic acid, sulfonated polyfluorostyrene, sulfonated polystyrene-divinylbenzene, perfluorosulfonimide, and perfluoro carboxylate membranes) or anion exchange membranes (e.g., quaternary ammonium polystyrene-divinylbenzene and doped polybenzimidazole membranes), for example. Separator 614 may be formed into a tubular shape by casting, extrusion, or rolling flat sheets and bonding a seam. In an embodiment, separator 614 is a tubular perfluorosulfonic acid membrane such as NafionTM.

[00119] In an embodiment, cathode 612, also known as a cathode electrode, is a high porosity or high surface area material that can conform to a tubular shape and be continuously conductive down the length of its form. Cathode 612 may be a pure metal, an alloy, a conductive polymer, a carbonized or graphitized polymer. In an embodiment cathode 612 has a coating that imparts conductivity, reaction selectivity, catalysis, adsorption, resistance to hydrogen evolution, increased surface area or modifies wettability. In an embodiment, cathode 612 may be made of one or more porous material formats including sintered or bonded particles, sintered or bonded fibers, woven mesh, continuous fibers or filaments, cloths, felts, and electro-spun or melt-spun filamentous forms. In an embodiment the electrode porosity and pore structure of cathode 612 may be uniform, graded or random. In an embodiment cathode 612 has an electrode specific surface area greater than about 10 m^2 per 1 m^2 superficial area. In an embodiment cathode 612 has an electrode specific surface area greater than about 100 m^2 per 1 m^2 superficial area. In an embodiment cathode 612 is continuous carbon fibers. The carbon fiber surfaces cathode 612 may be modified to possess carbon oxide species. In another embodiment, the carbon fiber surfaces of cathode 612 are coated with a catalyst that may be an organic material (e.g., adsorbed or bonded molecules or polymers) or an inorganic material (e.g., adsorbed, bonded or electrodeposited metals, semiconductors, alloys and their oxide or sulfide derivatives) or a mixture thereof.

[00120] In one embodiment, anode 616, also known as an anode electrode, can be a dimensionally stable anode consisting of an expanded titanium mesh coated with a catalyst. The catalyst is optimized for oxidation of species in an anolyte solution filling anolyte chamber 618, such as water or halides or other redox active materials, at reduced overpotentials or voltage. In some embodiments, the catalyst is a precious metal, noble metal, platinum group metal or oxides of such metals. In an embodiment, the catalyst is iridium oxide.

[00121] In an embodiment, anode 616 is in a tubular form, and may be in direct contact with separator 614, and may provide mechanical support to separator 614. In an embodiment, at least one titanium anode current collector tab 626 is affixed to the side of anode 616 and provides a point of attachment for the anode electrical feed-through post 628, which is also titanium.

[00122] In one embodiment, a heat transfer coil, which is not depicted in FIG. 6A or FIG 6B, can be positioned in anolyte chamber 618 with feedthroughs using two of the anolyte inlet and outlet/vent ports 622 and 624, respectively. If required, the heat transfer coil may be used in the reactor process for cooling or heating the anolyte solution. In an embodiment, the heat transfer coil is a metal or plastic tube made of a non-corrosive material such as stainless steel alloys, high purity titanium, high nickel alloys, polyvinyl chloride, polypropylene, polyvinylidene difluoride, polytetrafluoroethylene. The heat transfer fluid circulated through the coil may be water, catholyte solution, gas, air, glycol solutions, for example.

[00123] FIG. 7 depicts an embodiment of a reactor system 700 that has a reactor system fluid process flow, also known as a flow pathway, that enables gas recirculation within reactor system 700. A regulated gas makeup stream enters the gas circulation loop through the gas inlet line 702. The gas passes through the gas feed flow control valve 704 and the gas feed flow meter 706 and then enters the gas chamber 708 of the reactor. At least one boundary of the gas chamber is a gas distributor (not depicted in FIG. 7, but described above and depicted in FIG 6 as gas distributor 606). The gas passes through the gas distributor and into the cathode chamber 710. Excess gas not consumed in electrochemical process exits cathode chamber 710 co-linearly with liquid catholyte and cathodic products formed through the cathode product line 712. The liquid and gas mixture passes through a cooling coil 714 prior to entering a gas-liquid separator 716. The separated liquid, which can contain products formed in cathode chamber 710, is collected in a cathode product tank 718. The separated gas flows through a gas recirculation line 720, through a gas pump 722 and is returned to gas inlet line 702. A portion of the separated gas is removed from the system through a gas bleed flow control valve 724 and a gas bleed flow meter 726. Bleed rate of gas from the system is preferably the same as the mass flow of the gas makeup stream entering the system less the mass consumption of gas in the reactor less the mass production of gas recovered from the anode chamber 746 and added to the gas makeup stream through an anode gas vent 754.

[00124] While gas is passing through the system described in reference to FIG. 7, a catholyte solution makeup 730 is added to the cathode feed tank 732 where the head space of the tank can be open to the gas makeup stream through a gas pressure line 728. In some embodiments, the pneumatic pressure for the gas makeup stream may be used to feed the catholyte solution into cathode chamber 710 of the reactor. In additional embodiments, the hydraulic pressure of the catholyte solution makeup may be used to feed the catholyte solution into cathode chamber 710 of the reactor. The catholyte flows from cathode feed tank 732 through the catholyte inlet line 734, passes through a catholyte flow control valve 736 and catholyte flow meter 738 and enters cathode chamber 710 of the reactor. Excess liquid catholyte not consumed in electrochemical process and cathodic products formed exit cathode chamber 710 co-linearly with gas through cathode product line 712. The liquid and gas mixture passes through cooling coil 714 prior to entering gas-liquid separator 716. The separated liquid, which can contain products formed in cathode chamber 710, is collected in cathode product tank 718. The liquid cathode product can be removed from the system during or after operation through the cathode product drain 740.

[00125] While gas and catholyte is passing through the system described in reference to FIG. 7 an anolyte solution makeup 742 is added to the anode feed tank 744. The anolyte is supplied through anolyte feed line 746 to the anode chamber 748 by the action of gravity or a pump (not shown). Excess liquid anolyte not consumed in electrochemical process and anodic products formed, including gas, exit the anode chamber collinearly through the anode product line 750 and then pass through a gas-liquid separator 752. The separated liquid is returned to anode feed tank 744 while the separated gas is optionally fed to the gas makeup stream through anode gas vent 754. Anode gas vent 754 also serves to expose anode chamber 748 to the gas inlet line pressure such that the differential pressure between anode chamber 748 and cathode chamber 710 remains constant at any gas inlet line pressure or during pressure fluctuations in the system. The liquid anode or anode product can be removed from the system during or after operation through the anode product drain 756. While gas, catholyte, and anolyte are passing through the system described in reference to FIG. 7 a voltage or current is applied to the reactor by a controller (not shown in FIGs. 6 or 7).

[00126] Referring back to FIG. 5, it is noted that the present embodiments herein are not limited to only the electrochemical reactor 600 discussed above, or those

disclosed in published International application WO2012/166997; thus, alternative electrochemical reactors may be incorporated and used in the embodiments herein.

[00127] In one embodiment, electrochemical reactor 514 creates two outputs including alkaline hydrogen peroxide 524 output and acid concentrate 526 output, as discussed below with reference to Examples 1-3.

[00128] In one embodiment, brine 504 is a solution that contains ions necessary for producing alkaline hydrogen peroxide and acids in two separate streams. The brine 504 may also contain pH buffers and co-solvents compatible with the reaction process, which contribute to the reactive oxygen species output 522 formulation. For example, pH buffers include weak chemical electrolytes chosen from the group including: acetate, citrate, propionate, phosphate and sulfate.

[00129] Acyl or acetyl donor 510 includes, but is not limited to, an acyl or acetyl donor chosen from the group including: monoacetin, diacetin, triacetin, acetylsalicylic acid, methyl benzoate, ethyl lactate and tetraacetylenediamine (TAED). In alternative embodiments, other synthetic or natural esters, mono-, di- and triacylglycerides and phospholipids having acyl substituents possessing more than one carbon can provide other types of organic peracids by the non-equilibrium reaction mechanism. Acyl or acetyl donor 510 or mixture of donors may be in liquid or solid form, or dissolved in a solvent when reacted with a solution of hydrogen peroxide. Additives concentrate 512, for example, include at least one of the following additives chosen from the group including: salts, surfactants, co-solvents, stabilizers, and emulsifiers.

[00130] FIG. 8 shows an exemplary method 800 for generating a diluted reactive oxygen species output 522 using system 500 of FIG. 5. FIG. 8 is illustrated with use of an acetyl donor, but as discussed herein can more generally use an acyl donor. In step 802, method 800 generates an alkaline hydrogen peroxide 524 output, and an acid concentrate 526 output. Acid concentrate output 526 is then stored in holding tank 518(1). Exemplary processes for generating outputs 524 and 526 are discussed below in Examples 1-3. In one embodiment, both output streams 524 and 526 are in concentrated liquid forms produced at a constant rate. For example, the alkaline hydrogen peroxide 524 output may contain 0.1 wt% to 3 wt% hydrogen peroxide at pH 12.0 to 13.0. Typical alkaline hydrogen peroxide 524 output may contain 0.3 wt% to 0.8 wt% hydrogen peroxide at pH 12.1 to 12.6. The acid concentrate 526 output may contain 0.1 wt% to 20 wt% depending on the concentration and composition of anolyte solution

makeup 742. For example, a 20 wt% sodium acetate solution as anolyte solution makeup 742 may produce 13.5 wt% acetic acid at 85% conversion efficiency. In an alternative embodiment, an anolyte solution makeup 742 is a 5 wt% sodium sulfate solution that may produce 3.6 wt% bisulfate acid at 85% conversion efficiency.

[00131] In step 804, the alkaline hydrogen peroxide 524 output is combined with acyl or acetyl donor 510 in mixing tank 520(1) to create alkaline peracid concentrate 524'. In one embodiment, alkaline peracid concentrate 524' may be peroxyacetic acid. In one embodiment, the acyl or acetyl donor 510 is added in proportion to the hydrogen peroxide 524. In one embodiment, the molar ratio of H₂O₂ 524 to acyl or acetyl donor 510 reactive group equivalents may range from 1:1.25 to 1:4. For example, a preferred molar ratio range is 1:1.5 to 1:2.5, more preferably the molar ratio range is 1:1.9 to 1:2.1 and most preferably the molar ratio is 1:2. If the ratio is too low a high hydrogen peroxide residual will remain in the peracid concentrate where it will significantly quench singlet oxygen. If the ratio is higher than needed to achieve a low hydrogen peroxide residual that does not significantly quench singlet oxygen, then excess acyl or acetyl donor remains unused. In one embodiment, the acyl or acetyl donor is an oxygen–acyl or oxygen–acetyl donor shown in Equation 2a below:



Where Ac is acyl [-C(O)R'] or acetyl [-C(O)CH₃] and R and R' are hydrocarbon-based substituents and more specifically are alkyl or aryl groups. In an alternative embodiment, the acyl or acetyl donor is a nitrogen-acyl or nitrogen-acetyl donor as shown in Equation 2b below:



Where Ac is acyl [-C(O)R'] or acetyl [-C(O)CH₃] and R and R' are hydrocarbon-based substituents and more specifically are alkyl or aryl groups.

[00132] In Equations 2a/2b above, the reaction between an acyl or acetyl donor 510 and alkaline hydrogen peroxide 524 occurs at alkaline pH by nucleophilic attack of the acyl carbonyl carbon atom by the hydrogen peroxide anion, which displaces the donor molecule fragment as an alcohol or amine in a manner analogous to saponification. In some embodiments, the non-equilibrium reactions generalized in Equations 2a/2b are conducted between pH 10 and pH 13.

[00133] A particular advantage of the use of non-equilibrium reaction in Equations 2a/2b is that peracid solutions 524' with concentrations of less than approximately 10 wt% peroxyacetic acid and/or other organic peracids can be produced

efficiently and rapidly. Peracid solutions 524" with concentrations of less than approximately 5wt% peroxyacetic acid and/or other organic peracids can be produced. Using the non-equilibrium reaction allows the hydrogen peroxide residual to be minimized if necessary. In one embodiment, for example, the peroxyacetic acid water/peroxide concentration ratios can be 10, 100, or 1000 depending on the ratio of hydrogen peroxide to acyl donor ratio in Equations 2a/2b. Hydrogen peroxide is preferably minimized in alkaline peracid concentrate. Hydrogen peroxide is preferably less than 3% the mass concentration of peroxyacetic acid or other peracid, and more preferably less than 0.5% the mass concentration of peroxyacetic acid or other peracid. Concentrates having only trace or no detectible levels of hydrogen peroxide are preferred. In one embodiment, at least one molar equivalent of acyl or acetyl donor 510 reactive groups is added for each equivalent of hydrogen peroxide in alkaline hydrogen peroxide anion solution 524 used in Equations 2a/2b to consume all of the hydrogen peroxide.

[00134] In optional step 806, as indicated by the dashed lines, method 800 entrains byproducts 528 produced by the reactions of Equations 2a/2b. In one embodiment, byproducts 528 are entrained in solution with the alkaline peracid concentrate 524'. In one embodiment, byproducts 528 are useful as co-solvents, pH buffers, chelating agents or stabilizers and carbon substrates for microbial processes after a chemical oxidation process. For example, the byproduct 528 of acetyl donors 510 of monacetin, diacetin and triacetin is glycerol, a potential co-solvent and favorable carbon source for microbes. In another embodiment, byproduct 528 of acetyl donor 510 of TAED, diacetylenediamine, acts as a chelating agent for transition metal ions and potentially serves as a peroxide stabilizer. In yet another embodiment, byproduct 528 is the carboxylic acid produced after alkaline peracid concentrate 524' reacts with a material or decomposes. Alternatively, acetic acid, a byproduct 528 of peroxyacetic acid, serves as a co-solvent, a pH buffer, a chelating agent, and a biological substrate.

[00135] In step 808, the resulting alkaline peracid concentrate 524' is then diluted with makeup water 502(2) introduced by pump 516(2) to create a diluted peracid 524" to nearly the point of use concentration and is stored in holding tank 518(2). In optional step 810, as indicated by the dashed outline, additional additives concentrate 512 is combined with diluted peracid 524" and then stored into holding tank 518(2).

[00136] In step 812, the diluted peracid's 524" pH is adjusted, by combining diluted peracid 524" with created acid concentrate 526, to the activated pH level for

producing reactive oxygen species output 522. The resulting reactive oxygen species output 522 is then distributed to its point of use in liquid form. The reactive oxygen species output 522 may then be used in the form of a liquid, an ice, a foam, an emulsion, a micro-emulsion or an aerosol applied by means such as injection, flooding, spraying, circulation or any other means of conveying a fluid. In one embodiment, the diluted peracid's 524" pH does not require the addition of acid concentrate 526 and is ready for immediate distribution to its point of use.

[00137] In one embodiment, during step 812, an acid concentration 526 is combined with diluted peracid 524" such that there is a population of both peracid (e.g., peracetic acid) and the corresponding peracid anion (e.g., peracetate anion) which react together to generate singlet oxygen according to Equation 3 below:



Wherein the reaction rate for Equation 3 above follows a second order kinetics and is maximized when the ratio of the two forms of peroxyacetic acid is equivalent at its pKa of 8.3. The evolution and release of singlet oxygen occurs over time ranging from minutes to several hours depending on the rate of reaction in Equation 3 above. In one embodiment, the evolution of singlet oxygen from peroxyacetic acid, or other organic peracid having a similar pKa, the pH is between 6 and 11 or more specifically between 6.5 and 9.5.

[00138] In optional step 814, as indicated by the dashed outline, the reactive oxygen species output 522 may further be activated by means of a Fenton or Fenton-like catalyst, ultrasound, ultraviolet radiation, or thermal activation to produce other reactive species, which can include additional reactive oxygen species, such as hydroxyl radical, or reactive species other than reactive oxygen species, e.g., hydrocarbon radicals, such as alkyl radicals.

[00139] FIG. 9 shows an exemplary system 900 for generating chemicals using an electrochemical reactor 914 and mixing the reactor's 914 outputs together and optionally with other materials to produce a concentrated reactive oxygen species output 922. In one embodiment, concentrated reactive oxygen species output 922 is used, for example, in applications where a concentrate is dosed into a liquid stream which is to be treated or used to distribute the precursor solution throughout a larger system while generating singlet oxygen, for example, as the primary reactive oxygen species in addition to the parent oxidant(s) at the point of use or in-situ. In some embodiments, applications include water and wastewater treatment; cooling tower water treatment and

cooling tower system cleaning; desulfurization and deodorization of gases; water treatment in forestry operations, pulp and paper making processes; oil and gas produced water and hydraulic fracturing flowback water treatment.

[00140] System 900 includes an electrochemical reactor 914 including inputs of a makeup water 902, brine 904, an oxygen gas 906, and power source 908, an acyl or acetyl donor 910, an additives concentrate 912, holding tanks 916, pumps 918, mixing chambers 920, and reactive oxygen species output 922. In one embodiment, the electrochemical reactor 914 is that embodied by published International application WO2012166997. An exemplary electrochemical reactor is shown in FIGs. 6-7.

[00141] In one embodiment, brine 904 is a solution that contains ions necessary for producing alkaline hydrogen peroxide and acids in two separate streams. In one embodiment, brine 904 may contain 5 wt% sodium sulfate. A small fraction of brine 904 may be fed as a side stream to the cathode feed tank 732 where it is diluted by a factor of 20 with water to 0.25 wt% sodium sulfate before being fed to the catholyte inlet line 734 to serve as an electrolyte. The remaining majority of brine 904 is fed to the anolyte solution makeup 742 and converted to approximately 3.6 wt% sodium bisulfate acid at 85% conversion efficiency. The sodium displaced from sodium sulfate is transported from anode to cathode to support current flow in the reactor and combines with anionic oxygen species produced at the cathode including hydroxide, hydroperoxide and superoxide. In an alternative embodiment, all of brine 904 is fed to anolyte solution makeup 742 while a separate brine (not shown) of different composition and concentration is fed separately into the catholyte feed tank 732. The brine 904 may also contain pH buffers and co-solvents compatible with the reaction process, which contribute to the reactive oxygen species output 922 formulation. For example, pH buffers include weak chemical electrolytes chosen from the group including: acetate, citrate, propionate, phosphate and sulfate. Co-solvents may include a substance chosen from the group including: alcohols such as methanol, ethanol, propanol, propylene glycol, glycol ethers, glycerol, ethyl lactate, soybean oil, vegetable oil, sunflower oil, peanut oil and guar gum.

[00142] Acyl or acetyl donor 910 or mixture of donors may be in liquid or solid form, or dissolved in a solvent when reacted with a solution of hydrogen peroxide. Additives concentrate 912, for example, include at least one of the following additives chosen from the group including: salts, surfactants, co-solvents, stabilizers, and emulsifiers.

[00143] FIG. 10 shows an exemplary method 1000 for generating a concentrated reactive oxygen species output 922 using system 900 of FIG. 9. FIG. 10 is illustrated with use of an acetyl donor, but as discussed herein can more generally use an acyl donor. In step 1002, method 1000 generates an alkaline hydrogen peroxide 924 output, and an acid concentrate 926 output. Alkaline hydrogen peroxide output 924 and acid concentrate output 926 is then stored in separate holding tanks 916(1), 916(2), respectfully, for immediate or later use. Alkaline hydrogen peroxide 924 has a longer lifetime prior to use which allows the alkaline hydrogen peroxide 924 to be stored for several minutes to a few hours in holding tank 916(1) without as much decomposition as a peracid at similar concentration. Exemplary processes for generating outputs 924 and 926 are discussed below in examples 1-3. In one embodiment, both output streams 924 and 926 are in concentrated liquid forms produced at a constant rate.

[00144] In step 1004, the alkaline hydrogen peroxide 924 output is combined with acyl or acetyl donor 910 in mixing tank 920(1) to create peracid 924'. In one embodiment, the acyl or acetyl donor is an acyl or oxygen-oxygen-acetyl donor shown in Equation 2a above where Ac is acyl $[-C(O)R']$ or acetyl $[-C(O)CH_3]$ and R and R' are hydrocarbon-based substituents and more specifically are alkyl or aryl groups. In an alternative embodiment, the acyl or acetyl donor is a nitrogen-acyl or nitrogen-acetyl donor as shown in Equation 2b above. Where Ac is acyl $[-C(O)R']$ or acetyl $[-C(O)CH_3]$ and R and R' are hydrocarbon-based substituents and more specifically are alkyl or aryl groups.

[00145] In Equations 2a/2b above, the reaction between an acetyl or acyl donor 910 and alkaline hydrogen peroxide 924 occurs at alkaline pH by nucleophilic attack of the acyl carbonyl carbon atom by the hydrogen peroxide anion, which displaces the donor molecule fragment as an alcohol or amine in a manner analogous to saponification. In some embodiments, the non-equilibrium reactions generalized in Equations 2a/2b are conducted between pH 10 and pH 13.

[00146] The use of non-equilibrium reaction in Equations 2a/2b provides peracid solutions 924' with concentrations of less than approximately 10 wt% peroxyacetic acid and/or other organic peracids that are produced efficiently and rapidly. Peracid solutions 924' with concentrations of less than approximately 5 wt% peroxyacetic acid and/or other organic peracids can be produced. Using the non-equilibrium reaction allows the hydrogen peroxide residual to be minimized if necessary. In one embodiment, for example, the peroxyacetic acid water/peroxide concentration ratios can be 10, 100, or

1000 depending on the ratio of hydrogen peroxide to acyl or acetyl donor ratio in Equations 2a/2b. Hydrogen peroxide is preferably minimized in alkaline peracid concentrate. Hydrogen peroxide is preferably less than 3% the mass concentration of peroxyacetic acid or other peracid, and more preferably less than 0.5% the mass concentration of peroxyacetic acid or other peracid. Concentrates having only trace or no detectible levels of hydrogen peroxide are preferred.

[00147] In one embodiment, at least one molar equivalent of acyl or acetyl donor 910 reactive groups is added for each equivalent of hydrogen peroxide in alkaline hydrogen peroxide anion solution 924 used in Equations 2a/2b to consume all of the hydrogen peroxide.

[00148] In optional step 1006, as indicated by the dashed lines, byproducts 928 produced by the reactions of Equations 2a/2b are collected. In one embodiment, byproducts 928 are useful as co-solvents, pH buffers, chelating agents or stabilizers and carbon substrates for microbial processes after a chemical oxidation process. For example, the byproduct 928 of acetyl donors 910 of monacetin, diacetin and triacetin is glycerol, a potential co-solvent and favorable carbon source for microbes. In another embodiment, byproduct 928 of acetyl donor 910 of TAED, diacetylenediamine, acts as a chelating agent for transition metal ions and potentially serves as a peroxide stabilizer. In yet another embodiment, byproduct 928 is the carboxylic acid produced after a peracid 924' reacts with a material or decomposes. Alternatively, acetic acid, a byproduct 928 of peroxyacetic acid, serves as a co-solvent, a pH buffer, a chelating agent, and a biological substrate.

[00149] In step 1008, the concentrated peracid's 924' pH is adjusted, by combining concentrated peracid 924' with created acid concentrate 926, to the activated pH level for producing reactive oxygen species output 922. The resulting reactive oxygen species output 922 is then distributed to its point of use in liquid form. The reactive oxygen species output 922 may then be used in the form of a liquid, an ice, a foam, an emulsion, a micro-emulsion or an aerosol applied by means such as injection, flooding, spraying, circulation or any other means of conveying a fluid.

[00150] In one embodiment, during step 1008, an acid concentration 926 is combined with concentrated peracid 924' such that there is a population of both peracetic acid and peracetic acid anion which react together to generate singlet oxygen according to Equation 3 above. Wherein the reaction rate for Equation 3 above follows a second order kinetics and is maximized when the ratio of the two forms of peroxyacetic acid is

equivalent at its pKa of 8.3. The evolution and release of singlet oxygen occurs over time ranging from minutes to several hours depending on the rate of reaction in Equation 3 above. In one embodiment, the evolution of singlet oxygen from peroxyacetic acid, or other organic peracid having a similar pKa, the pH is between 6 and 11, or more specifically 6.5 and 9.5.

[00151] In one embodiment, the concentrated peracid's 924' pH does not require the addition of acid concentrate 926 and is ready for immediate distribution to its point of use.

[00152] In optional step 1010, as indicated by the dashed outline, additional additives concentrate 912 is combined with concentrated peracid 924' and then distributed as reactive oxygen species output 922 to the point of use.

[00153] In optional step 1012, as indicated by the dashed outline, the reactive oxygen species output 922 may further be activated by means of a Fenton or Fenton-like catalyst, ultrasound or ultraviolet radiation to produce other reactive species, which can include other reactive oxygen species, such as hydroxyl or hydroperoxyl radicals, or reactive species other than reactive oxygen species, such as hydrocarbon radicals, e.g., alkyl radicals.

[00154] FIG. 11 shows an exemplary system 1100 for generating chemicals using an electrochemical reactor 1114 and mixing the reactor's 1114 outputs together and optionally with other materials to produce a superoxide reactive oxygen species output 1122. In one embodiment, the superoxide reactive oxygen species output 1122 is a concentrated superoxide precursor. Alternatively, the superoxide reactive oxygen species output 1122 is a diluted superoxide precursor. In one embodiment, superoxide reactive oxygen species output 1122 is used, but not limited to, applications where a concentrate is dosed into a liquid stream, or applied to a surface or material. In some embodiments, applications include water and wastewater treatment; cooling tower water treatment and cooling tower system cleaning; desulfurization and deodorization of gases; water treatment in forestry operations, pulp and paper making processes; oil and gas produced water and hydraulic fracturing flowback water treatment; in-situ chemical oxidation for remediation of soil and groundwater; ex-situ chemical oxidation for remediation of soil; construction or demolition debris; hard surface cleaning and decontamination; cleansing applications in food, dairy, beverage and biopharma production and processing; cleaning of membrane filtration systems.

[00155] System 1100 includes an electrochemical reactor 1114 including inputs of a makeup water 1102(1), brine 1104, an oxygen gas 1106, and power source 1108, an additives concentrate 1110, holding tanks 1116, pumps 1118, mixing chambers 1120, and superoxide reactive oxygen species output 1122. In one embodiment, the electrochemical reactor 1114 is that embodied by published International application WO2012166997. An exemplary electrochemical reactor is shown in FIGs. 6-7.

[00156] In one embodiment, brine 1104 is a solution that contains ions necessary for producing alkaline hydrogen peroxide and acids in two separate streams. The brine 1104 may also contain pH buffers and co-solvents compatible with the reaction process, which contribute to the reactive oxygen species output 1122 formulation. For example, pH buffers include weak chemical electrolytes chosen from the group including: acetate, citrate, propionate, phosphate and sulfate. Co-solvents may include a substance chosen from the group including: alcohols such as methanol, ethanol, propanol, propylene glycol, glycol ethers, glycerol, ethyl lactate, soybean oil, vegetable oil, sunflower oil, peanut oil and guar gum.

[00157] Additives concentrate 1110, for example, include at least one of the following additives chosen from the group including: salts, surfactants, co-solvents, stabilizers, and emulsifiers.

[00158] FIG. 12 shows an exemplary method 1200 for generating a concentrated superoxide reactive oxygen species output 1122 using system 1100 of FIG. 11, in one embodiment. In step 1202, electrochemical generator 1114 is used to create a superoxide solution 1124, as depicted below in Example 4. In one embodiment, superoxide solution 1124 additionally contains hydrogen peroxide co-generated with superoxide. In yet another embodiment, in step 1202, electrochemical generator 1114 creates superoxide solution 1124, with or without co-generation of hydrogen peroxide, and additionally co-generates an acid concentrate 1126. The proportion of superoxide to hydrogen peroxide co-generated can be adjusted by the nature of the cathode surface. For carbon cathodes, a higher degree of oxidation of the cathode surface can correlate with higher superoxide to hydrogen peroxide ratios. Also, when using such cathodes increasing cathodic current density can provide relatively minor increases in the superoxide to hydrogen peroxide production ratios. The molar ratio of superoxide to hydrogen peroxide co-generated by the reactor can range from approximately 0.01:1 to 10:1. Molar ratios of superoxide to hydrogen peroxide can range between 0.5:1 to 1.5:1, 1.5:1 to 3:1 or 3:1 to 5:1. One preferred molar ratio range-of superoxide to hydrogen

peroxide is 1:1 to 6. Another preferred molar ratio range of superoxide to hydrogen peroxide is 3:1 to 5:1. Variation in the molar ratio of superoxide to hydrogen peroxide in these formulations can affect the oxidation properties of the formulations.

[00159] Electrochemically generated superoxide solutions in the above ranges are more stable than those solutions generated from bulk chemicals. Superoxide solutions produced from bulk chemicals, at modestly alkaline pH's, i.e. 10-12.5 pH, contains HOOH in equilibrium with NaOOH, causing the bulk chemical superoxide solutions to have less stability. In contrast, electrochemically generated superoxide solutions at pH greater than about 12.5 can be made to initially contain HOO⁻ (e.g., NaOOH), which in the presence of only O₂⁻ (e.g., NaO₂) and HO⁻ (e.g., NaOH) produces more stable solutions. Upon adding a proton source, such as an acid, the degradation of electrochemically generated superoxide solutions accelerates.

[00160] In alternate embodiments, hydrogen peroxide may be added from an independent source including bulk chemical concentrate production as described in conjunction with FIGS. 1-4. Superoxide solution 1124 may then be used as formed, or stored in holding tank 1116(1). Co-generated acid is stored in holding tank 1116(2). Hydrogen peroxide addition from an independent source facilitates adjustment of the molar ratio of superoxide to hydrogen peroxide in formulations.

[00161] In step 1204, the superoxide solution 1124 is combined with additives 1110, such as salts, co-solvents, or surfactants to increase lifetime and working time of superoxide formulations; the resulting solution may then be distributed to its point of use. In step 1206, superoxide solution 1124 is combined with additives concentrate 1126 to adjust the pH level of the superoxide for pH sensitive applications such as groundwater and soil remediation. The initial pH can range from pH 8 to pH 13. A preferred initial pH range is pH 9 to pH 12. As the superoxide solution reacts and is consumed, the pH decreases, as shown by the superoxide data examples below, leaving a final pH closer to neutral. In step 1208, the superoxide solution 1124 is diluted with makeup water 1104(2) for concentration sensitive applications.

[00162] In step 1210, the electrochemical reactor 1114 creates an output of both hydrogen peroxide and superoxide; method 1200 then generates the hydroperoxyl radical and hydroxyl radical according to the Equations 4-7 below.



Wherein the Haber-Weiss reaction of Equation 4 between superoxide radical anion and hydrogen peroxide form excited state (singlet) molecular oxygen, hydroxyl radical and

hydroxide anion. Hydroxyl radicals will react with an excess of hydrogen peroxide in an equilibrium reaction forming water and the hydroperoxyl radical as shown below in Equation 5:



In one embodiment, hydroperoxyl radicals further subsequently react with excess hydrogen peroxide to form water, ground state molecular oxygen and hydroxyl radical as shown below in Equation 6:



[00163] In step 1210, as the superoxide solution 1124 pH decreases the population of hydroperoxyl radical increases via the equilibrium in Equation 7 below:



In one embodiment, hydroxyl radical evolution is most relevant at lower concentrations of parent oxidants since hydroxyl radicals rapidly react with the parent oxidants. In one embodiment, evolved hydroxyl radicals initiate oxidation reactions which the parent oxidants are not capable of, thereby enhancing the oxidative activity.

[00164] In yet another embodiment, in step 1212, the superoxide formulation 1124 containing hydrogen peroxide may be exposed to a Fenton catalyst, Fenton-like catalyst, ultrasound, ultraviolet radiation, or thermal activation (not shown in FIG. 11) to produce radical species such as hydroxyl radicals.

[00165] Steps 1204-1212 are all optional steps as shown by the dashed outlines. The implementation of steps 1204-1212 depends on the application required. For example, pH sensitive uses such as soil and groundwater remediation require diluted superoxide solution 1124, and additional additives may be required to be combined with the solution.

[00166] In step 1214, the superoxide solution 1124, and any additional components combined in optional steps 1204-1212 are distributed to the point of use. In one embodiment, the point of use is various substrates including materials, compounds, atoms or ions (organic or inorganic) to be reduced, oxidized or degraded and microorganisms to be denatured or killed. In one embodiment, the superoxide solution 1124 is used soon after its production due to its relatively short half life determined by initial concentration, salinity, pH, temperature and other oxidants and constituents present. In another embodiment, the resulting superoxide solution as distributed as superoxide reactive oxygen species output 1122 is then used in the form of, for example, a liquid, an ice, a foam, an emulsion, a microemulsion or an aerosol applied by means

such as injection, flooding, spraying, circulation or by any other means of conveying a liquid.

[00167] In this invention, formulations containing both superoxide and hydrogen peroxide are preferably prepared by electrochemical reaction as described above. Bulk chemical mixing is not an effective method for making such formulations. Superoxide in the form of KO_2 is commercially available, but is currently a relatively expensive specialty chemical. Further, dissolution of KO_2 in water results in formation of oxygen, KOH and hydrogen peroxide making the formation of superoxide/hydrogen peroxide solutions inefficient. In contrast addition of hydrogen peroxide to electrochemically prepared mixtures of superoxide and hydrogen peroxide allows ready adjustment of the ratio of superoxide to hydrogen peroxide.

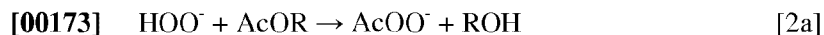
[00168] The exemplary system of Fig. 5 can be adapted and employed to prepare a superoxide + PAA formulation which generates singlet oxygen and other reactive species (S-PM formulations). In one embodiment, electrochemical reactor 514 is adapted to create two outputs including superoxide with hydrogen peroxide 524 output and acid concentrate 526 output.

[00169] In one embodiment, brine 504 is a solution that contains ions necessary for producing alkaline superoxide with hydrogen peroxide and acids in two separate streams. The brine 504 may also contain pH buffers and co-solvents compatible with the reaction process, which contribute to the reactive oxygen species output 522 formulation. For example, pH buffers include weak chemical electrolytes chosen from the group including: acetate, citrate, propionate, phosphate and sulfate.

[00170] Acetyl donor 510 (exemplified with acetyl, but acyl donor can be used) includes, but is not limited to, an acyl or acetyl donor chosen from the group including: monoacetin, diacetin, triacetin, acetylsalicylic acid, methyl benzoate, ethyl lactate and tetraacetylenediamine (TAED). In alternative embodiments, other synthetic or natural esters, mono-, di- and triacylglycerides and phospholipids having acyl substituents possessing more than one carbon can provide other types of organic peracids by the non-equilibrium reaction mechanism. Acyl or acetyl donor 510 or mixture of donors may be in liquid or solid form, or dissolved in a solvent when reacted with a solution of hydrogen peroxide. Additives concentrate 512, for example, include at least one of the following additives chosen from the group including: salts, surfactants, co-solvents, stabilizers, and emulsifiers.

[00171] FIG. 8 shows an exemplary method 800 for generating a diluted reactive oxygen species output 522 using system 500 of FIG. 5. In step 802, method 800 adapted for production of PAA + superoxide formulations generates an alkaline superoxide with hydrogen peroxide 524 output, and an acid concentrate 526 output. Acid concentrate output 526 is then stored in holding tank 518(1). In one embodiment, both output streams 524 and 526 are in concentrated liquid forms produced at a constant rate. For example, the alkaline superoxide with hydrogen peroxide 524 output may contain 0.1 wt% to 1 wt% hydrogen peroxide and 0.1 wt% to 2 wt% superoxide at pH 12.5 to 14.0. Typical alkaline hydrogen peroxide and superoxide 525 output may contain 0.2 wt% to 0.3 wt% hydrogen peroxide and 0.5 wt% to 1.2 wt% superoxide at pH 12.8 to 13.5. The acid concentrate 526 output may contain 0.1 wt% to 20 wt% depending on the concentration and composition of anolyte solution makeup 742. For example, a 20 wt% sodium acetate solution as anolyte solution makeup 742 may produce 13.5 wt% acetic acid at 85% conversion efficiency. In an alternative embodiment, an anolyte solution makeup 742 is a 5 wt% sodium sulfate solution that may produce 3.6 wt% bisulfate acid at 85% conversion efficiency.

[00172] In step 804, the alkaline superoxide with hydrogen peroxide 524 output is combined with acyl or acetyl donor 510 in mixing tank 520(1) to create alkaline superoxide with peracid concentrate 524'. In one embodiment, alkaline superoxide with peracid concentrate 524' may be superoxide with peroxyacetic acid. In one embodiment, the acyl or acetyl donor 510 is added in proportion to the hydrogen peroxide in the superoxide with hydrogen peroxide 524 output solution. In one embodiment, the molar ratio of H₂O₂ in 524 to acyl or acetyl donor 510 reactive group equivalents may range from 1:3 to 1:4. For example, a preferred molar ratio is 1:3 when the alkaline superoxide with hydrogen peroxide 524 output pH is 13.0-13.4. In one embodiment, the acyl or acetyl donor is an oxygen-acyl or oxygen-acetyl donor shown in Equation 2a below:



[00174] Where Ac is acyl [-C(O)R'] or acetyl [-C(O)CH₃] and R and R' are hydrocarbon-based substituents. In an alternative embodiment, the acyl or acetyl donor is a nitrogen-acyl or nitrogen-acetyl donor as shown in Equation 2b below:



[00176] Where Ac is acyl [-C(O)R'] or acetyl [-C(O)CH₃] and R and R' are hydrocarbon-based substituents. The acetyl donor and its reaction products and

byproducts should be compatible with, or provide synergistic behavior in combination with, superoxide.

[00177] In Equations 2a/2b above, the reaction between an acetyl or acyl donor 510 and alkaline hydrogen peroxide 524 occurs at alkaline pH by nucleophilic attack of the acyl carbonyl carbon atom by the hydrogen peroxide anion, which displaces the donor molecule fragment as an alcohol or amine in a manner analogous to saponification. In some embodiments, the non-equilibrium reactions generalized in Equations 2a/2b are conducted between pH 10 and pH 14.

[00178] A particular advantage of the use of non-equilibrium reaction in Equations 2a/2b is that peracid solutions 524" with concentrations of less than approximately 10 wt% peroxyacetic acid and other organic peracids or less than 5 wt% peroxyacetic acid and other organic peracids can be produced efficiently and rapidly. Using the non-equilibrium reaction allows the hydrogen peroxide residual to be minimized if necessary. In one embodiment, for example, the peroxyacetic acid water/peroxide concentration ratios can be 10, 100, or 1000 depending on the ratio of hydrogen peroxide to acyl or acetyl donor ratio in Equations 2a/2b. Hydrogen peroxide is less than 3% the mass concentration of peroxyacetic acid, more preferably less than 0.5% the mass concentration of peroxyacetic acid, and preferably 0% the mass concentration of peroxyacetic acid.

[00179] In one embodiment, at least one molar equivalent of acetyl or acyl donor 510 reactive groups is added for each equivalent of hydrogen peroxide in alkaline hydrogen peroxide anion solution 524 used in Equations 2a/2b to consume all of the hydrogen peroxide. In alternative embodiments, excess acetyl or acyl donor 510 reactive groups is used to minimize the hydrogen peroxide residual due to the competing conversion of acetyl or acyl donor 510 reactive groups to the corresponding carboxylic acid by the alkali in the superoxide with hydrogen peroxide 524 output. The molar ratio of hydroxide to hydrogen peroxide affects the preferred ratio of acetyl donor reactive groups to hydrogen peroxide. For example, in one embodiment, the preferred molar ratio of sodium hydroxide to hydrogen peroxide is 1:1 resulting in a preferred ratio of acetyl donor reactive groups to hydrogen peroxide of about 2:1 to ensure the preferred low HP:PAA. In another embodiment the molar ratio of sodium hydroxide to hydrogen peroxide is about 2:1 resulting in a preferred ratio of acetyl donor reactive groups to hydrogen peroxide of at least 2:1 and preferably about 2.3:1. In another embodiment, for example where the electrochemical reactor of FIG. 11 is adapted to produce alkaline HP

+ superoxide in its cathode output, the molar ratio of sodium hydroxide to hydrogen peroxide is about 4.5:1 resulting in a preferred ratio of acetyl donor reactive groups to hydrogen peroxide of at least 3:1. In the above examples the ratio of acetyl donor reactive groups to hydrogen peroxide can be increased by 2-fold or more without significantly impacting performance.

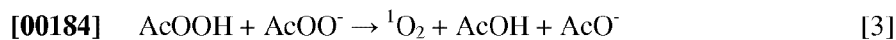
[00180] In optional step 806, as indicated by the dashed lines, method 800 entrains byproducts 528 produced by the reactions of Equations 2a/2b. In one embodiment, byproducts 528 are entrained in solution with the alkaline superoxide with peracid concentrate 524'. In one embodiment, byproducts 528 are useful as co-solvents, pH buffers, chelating agents or stabilizers and carbon substrates for microbial processes after a chemical oxidation process. For example, the byproduct 528 of acetyl donors 510 of monacetin, diacetin and triacetin is glycerol, a potential co-solvent and favorable carbon source for microbes. In another embodiment, byproduct 528 of acetyl donor 510* of TAED, diacetylenediamine, acts as a chelating agent for transition metal ions and potentially serves as a peroxide stabilizer. In yet another embodiment, byproduct 528* is the carboxylic acid produced after alkaline peracid concentrate 524' reacts with a material or decomposes. Alternatively, acetic acid, a byproduct 528 of peroxyacetic acid, serves as a co-solvent, a pH buffer, a chelating agent, and a biological substrate.

[00181] In step 808, the resulting alkaline superoxide with peracid concentrate 524' is then diluted with makeup water 502(2) introduced by pump 516(2) to create a diluted superoxide with peracid 524" to nearly the point of use concentration and is stored in holding tank 518(2)*. In optional step 810, as indicated by the dashed outline, additional additives concentrate 512 is combined with diluted peracid 524" and then stored into holding tank 518(2).

[00182] In step 812, the diluted superoxide with peracid 524" solution pH is adjusted, by combining diluted superoxide with peracid 524" with created acid concentrate 526, to the activated pH level for producing reactive oxygen species output 522*. The resulting reactive oxygen species output 522 is then distributed to its point of use in liquid form. The reactive oxygen species output 522 may then be used in the form of a liquid, an ice, a foam, an emulsion, a micro-emulsion or an aerosol applied by means such as injection, flooding, spraying, circulation or any other means of conveying a fluid. In one embodiment, the diluted superoxide with peracid 524" solution pH does not

require the addition of acid concentrate 526 and is ready for immediate distribution to its point of use.

[00183] In one embodiment, during step 812, an acid concentration 526 is combined with diluted superoxide with peracid 524" such that there is a population of both peracetic acid and peracetic acid anion which react together to generate singlet oxygen according to Equation 3 below:



[00185] Wherein the reaction rate for Equation 3 above follows a second order kinetics and is maximized when the ratio of the two forms of peroxyacetic acid is equivalent at its pKa of 8.3. The evolution and release of singlet oxygen occurs over time ranging from minutes to several hours depending on the rate of reaction in Equation 3 above. In one embodiment, the evolution of singlet oxygen from peroxyacetic acid, or other organic peracid having a similar pKa, the pH is between 6 and 11, or between 6.5-9.5.

[00186] In one embodiment the diluted superoxide with peracid 524" is held in Holding Tank 518(2) less than 5 minutes to utilize the synergistic activity of superoxide combined with a peracid, singlet oxygen and other beneficial reactive species evolved in the 524" solution. The freshly-made diluted superoxide with peracid 524" exhibits a significantly higher chemical reactivity than the diluted peracid 524" [in Fig 5] solution without an elevated concentration of superoxide.

[00187] In another embodiment the diluted superoxide with peracid 524" having a pH between 6 and 11 [adjusted before entering Tank 518(2)] is held in Holding Tank 518(2) for 20 to 35 minutes before use to allow a synergistic interaction between superoxide and singlet oxygen in the presence of a peracid to evolve a new reactive chemical species, complex or formulation exhibiting a significantly elevated ORP and reduced chemical reactivity relative to the freshly-made diluted superoxide with peracid 524" and relative to the diluted peracid 524" [in Fig 5].

[00188] In optional step 814, as indicated by the dashed outline, the reactive oxygen species output 522* may further be activated by means of a Fenton or Fenton-like catalyst, ultrasound, ultraviolet radiation, or thermal activation to produce other reactive species.

[00189] The molar ratio of superoxide to hydrogen peroxide co-generated by the reactor can range from approximately 0.01:1 to 10:1. A preferred molar ratios ranges of superoxide to hydrogen peroxide is 1:1 to 6:1. Another preferred molar ratio range of

superoxide to hydrogen peroxide is 3:1 to 5:1. The molar ratio range of superoxide to hydrogen peroxide include the ranges 0.5:1 to 1.5:1, and 1.5:1 to 3:1. Electrochemically generated superoxide solutions in the above ranges are more stable than those solutions generated from bulk chemicals. Superoxide solutions produced from bulk chemicals, at modestly alkaline pH's, i.e. 10-12.5 pH, contain HOOH in equilibrium with NaOOH, causing the bulk chemical superoxide solutions to have less stability. In contrast, electrochemically generated superoxide solutions at pH greater than approximately 12.6 can be made to initially contain NaOOH, which in the presence of only NaO_2 and NaOH produces more stable solutions. Upon adding a proton source, such as an acid, the degradation of electrochemically generated superoxide solutions accelerates.

DEFINITIONS

[00190] Generally, terms used herein not otherwise specifically defined have meanings corresponding to their conventional usage in the fields related to the invention.

[00191] "Reactive Oxygen Species" means a species such as singlet oxygen, superoxide, the hydroxyl radical and the hydroperoxyl radical, for example. Reactive species are often characterized by their strong oxidizing or reducing activity, high chemical reactivity and often short or transient lifetimes in aqueous media.

[00192] An acyl group, as known in the art, is a $-\text{C}(\text{O})\text{R}'$ group, where R is generally a hydrocarbon-based group and more specifically is an alkyl group, or aryl group (e.g., phenyl or benzyl). An acetyl group is a type of acyl group where R' is a methyl group, i.e., $-\text{C}(\text{O})\text{CH}_3$. An "Acyl donor" or particularly an "Acetyl donor" functions to transfer an acyl or particularly an acetyl group, respectively, to another chemical species as shown in equations 2a and 2b above. Acyl or acetyl donors can be oxygen-acyl or oxygen-acetyl donors as shown in Equation 2a or nitrogen-acyl or nitrogen-acetyl donors as shown in Equation 2b above. "Acyl Donor" includes, but is not limited to, an acetyl donor chosen from the group including: monoacetin, diacetin, triacetin, acetylsalicylic acid, and tetraacetylenediamine (TAED). Acyl donors that are not acetyl donors include methyl benzoate and ethyl lactate. In alternative embodiments, "Acyl Donor" may include other synthetic or natural esters, mono-, di- and triacylglycerides and phospholipids having acyl substituents possessing more than one carbon which provide other types of organic peracids by the non-equilibrium reaction mechanism. An "Acyl donor" may be capable of reacting to transfer one or more acyl groups.

[00193] “Parent Oxidant” is generally defined as an oxidant, which may constitute a majority or minority of the oxidant in a formulation, from which other Reactive Oxygen Species or Other Reactive Species are derived from. There may be more than one parent oxidant present in an oxidizing solution. The Parent Oxidant can transform or re-speciate in the presence of Reactive Oxygen Species or Other Reactive Species; or the Parent Oxidant can form complexes, clusters, ion pairs, hydrogen bonds or other associations with Reactive Oxygen Species or Other Reactive Species which provide synergistic properties including enhanced stability or lifetime and increased activity or decreased activity towards chemical and biological substrates.

[00194] “Reactive Oxygen Species” include hydroxyl radical, superoxide, hydroperoxyl radical, hydrogen trioxide and singlet oxygen.

[00195] “Other Reactive Species” include trioxyacetic acid, trioxyorganoacids, organo-peroxyl radicals, acyl radical, methyl radical, carboxyl radicals, and other radicals depending on the parent oxidant composition, structure and reactivity.

[00196] “Catalyst” includes transition metal ions, complexes, oxides, mixed-valence compounds, halides, sulfides, particles and surfaces. Transition metals include copper, iron, manganese, and any other suitable metal with chemical reactivity towards a Parent Oxidant leading to the formation of Reactive Oxygen Species and Other Reactive Species. Catalyst can be used to activate generation of reactive oxygen species.

[00197] “Activating Materials” includes Catalysts, chemical compounds, oxidants and other materials that react with the parent oxidant in a manner that produces Reactive Oxygen Species and Other Reactive Species.

[00198] “Activation event” or “Activation method” are events or methods that generate one or more reactive oxygen species. An activation event can be adjustment of pH to a selected range or the addition of an activating material. An activation method can be irradiation with electromagnetic radiation or application of ultrasound, among others.

[00199] “Ultraviolet Light” includes any wavelength of light or combination of wavelengths of light suitable for activating or cleaving a peroxide’s oxygen-oxygen bond, oxygen-hydrogen bond, or oxygen-carbon bond thereby producing reactive radicals including hydroxyl radical, superoxide, hydroperoxyl radical organo-peroxyl radicals, acyl radical, carboxyl radicals, and other oxygen-centered or carbon-centered radicals depending on the parent oxidant composition, structure and reactivity.

[00200] Other possible activation methods:

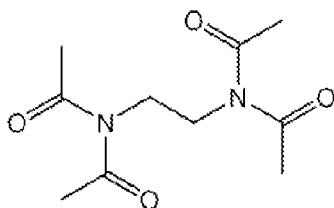
[00201] Other types of radiation can perform similarly to ultraviolet light activation, including ultrasound, sonic cavitation and microwave (sonic and electromagnetic energy).

[00202] Activation can also be conducted by energy transfer from a material (e.g., a photo-activated dye or an activated semiconductor surface activated by light or electrical field).

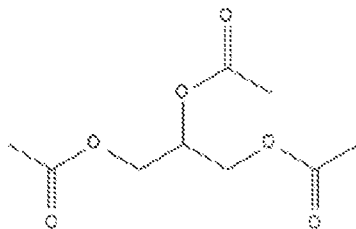
[00203] Thermal activation can be used as is practiced in wet peroxide oxidation processes.

[00204] Synergistic benefits of the activated PeroxyMax systems are demonstrated in comparative ORP measurements, oxidation experiments (e.g., MB oxidation assays) and biocidal data.

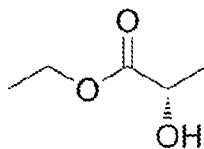
[00205] "Reactive groups" in association with "acetyl donor" distinguish between those acetyl or acyl groups that will react with alkaline hydrogen peroxide and those that are non-reactive. One example is TAED, shown below, where only two of the four acetyl groups are reactive.



Another example is triacetin, shown below, where all three acetyl groups are reactive.



Yet another example is ethyl lactate, shown below, where only one group is reactive.



[00206] "Additives concentrate" or "Additives" means any additional substance added to the chemical formulations described herein. "Additives concentrate", or "additives" includes, for example, at least one of the following additives chosen from the group including: salts, surfactants, co-solvents, stabilizers, emulsifiers, mineral acids,

organic acids, alkali, pH buffers, non-oxidizing molecules, ionized molecules and ionized atoms.

[00207] "Alkali concentrate" or "Alkali" includes any alkali material. In a preferred embodiment, alkali concentrate is an aqueous sodium hydroxide solution, or an aqueous potassium hydroxide solution.

[00208] "Salts" include, for example, at least one salt chosen from the group including: lithium, sodium and potassium chloride; lithium, sodium and potassium sulfate; calcium chloride or magnesium sulfate below pH 9; and lithium, sodium and potassium salts of acetate, citrate, propionate, phosphate and polyphosphates.

[00209] "Surfactants" may be anionic and nonionic for charge compatibility and include at least one surfactant chosen from the group including: sulfonic acid salts, alcohol sulfates, carboxylic acid salts, fatty acids, polyether alcohols and sodium dodecyl sulfate.

[00210] "Co-solvents" include, for example, at least one co-solvent chosen from the group including: alcohols such as methanol, ethanol, propanol, propylene glycol, glycol ethers, glycerol, ethyl lactate, soybean oil, vegetable oil, sunflower oil, peanut oil and guar gum.

[00211] "Stabilizers" include, chemical species which may be organic or inorganic which function to stabilize a reactive species of the formulations herein. A given stabilizer may be selected to stabilize a parent oxidant, such as PAA or superoxide. A stabilizer may be selected to stabilize a reactive oxygen species such as single oxygen. Such stabilizers of parent oxidants or reactive oxygen species are particularly useful when formulations or formulation precursors containing parent oxidant are to be stored or held before activation or before use. It will be appreciated that stabilizers are intended for temporary stabilization during such storage or to reduce the rate of reactivity, if desired for a given application, as the reactive species in the formulations herein are intended to react when activated to form other reactive species or to be active for their application. A stabilizer can be chosen from the group including: phosphoric acid, phytic acid, tetrasodium pyrophosphate, sodium hexametaphosphate, sodium tetrametapyrophosphate, organic phosphates, ethylenediamine tetraacetic acid and citric acid, chelating agents, and saline water. Useful organic phosphonates, include diethylenetriamine-NNN'N"N"-penta(methylphosphonic acid) commercially available as Dequest[®] 2060S. A stabilizer may be a peroxide stabilizer. Chelating agents which function to chelate metals which may be present in water, soil or other substrates to be

treated may be used to protect formulations from undesired reaction with metals. It will be appreciated by those of ordinary skill in the art that dilution, pH adjustment or lowered temperature can function to stabilize parent oxidants and reactive oxygen species.

[00212] "Emulsifiers" include, for example, at least one foaming and antifoaming agents chosen from the group including: surfactants, oils, co-solvents and polymers including polyethylene glycol.

[00213] "Foaming" and "antifoaming agents" include, for example, surfactants, oils, co-solvents and polymers including polyethylene glycol.

[00214] "Byproducts" means any additional substance that results from a chemical reaction. Byproducts may be useful as co-solvents, pH buffers, chelating agents or stabilizers and carbon substrates for microbial processes after a chemical oxidation process. For example, the byproduct of monoacetin, diacetin and triacetin is glycerol, a potential co-solvent and favorable carbon source for microbes. Another example is the byproduct of TAED, diacetylenediamine, which can act as a chelating agent for transition metal ions and potentially serve as a peroxide stabilizer. Another example of a byproduct is the carboxylic acid produced after a peracid reacts with a material or decomposes. Acetic acid, a byproduct of peroxyacetic acid, can serve as a co-solvent, a pH buffer, a chelating agent, and a biological substrate.

[00215] Oxygen-based oxidants have a wide variety of oxidation potentials, reaction pathways, and oxidation kinetics depending on what reactive materials are present and the conditions under which they are used. Because of these differences the oxidation products and oxidation byproducts will vary between oxidant type, amount used and other conditions such as pH and temperature. Oxidation products of organic materials are typically organic acid fragments, small organic acids, alcohols and substituted alkanes. Complete mineralization of organic materials to carbon dioxide and water can occur. Often, the organic oxidation products are more readily consumed by biological activity than the original materials. Oxidation using formulations containing reactive oxygen species of this invention can, for example, in an embodiment by at least partial oxidation, facilitate biodegradation of organic materials.

[00216] Formation of other undesirable or regulated oxidation byproducts will depend on both the oxidant and the reactive material(s) present that may be oxidized. Organic materials possessing nitrogen atoms may be oxidized and release nitrate as a byproduct. This is a particular issue during the oxidation of natural organic material

(NOM) such as humic substances and reduced hydrocarbons from conventional oil reservoirs, oil sands and natural gas shales.

[00217] "Hydrogen Peroxide Concentrate" typically means an aqueous hydrogen peroxide solution. However, in alternative embodiments, hydrogen peroxide concentrate may include other chemical forms of hydrogen peroxide chosen from the group including: calcium peroxide, potassium peroxide, sodium peroxide, lithium peroxide, percarbonates, and perborates.

[00218] "Brine" contains ions necessary for producing alkaline hydrogen peroxide and acids in two separate fluid streams, for example. Brine may also be formulated to contain pH buffers and co-solvents compatible with the generation process, which contribute to the hydrogen peroxide solution formulation.

Oxidative Reduction Potential (ORP)

[00219] The oxidative reductive potential (ORP) is a measure of how oxidizing or reducing a solution is relative to a standard reference potential measured in volts. Standard reference potentials are measured relative to the hydrogen/hydrogen ion reduction-oxidation potential of 0.000 V at unit activity for the standard hydrogen electrode (SHE). Generally, solutions with potentials greater than 0 V vs SHE are considered oxidizing (electron accepting) while solutions with potentials less than 0 V vs SHE are considered reducing (electron donating). The measured ORP of water is influenced by its pH or hydrogen ion activity. As the hydrogen ion activity (e.g., concentration, temperature) increases, the ORP of water increases to more positive values. ORP is also influenced by the presence of reducing or oxidizing agents relative to their standard reduction-oxidation potentials and solution activities.

[00220] Standard oxidation potentials are often cited to compare the oxidative strength of oxidants (Table 1). The standard potential is a thermodynamic value which is always lower than the measured ORP in solution. This difference is caused by kinetic factors, such as the overpotential or activation barrier of electron transfer at an electrode surface and the solution activity of the oxidant, which is proportional to the concentration. Neither the standard potential nor ORP reflect the chemical reactivity of an oxidant regarding its reaction mechanism with a substrate, which is an additional kinetic factor.

[00221] For example, according to the standard potentials (Table 1) hydrogen peroxide is a stronger oxidant than hypochlorous acid. However, the ORP of hypochlorous acid (29 mM) at pH 7 is over 1.1 V (SHE)m while the ORP of hydrogen

peroxide (29 mM) at pH 7 is about 0.5 V (SHE) indicating that hypochlorous acid is the stronger oxidant. Free radicals of chlorine are strong electron acceptors and also rapidly attack and substitute unsaturated and aromatic hydrocarbons, amines, thiols, aldehydes, ketones, and biological materials such as DNA and proteins. Hydrogen peroxide is a strong electron acceptor, but it is not a free radical and is less chemically reactive than chlorine. This difference in chemical reactivity is reflected in the ORP. In practice, chlorine is used as a broad-spectrum biocide in water treatment whereas hydrogen peroxide is not. Hydrogen peroxide can be activated to form highly reactive free radicals (i.e., hydroxyl radical, superoxide) in various ways, e.g., by addition of a catalyst or irradiation with ultraviolet light.

[00222] Table 1: Standard Potentials of Oxidants (values at pH 7 unless noted)

Oxidant	Standard Potential (V)
Hydroxyl Radical	2.80
Ozone Gas	2.07
Ozone (pH 0)	2.08
Ozone (pH 14)	1.24
Sodium Peroxodisulfate (pH 0)	2.12
Sodium Persulfate (peroxodisulfate)	2.0
Oxone (peroxymonosulfate)	1.82
Caro's Acid (pH 0)	1.81
Peroxyacetic Acid	1.81
Hydrogen Peroxide	1.78
Hydrogen Peroxide (pH 0)	1.80
Hydrogen Peroxide (pH 14)	0.87
Potassium Permanganate	1.68
Hypochlorous Acid	1.61
Hypobromous Acid	1.57
Chlorine Dioxide	1.57
Chlorine Dioxide (pH 0)	0.93
Chlorine Gas	1.36
Oxygen Gas	1.23
Bromine (aq)	1.07
Hypochlorite	0.81
Hypobromite	0.76
Singlet Oxygen	0.65
Superoxide	-0.33

[00223] ORP is used as a general measure of the antimicrobial strength of a solution containing an oxidizing antimicrobial agent, biocide or disinfectant. ORP can be correlated to relative oxidant concentration for lower oxidant concentrations at

constant pH and temperature. This feature is the basis for ORP monitoring systems sometimes used in water treatment and disinfection processes where oxidant dose can be adjusted to maintain a desired ORP and corresponding biocidal activity for a particular oxidant.

[00224] Water solutions containing oxidizing biocides which have ORP's of greater than about 650 mV (SHE) are generally considered to be suitable for disinfection (Suslow, T. "Oxidation-Reduction Potential (ORP) for Water Disinfection Monitoring , Control , and Documentation" Univ. California Publication 8149 <http://anrcatalog.ucdavis.edu>) while ORP's above about 800 mV (SHE) are suitable for sterilization. Below about 475 mV (SHE) there is typically little to no biocidal activity for oxidizing biocides even after long contact times. Known exceptions to these ORP benchmarks include in-situ generation of short-lived reactive oxygen species such as hydroxyl radical, by ultraviolet-activated hydrogen peroxide, or singlet oxygen, by dye-sensitized photo-activation of molecular oxygen.

[00225] There are several limitations to ORP measurement as a method for evaluating antimicrobial activity. ORP is not sensitive to very short-lived reactive oxygen species such as hydroxyl radicals, singlet oxygen, hydrogen trioxide and hydroperoxide radical in the presence of parent oxidants such as, for example, hydrogen peroxide, peroxyacetic acid, molecular oxygen and ozone. ORP is not sensitive to non-oxidizing biocides and chemical reactivity which impart other mechanisms for disrupting cellular viability. Examples of non-oxidizing chemical biocides include glutaraldehyde, which acts by crosslinking protein structures, and antimicrobial quaternary ammonium compounds, which disrupt cell membranes. ORP is also insensitive to the tolerance of various microorganisms to a given biocide, which affects the concentration and contact time required to inactivate or destroy a specific microorganism. For example, chlorine use in water treatment is not effective against certain spores (e.g., *Cryptosporidium* oocysts) while chlorine dioxide and ozone are.

[00226] In the present invention the production of reactive oxygen species including singlet oxygen in the absence of hydrogen peroxide, production of superoxide by electrochemical generation and the combining of these reactive oxygen species in the presence of hydroperoxides is conducted to produce liquid formulations with enhanced ORP's and oxidation capabilities.

Applications of Reaction Oxygen Species Formulations

[00227] The invention provides methods of oxidation which employ reactive oxygen species formulations as described herein. The oxidation method includes application of one or more selected reactive oxygen species formulations to an environment, a substrate in an environment or to a substrate that is to be subjected to oxidization. The terms environment and substrate are used herein broadly to refer to a place, a material, a chemical and/or a biological species that is to be subject to at least partial oxidation. The environment can be, among others, water in situ, for example, ground water, a pool, a pond, a tailing pond, an area of contaminated soil, industrial processing equipment (e.g., pipes, pumps, tanks and other container, filters, etc. to be cleaned in place). A substrate can be any item or place that are to be oxidatively cleaned for example, containers, tanks, pipes, counter tops, appliances, food preparation surfaces and equipment, food and beverage containers, filters, food items during food processing, that are subjected to oxidative cleaning. In specific embodiments, the substrate is water containing undesirable chemical or biological species that are to be at least in part removed by oxidative treatment. Water to be treated includes waste water, greywater, raw water, ground water, tailing pond water, refinery waste water, frac flowback water, produced water, water from oil sands extraction processes, various industrial and food processing waters. In an embodiment, the environment or substrate is contaminated with higher than desirable levels of microorganisms wherein the environment or substrate is to be disinfected. The reactive oxygen species formulations can be used as antimicrobial agents, disinfectants and biocides. For example, the formulations can be used for cleaning and disinfection of medical or dental equipment, food processing equipment, containers and surfaces.

[00228] The formulations of the invention can be used in various applications as oxidants and/or biocides. As described herein, different formulations, as assessed by ORP measurement and dye oxidation rate among other properties, can exhibit enhanced activity as a chemical oxidant or as a disinfectant or biocide.

[00229] The invention provides uses of the reactive oxygen species formulations herein for various industrial or domestic oxidation, clean up and disinfection applications.

[00230] Exemplary non-limited applications of formulation of the invention include: general industrial clean up, clean in place applications, equipment cleaning, water treatment, soil treatment and decontamination, cleaning for packing and bottling, fruit, vegetable and other food processing (e.g., meat and fish) cleaning and disinfection

applications, food preparation cleaning and disinfection applications, medical and dental equipment clean up and disinfection; or bleaching applications to pulp and paper, textiles or in laundry or related applications.

[00231] More specific applications include without limitation, Frac flowback water treatment and reuse; produced water treatment, refinery wastewater treatment, oilsands extraction and process water treatment; process water cleaning and reuse, waste water treatment, mine water treatment, cooling tower cleaning, cleaning/disinfections of water wells, pipes and containers, flue gas scrubbing water treatment, textile dye recycle and waste water treatment, pulp and paper processing waste water treatment and recycle, specialty bleaching applications, clean in place applications in food and beverage processing, water filter cleaning, membrane clean up, more general in situ antimicrobial filter cleaning and disinfection, cleaning and disinfection of vehicles, cleaning and disinfection in food preparation services.

[00232] Formulations of the invention can be used in various antimicrobial, disinfection and biocide applications including without limitation: fruit and vegetable washing, meat and fish processing and storage, food equipment clean up, water disinfection and maintenance, pool cleaning and disinfection applications.

[00233] In various water and soil applications, it can be desirable to employ biological treatment processes for removal of organic contaminants. In specific embodiments, for decontamination applications, particularly as applied to water and soil treatments, one or more oxygen reactive species formulations of the invention are employed to provide at least partial oxidation of more recalcitrant organic contaminants, for example, with certain activated formulation of the invention prior to application of known biological treatment processes to allow for more rapid treatment of smaller organics in the biological treatment process. In a water treatment, contact of the water with the formulations of the invention or activated formulations of the invention can be configured upstream of a biological treatment process.

[00234] Reactive oxygen species formulations can be employed as an antimicrobial agent or oxidizing agent for treatment of water, including without limitation, process streams or waste streams. Reactive oxygen species formulations can be used in water treatment: to cause chemical transformation or degradation of components or contaminants; to promote or enhance flocculation, micro-flocculation, coagulation and subsequent clarification and separation of inorganic and organic materials; to promote or enhance biological treatment processes; to promote or enhance

wet peroxide oxidation processes; as a pretreatment, intermediary treatment or post treatment process to other treatment and separation processes.

[00235] In water treatment processes, the chlorine-free and bromine-free reactive oxygen species formulations of the invention can be used to provide for treatment without formation of undesired chlorinated or brominated byproducts. In water treatment processes, the chlorine-free and bromine-free active oxygen species formulations of the invention can be used to provide for treatment in the absence of chlorine dioxide and/or ozone.

[00236] In water treatment process, the reactive oxygen species formulations of the invention can be used in place of or in combination with wet peroxide oxidation or ultraviolet (UV) light-activated advanced oxidation processes (AOP).

[00237] For applications of the formulations herein the formulation is contacted with a substrate or environment to be oxidized or treated. Any means of contacting can be employed, that is suitable for retention of the oxidation activity of the formulation and that is suitable for the environment and/or substrate. Formulations are liquid and can be employed in a concentrated form or a diluted form. Formulations can be diluted, if desired, before, during or after initial contact. The concentration of formulations in contact with an environment and/or substrate may be varied during contact.

[00238] A given application may employ separate contacting events which may be the same or different and which may employ the same formulation or precursor formulation. A given application may employ contact with more than one formulation or precursor thereof. The environment and/or substrate can, for example, be contacted with an activated liquid formulation containing reactive oxygen species. Alternatively, the environment and/or substrate can be contacted with a liquid precursor formulation that will generate reactive oxygen species on activation and the formulation is activated as or after it comes into contact with the environment or substrate.

[00239] For example, the environment or substrate may itself provide for activation, such as a pH adjustment to the activation pH. One or more additional steps of activation to form additional reactive species can occur after the contact of the formulation or the precursor formulation with the environment and/or substrate. For example, steps of pH adjustment may occur after contact between the formulation and the environment or substrate. Contact with the environment or substrate may be controlled by addition of a selected volume or concentration of formulation or its

precursor to the environment or in contact with the substrate. Alternatively, contact can occur by addition, including controlled addition of the substrate to the formulation or a precursor thereof.

[00240] The time between formulation activation and contact can be controlled. The timing of additional steps of activation can be controlled with respect to initial contact, initial activation or other steps of activation.

[00241] Contact can be combined with stirring or other agitation, with scrubbing, scrapping or other abrasive method if appropriate for the environment and/or substrate. Contact may be combined with removal of flocculant, precipitant or other solids present or formed in the environment or on contact with the substrate. The environment or substrate may be pre-treated prior to contact. The treated environment to substrate may be subject to another form of cleaning or disinfection.

[00242] When a Markush or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure. Every formulation or combination of components described or exemplified can be used to practice the invention, unless otherwise stated.

[00243] Without wishing to be bound by any particular theory, there can be discussion herein of beliefs or understandings of underlying principles relating to the invention. It is recognized that regardless of the ultimate correctness of any mechanistic explanation or hypothesis, an embodiment of the invention can nonetheless be operative and useful.

[00244] One of ordinary skill in the art will appreciate that process methods (adding, mixing, dispensing, etc.), device elements, materials (e.g., salts, acids, bases, etc.), analytical and spectroscopic methods, and system configurations other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such methods, device elements, materials, and configurations are intended to be included in this invention. Whenever a range is given in the specification, for example, range of ratios, a temperature range, a time range, or a composition range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure.

[00245] The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such

terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[00246] References provide additional description of device and system elements, for example, electrochemical reactors, processes for use of such device and system elements and additional applications of the process and formulations of the invention.

EXAMPLES

Example 1: Cogeneration of Alkaline Hydrogen Peroxide and Citric Acid

[00247] A reactor system with the reactor of FIG. 6A and fluid process flow illustrated in FIG. 4 was used in this example. The cathode's active superficial area was approximately 255 cm². The anolyte reservoir and chamber were charged with a 10% weight to volume solution of trisodium citrate in distilled water. A filtered compressed air stream was fed into the gas feed line at a rate of 5 liters per minute at 1.3 psig. A solution of 0.05 molar sodium sulfate and 0.01 molar sodium chloride in distilled water was fed into the catholyte feed line at a rate of 13 mL per minute at approximately 1.0 psig. A DC current was applied to the reactor at 5.0 amps and 4.55-4.65 volts. The catholyte output reached a steady state composition of 720 mg/L hydrogen peroxide with a pH of 12.4 (pH measured at a 20-fold dilution) within twelve minutes of applying the electric current and remained there at ambient temperature near 15 degrees centigrade until the process conditions were changed after 29 minutes. The air feed rate was then increased to ca. 15 liters per minute at 2 psig. The catholyte inlet pressure increased to 1.5 psig. The DC current was maintained at 5.0 amps while the voltage increased to 4.74 volts. The catholyte output reached a new steady state composition of 1040 to 1080 mg/L hydrogen peroxide at a pH of 12.3 (pH measured at a 20-fold dilution) within five minutes of changing the air feed rate until the reactor was shut down after 46 minutes.

[00248] To the existing catholyte feed was added 0.001 molar trisodium citrate and the reactor restarted under the previous process conditions and nearly the same catholyte output was achieved at 1000-1080 mg/L hydrogen peroxide at a pH of 12.3 decreasing to 12.0 (pH measured at a 20-fold dilution) during the first 35 minutes of operation. While maintaining the current at 5.0 amps (air feed was reduced to 5 liters per minute at 46 minutes) the pH of the catholyte output continued to decrease to a pH of 10.2 (not diluted) at 2 hours 25 minutes when the system was shut down. The anolyte solution was drained from the reactor and had a pH of 2.5 indicating the production of citric acid.

Example 2: Generation of Hydrogen Peroxide by Cogeneration of Alkaline Hydrogen Peroxide and Sulfate Acids

[00249] A reactor system with the reactor of FIG. 6A and fluid process flow illustrated in FIG. 4 was used in this example. The cathode's active superficial area was approximately 255 cm². The anolyte reservoir and chamber were charged with a 1.9 L solution of 0.25 molar sodium sulfate in distilled water, initial pH = 9.5. A ca. 93% oxygen gas stream generated by a pressure swing adsorption oxygen concentrator was circulated through the gas feed line at a rate of 14.5 liters per minute at 2.9 psig. A 0.02 molar solution of sodium sulfate in distilled water was fed into the catholyte feed line at a rate of 12.8 mL per minute at 1.5 psig. A DC current was applied to the reactor at 7.0 amps and 3.7 volts between anode and cathode posts. The catholyte output reached a steady state composition of 2400 to 2450 mg/L hydrogen peroxide at a pH of 12.5 within twenty minutes of applying the electric current and remained there with an output product temperature of 19 to 20 °C until about 60 minutes. Over the following 75 minutes the hydrogen peroxide output concentration decreased to about 2000 mg/L with a pH of 12.5 and temperature increasing to 21 °C. The process was shut down after a total operating time of 135 minutes. The total collected hydrogen peroxide product stream had a volume of 1.7 L with a measured composition of 2300 mg/L hydrogen peroxide at pH 12.5. The anolyte was removed from the reactor with a volume of 1.8 L and a measured pH of 1.42 indicating conversion of sodium sulfate to its acid forms. The hydrogen peroxide and anolyte product streams were combined producing a pH neutralized product with a measured composition of 1050 mg/L hydrogen peroxide at a pH of 9.8, 0.2 pH units higher than the starting anolyte solution, and a calculated sodium sulfate content of 0.15 M.

Example 3: Cogeneration of Alkaline Hydrogen Peroxide and Sodium Hypochlorite

[00250] A reactor system with the reactor of FIG. 6A and fluid process flow illustrated in FIG. 4 was used in this example. The cathode's active superficial area was approximately 255 cm². The anolyte reservoir and chamber were charged with a 1.8 L solution of 0.25 M sodium hydroxide and 0.067 M sodium chloride in distilled water, initial pH = 13.2. A ca. 93% oxygen gas stream generated by a pressure swing adsorption oxygen concentrator was circulated through the gas feed line at a rate of 14.5 liters per minute at 3.0 psig. A 0.02 M solution of sodium sulfate in distilled water was fed into the catholyte feed line at a rate of 12.8 mL per minute at 1.7 psig. A DC current was applied to the reactor at 7.0 amps and 2.7 volts between anode and cathode posts. The catholyte output reached a steady state composition of 2300 to 2450 mg/L hydrogen peroxide at a pH of 12.6 within twenty minutes of applying the electric current and remained there with an output product temperature of 19 to 21 °C until the process was shut down after 138 minutes of operation. The final output pH had decreased slightly to 12.5. The total collected hydrogen peroxide stream had a volume of 1.7 L with a measured composition of 2350 mg/L hydrogen peroxide at pH 12.6. The anolyte was removed from the reactor with a volume of 1.75 L and a measured pH of 12.0. The total chlorine content was measured to be near 40 mg/L +/- 10 mg/L.

Example 4: Superoxide Production

[00251] Evidence for enhanced superoxide production was observed using the electrochemical reactor of FIG. 6A and process flow of Fig. 7. At 5 amps a relatively low hydrogen peroxide production current efficiency of less than 60% is accompanied by a lower than normal pH (e.g., 2000-2400 mg/L hydrogen peroxide and pH 12.40). As the current density is increased to 8 amps, the hydrogen peroxide production current efficiency decreases rapidly to less than 40% and the pH decreases by at least 0.1 pH units (e.g., 2600 mg/L hydrogen peroxide and pH 12.26). This change of efficiency at high current is explained by production of superoxide. If the loss of hydrogen peroxide production efficiency were due to current going into the four electron reduction of molecular oxygen as shown in Equation 8 below, or into the splitting of water as shown in Equation 9 below, then a significant amount of hydroxide would have been generated thereby raising the pH significantly. This was not observed.





Furthermore, significant electrolytic splitting of water at the cathode would require a larger overpotential at the cathode (ca. 0.5 V more negative) and be reflected in a higher cell voltage. However, the cell voltage remained unchanged relative to higher efficiencies as in the examples above. Based on these data, substantial reaction by Equation 8 or 9 does not appear to occur.

[00252] Additional evidence in support of superoxide production is the decoloration of methylene blue (MB) dye with the fresh cathode output solution produced with the above characteristics. A 25 mg/L solution of methylene blue can be decolorized to the eye, partially within minutes and completely within 5 hours of mixing with the aforementioned freshly produced cathode product (e.g., 2600 mg/L hydrogen peroxide and pH 12.26). The decoloration of methylene blue does not occur on this time scale or at all when using catholyte product aged for at least 24 hours or using store bought hydrogen peroxide to make a simulated catholyte product in control experiments. The decoloration of methylene blue dye is thought to be caused by or at least initiated by the direct action of generated superoxide or by the evolution of hydroxyl radicals via the Haber-Weiss reaction in Equation 4, below, over time relative to the control experiments.



Example 5: Generation of Singlet Oxygen Using Bulk Chemical Precursors:

[00253] A generation system from FIG. 1 and associated method from FIG. 2 was used to producing a singlet oxygen precursor formulation using bulk chemical precursors. A 30 g/L aqueous hydrogen peroxide solution 102 is pH adjusted with sodium hydroxide alkali concentrate 104 to pH 12.0 to 12.4, using approximately 50 g sodium hydroxide per liter of 30 g/L hydrogen peroxide. The resulting alkaline hydrogen peroxide solution is mixed 120(1) and reacted with an acetyl donor 106, triacetin in a ratio of 128 g triacetin per liter of alkaline hydrogen peroxide solution. The resulting alkaline peracid concentrate 122' will contain approximately 65 g/L peroxyacetic acid and 0.9 g/L hydrogen peroxide, assuming 97 % conversion of the hydrogen peroxide to peroxyacetic acid. The resulting alkaline peracid concentrate 122' will also contain about 54 g/L glycerol byproduct 124.

[00254] The peroxyacetic acid concentrate is then diluted to its point of use concentration before or during pH adjustment to minimize losses resulting from accelerated peroxyacetic acid decomposition at higher concentrations when in its

activated pH range. In the present example, the above peroxyacetic acid concentrate is diluted to 1.5 g/L, a dilution factor of 41.5 times. The peroxyacetic acid solution is diluted with 40.5 L of make up water 108 (e.g., fresh water or salt water) and then mixed with an acid concentrate 112 necessary for adjusting the pH to activate singlet oxygen evolution, where an initial pH range is between pH 8 and pH 9. For example, 12 g hydrochloric acid (100% base) is added per 1 L of concentrate. Additionally, other additives may be added to the solution by combining them with water 108 used to dilute alkaline peracid concentrate 122', for example, additives can include, for example, sodium or calcium chloride, tetrasodium pyrophosphate, sodium lauryl sulfate and/or glycerol.

[00255] For the above exemplary singlet oxygen precursor formulation the hydrogen peroxide stock solution, alkali types, and acid types and other additives including salts, surfactants, co-solvents, stabilizers, and emulsifiers can be substituted with compatible alternatives known in the art to accommodate specific application requirements. The resulting singlet oxygen reactive oxygen species output 116 may then be used in the form of a liquid, an ice, a foam, an emulsion, a microemulsion or an aerosol applied by means such as injection, flooding, spraying, circulation or by any other means of conveying a fluid.

[00256] The above Example 5 may also be implemented using the system of FIG. 3 and method of FIG. 4, without diluting the alkaline peracid concentrate 122'.

Example 6: Singlet Oxygen from Electrochemically Generated Chemicals

[00257] A generation system from FIG. 5 and associated method from FIG. 8 was used in the present example, in an embodiment, to produce a singlet oxygen precursor formulation using an electrochemical generator. In the present example, the hydrogen peroxide, alkali, and acid may be generated electrochemically and on site as an alternative to supplying them as bulk chemicals. Alkaline hydrogen peroxide 524 and acid concentrate 526 are generated by electrochemical reduction. Electrochemical reduction of oxygen is conducted at a suitable cathode and water is oxidized at a suitable anode in an electrochemical reactor 514 in which the anode and cathode chambers are separated by a membrane. Oxygen gas 506 and a 4 g/L aqueous sodium acetate solution 504 are supplied to the cathode while 50 g/L aqueous sodium acetate solution 504 is supplied to the anode. A direct current 508 is applied to the electrodes thereby driving the reduction of oxygen at the cathode to produce hydrogen peroxide 524 and sodium

hydroxide as the majority products from the cathode while water is oxidized at the anode to produce acetic acid 526 and oxygen gas as majority products from the anode.

[00258] In this example, the cathode product solution has a composition of approximately 6 g/L hydrogen peroxide (as H_2O_2), 4 g/L sodium acetate and a pH of about 12.4 (as NaOH), assuming a 94% current efficiency for oxygen reduction to hydrogen peroxide. The anode product solution has a composition of approximately 31 g/L acetic acid and 7/5 g/L sodium acetate assuming an 85% sodium acetate to acetic acid conversion. The anode product solution volume is about 0.46 L per 1L of cathode product solution.

[00259] The alkaline hydrogen peroxide cathode product solution is mixed and reacted with an acetyl donor 510, for example, triacetin in a ratio of 25.5 g triacetin per liter of alkaline hydrogen peroxide solution 524. The resulting concentrate will contain approximately 13 g/L peroxyacetic acid 524' and 0.17 g/L hydrogen peroxide, assuming 97% conversion of the hydrogen peroxide to peroxyacetic acid. The concentrate will also contain about 11 g/L glycerol byproduct 528.

[00260] In the present example, the above peroxyacetic acid concentrate 524' is diluted to 1.5 g/L, a dilution factor of 8.7 times. Dilution is achieved by diluting the acidic anode product solution with 7.24 L of water 502(2) (e.g., fresh water or salt water). Additional additives 512 can also be added, such as sodium or calcium chloride, tetrasodium pyrophosphate, sodium lauryl sulfate, and glycerol. The solution is then combined with acid concentrate 526 to produce a singlet oxygen reactive oxygen species output 522 with a pH in the range of pH 8 to pH 9.

[00261] For the above exemplary singlet oxygen precursor formulation the hydrogen peroxide stock solution, alkali types, and acid types and other additives including salts, surfactants, co-solvents, stabilizers, and emulsifiers can be substituted with compatible alternatives known in the art to accommodate specific application requirements. The resulting singlet oxygen reactive oxygen species 522 may then be used in the form of a liquid, an ice, a foam, an emulsion, a microemulsion or an aerosol applied by means such as injection, flooding, spraying, circulation or by any other means of conveying a fluid.

[00262] The above Example 6 may also be implemented using the system of FIG. 9 and method of FIG. 10, without diluting the peroxyacetic acid concentrate 524'.

Example 7: Electrochemical Generation of H_2O_2 as a "Control" for Superoxide Production Experiments (Experiments 8-9).

[00263] A reactor system with an electrochemical reactor of Figure 6 and fluid process flow illustrated in Figure 7 was used in this example. A carbon fiber cathode suitable for high efficiency hydrogen peroxide production was installed in the reactor with an active superficial area of 255 cm². The anolyte reservoir and chamber were charged with a 2.5 L solution of about 1.5 M sodium hydroxide in distilled water. The anolyte was recirculated through the anode chamber over time. A ca. 93% oxygen gas stream generated by a pressure swing adsorption oxygen concentrator at about 5 L per minute was circulated through the gas feed line and reactor by a pump at a rate of 10 liters per minute at 2.6 psig while a 5 L per minute bleed stream of oxygen gas was released from the system. The catholyte was a 0.05 M solution of sodium sulfate in distilled water adjusted to pH 11.2 with sodium hydroxide to precipitate trace magnesium in the electrolyte. The catholyte solution was fed into the catholyte feed line at a rate of 12.8 mL per minute at 1.3 psig (single pass, flow through). A DC current was applied to the reactor at 5.0 amps (current control). The negative pole of the power supply was grounded. Hydrogen peroxide concentration was analyzed by titration using a Hach Inc. HYP-1 Hydrogen Peroxide Test and pH was measured using an Oakton pH 11 Series meter with a temperature compensated double junction pH electrode.

[00264] The catholyte output reached a steady state composition of 3700 +/- 50 mg/L hydrogen peroxide and pH 12.25 +/- 0.04 at 25 to 26 °C. The current efficiency for hydrogen peroxide production was calculated to be 90.8% assuming a two electron reduction of molecular oxygen.

Example 8: Superoxide Generation Using Electrochemical Reactor

[00265] A generation system from FIG. 11 and associated method from FIG. 12 was used in the present example to show an exemplar of producing a superoxide precursor formulation using an electrochemical generator, in one embodiment. Superoxide concentrate 1124 and, optionally, acid concentrate 1126 are electrochemically generated using an electrochemical reactor 1114. Electrochemical reduction of oxygen is conducted at a suitable cathode and water is oxidized at a suitable anode in an electrochemical reactor 1114 in which the anode and cathode chambers are separated by a membrane. Oxygen gas 1106 and a 4 g/L aqueous sodium acetate solution 1104 are supplied to the cathode, while a 50 g/L aqueous sodium acetate solution 1104 is

supplied to the anode. A direct current 1108 is applied to the electrodes thereby driving the reduction of oxygen at the cathode to produce superoxide, hydrogen peroxide and sodium hydroxide as the majority products 1124 of the cathode, while water is oxidized at the anode to produce acetic acid and oxygen gas as the majority products 1126 of the anode.

[00266] In this example, the cathode product solution 1124 has a composition of approximately 3.0 g/L superoxide (as $O_2^{\cdot-}$), 3.2 g/L hydrogen peroxide (as H_2O_2), 4 g/L sodium acetate and a pH of about 12.2 (as NaOH), assuming a 90% current efficiency for oxygen reduction to superoxide and hydrogen peroxide. The anode product solution 1126 has a composition of approximately 31 g/L acetic acid and 7.5 g/L sodium acetate assuming 85% sodium acetate to acetic acid conversion. The anode product solution volume is about 0.46 L per 1 L of cathode product solution.

[00267] The superoxide-containing cathode product solution 1124 is then diluted to its point of use concentration before or during pH adjustment to minimize losses resulting from accelerated superoxide decomposition at lower pH. In this example, the superoxide is diluted to 1.0 g/L, a dilution factor of 3 times. In one example, dilution can be achieved by diluting the acidic anode product solution with 1.54 L of water (e.g., fresh water or salt water), adding other desirable additives to the diluted anode product solution and then combining the diluted anode product solution with the superoxide-containing cathode product solution. Examples of additives include sodium chloride, sodium lauryl sulfate, isopropanol and soybean oil.

[00268] Due to the decreasing lifetime of superoxide in aqueous media as the pH becomes less alkaline, non-aqueous co-solvents or emulsion compositions may be employed to improve the lifetime and activity of superoxide solution 1124. Alternatively, the alkaline superoxide-containing cathode product solution may be utilized directly, followed by pH neutralization or adjustment with the acidic anode product solution.

[00269] For the above exemplary singlet oxygen precursor formulation the hydrogen peroxide stock solution, alkali types, and acid types and other additives including salts, surfactants, co-solvents, stabilizers, and emulsifiers can be substituted with compatible alternatives known in the art to accommodate specific application requirements. The resulting singlet oxygen reactive oxygen species 1122 may then be used in the form of a liquid, an ice, a foam, an emulsion, a microemulsion or an aerosol applied by means such as injection, flooding, spraying, circulation or by any other means

of conveying a fluid. The above example may also be implemented without diluting the superoxide solution 1124.

Example 9: Dye Oxidation with Singlet Oxygen:

[00270] Methylene blue (MB) is a heterocyclic aromatic compound with the molecular formula $C_{16}H_{18}N_2S$ and is considerably resistant to oxidation. MB is a useful model dye for comparing the oxidative strengths of various oxidizers based on the rate of color loss from solutions when treated. Methylene blue dissolved in water has an intense absorption band maximum near 662 nm in the visible part of the electromagnetic spectrum resulting in its intense blue color. Observing the loss of this absorption and blue color by oxidation of the dye provides a preliminary comparison between oxidizers. Observing can be done by an observer noting color change, particularly using color standards, or by use of appropriate spectrometric measurement.

[00271] A series of MB oxidation trials were conducted near room temperature (17-22°C) by combining equal volumes of oxidant formulations with 100 mg/L MB stock solution resulting in a 50 mg/L MB initial concentration. The change in MB solution color was evaluated over time by visual comparison to a series of color standards made by serial dilution of the same 100 mg/L MB stock solution. Color standards were 50, 25, 10, 5, 1, and 0.5 mg/L MB. Color comparisons were made with test samples and color standards contained in 12 mm inner diameter Pyrex test tubes positioned in front of a back-lit, diffuse white field. Solution pH and temperature was measured with a temperature compensated pH electrode using an Oakton pH11 meter with three point calibration. Hydrogen peroxide concentration was measured using the HACH hydrogen peroxide test method based on ammonium molybdate-catalyzed triiodide titration with sodium thiosulfate.

[00272] The following bulk chemical reagents were purchased and used as received: Triacetin, 99%, (Acros Organics); Methylene Blue, 1% w/v aqueous solution (Ricca Chemical Company); Hydrogen peroxide, 2.7% w/v (measured) (Kroger Co.); Sodium Hydroxide, 100% (Roto Corp.); Sodium Sulfate, 100% anhydrous (Duda Diesel); and Distilled water from Kroger Co.

[00273] For example, electrochemically generated hydrogen peroxide concentrate solution was produced one to three days prior to use and stored at 2-4°C in a high density polyethylene bottle. The composition of the electrochemically generated hydrogen peroxide solution in distilled water at room temperature was 4800 mg/L (+/- 50

mg/L) hydrogen peroxide, pH 12.81 (+/- 0.04) as sodium hydroxide, and 7.1 g/L sodium sulfate. Hydrogen peroxide concentration was stable for several days.

[00274] Electrochemically co-generated sulfate acid concentrate with pH $\approx$ 1.40 (+/- 0.04) was produced from a 0.31 molar (44.0 g/L) sodium sulfate brine in distilled water. The approximate calculated composition of the acid concentrate at 20°C (pKa $\approx$ 0.973) was 0.091 M sodium sulfate and 0.24 M sodium bisulfate.

[00275] Peroxyacetic acid formulations were made by mixing electrochemically generated hydrogen peroxide solution with triacetin as the acetyl donor. The molar ratio of hydrogen peroxide to acetyl donor group was adjusted to produce non-equilibrium peroxyacetic acid solutions. The triacetin molecule possesses three molar equivalents of acetyl groups. A 2.00 mL volume of the oxidant formulation was combined with 2.00 mL of 100 mg/L MB aqueous solution. The initial pH was then adjusted by quickly titrating in electrochemically generated sulfate acid concentrate in amounts less than 0.5-2% of the total solution volume. The initial concentration of peroxyacetic acid was estimated based on the initial hydrogen peroxide concentration. The amount of unreacted hydrogen peroxide residual was not measured, but its effect was observed in the percent color removal results.

[00276] Table 2 below represents examples of MB oxidation test results demonstrating the relative effects of oxidant, pH, concentration and molar ratio of acetyl donor groups reacted with hydrogen peroxide. The initial MB concentration was 50 mg/L in all cases. Entry 1 used commercially produced hydrogen peroxide as the parent oxidant near neutral pH without adjustment. Entry 2 used electrochemically generated hydrogen peroxide at high strength without pH adjustment. Entry 3 used commercially produced hydrogen peroxide reacted with triacetin near pH 12.2, a known amount of hydrogen peroxide was added and then pH adjusted with electrochemically generated sulfate acid concentrate. Entries 4-13 used electrochemically generated hydrogen peroxide reacted with triacetin and diluted to varying initial concentrations of peroxyacetic acid as the parent oxidant.

[00277] The results in Table 2 demonstrate, for example, that singlet oxygen evolving formulations are significantly stronger oxidants than hydrogen peroxide or peroxyacetic acid solutions alone. Hydrogen peroxide by itself did not have any observed effects during this test and after the test solution in Entry 1 had sat for several days. Alkaline hydrogen peroxide in Entry 2 eventually caused a small amount of MB to precipitate after several hours more and has a slight shift in solution color to a purple

hue, but color loss did not progress significantly. A control test with 50 mg/L MB without any oxidant, but in the presence of 1M sodium hydroxide gave a similar result to Entry 2, indicating that hydrogen peroxide had little or no effect on the observed changes. Entry 3 demonstrates that the presence of a significant concentration of hydrogen peroxide in the peroxyacetic acid formulation severely inhibits oxidative activity toward MB and color removal.

Table 2: MB Oxidation Test Results

Entry no.	Molar reaction ratio, HP:acetyl equiv.	Initial Conc., Parent Oxidant	Initial pH	Final pH	Final Time (h)	% Color Removal
1	1:0	50 mg/L, HP	6.1-6.4	NR	3	0
2	1:0	2150 mg/L, HP	12.0-12.2	NR	3	0
3	1:2	7000 mg/L, PAA 5000 mg/L, HP	9.00	NR	48	<10
4	1:1	<240 mg/L, PAA	3.54	3.71	7	0
5	1:1	<240 mg/L, PAA	8.55	6.93	7	25
6	1:2	240 mg/L, PAA	4.50	4.55	8	0
7	1:2	240 mg/L, PAA	9.00	7.90	8	65
8	1:4	240 mg/L, PAA	4.60	4.73	7	0
9	1:4	240 mg/L, PAA	8.49	7.75	7	50
10	1:2	465 mg/L, PAA	3.97	3.70	7	20
11	1:2	465 mg/L, PAA	9.01	7.99	7	82
12	1:2	950 mg/L, PAA	9.01	8.16	7	93
13	1:2	1900 mg/L, PAA	9.00	8.46	5	99.5

HP = hydrogen peroxide; PAA = peroxyacetic acid; NR = not recorded

[00278] Entries 5, 7 and 9 in Table 2, above, demonstrate the effect of HP:acetyl donor equivalent ratio on oxidation activity as impacted by hydrogen peroxide residual, which leads to inhibited oxidative activity presumably due to singlet oxygen quenching. When the HP:acetyl donor equivalent ratio is 1:1, the MB color loss is significantly lower than when the ratio is 1:2 or 1:4. The difference in results between HP:acetyl donor equivalent ratios of 1:2 and 1:4 is minimal, when normalized to reaction time indicating that an excess of acetyl donor is not necessarily detrimental to oxidative activity.

[00279] When the initial peroxyacetic acid solution pH was above 8 the oxidation and color loss of MB was observed (Table 2). When the initial peroxyacetic acid solution pH was below 5, there was little to no color loss observed. When the pH remained above approximately 6.5 an increase in the peroxyacetic acid concentration resulted in faster and greater color loss of MB. This trend is demonstrated by the results

in graph 1300 of FIG. 13 showing the percent color removal of 50 mg/L MB solutions observed over time starting with different initial peroxyacetic acid concentrations. The results in graph 1300 of FIG. 13 also demonstrate that the singlet oxygen evolution occurs over a period of several hours. This result is reinforced by the observation of gas bubble evolution, which persists for several hours when the initial peroxyacetic acid concentrations are significantly greater than 1900 mg/L.

Example 10: pH Control and Formulation of Nitrate Oxidation Byproduct

[00280] As materials are oxidized and the peroxyacetic acid transforms to acetic acid, the pH of the treatment solution decreases. The initial pH and/or pH buffer concentration of the singlet oxygen precursor solutions should be adjusted to control the change in pH during the active oxidation period, such that the final pH is in a desirable range. Table 3 shows oxidation results for raw hydraulic fracturing and flowback water with singlet oxygen precursor formulations. Data in Table 3, below, demonstrate how the initial pH, the amount of parent oxidant and the amount of oxidation can be used control the final pH of the oxidized water. This example also illustrates the production of nitrate as a byproduct of the oxidation of nitrogen-containing organic materials with singlet oxygen formulations.

Table 3: Oxidation Results For Raw Hydraulic Fracturing and Flowback Water

Sample No.	PAA:TOC mass ratio	Raw water volume (mL)	Total oxidation volume (mL)	Initial oxidation pH	Final (6 h) oxidation pH	Nitrate byproduct (mg/L)
1	0:1	37	56.7	8.19	8.19	BDL
2	2.4:1	37	56.7	8.87	6.73	0.92
3	1.2:1	37	56.7	8.77	6.81	0.52
4	0.6:1	37	56.7	8.67	7.00	0.31

BDL = below detection limit of 0.1 mg/L

[00281] Raw hydraulic fracturing and flowback water generated by oil and gas development operations was obtained from an undisclosed location in Colorado, USA after temporary impoundment in a lagoon. The composition of the raw water was approximately 5000 mg/L total organic carbon (hereinafter "TOC"), approximately 10,000 mg/L total dissolved solids (hereinafter "TDS"), appeared opaque with suspended silt and dark brown organic material and had a pH of 8.19 indicating alkalinity content. The raw water also possessed a mild odor of volatile organic compounds (i.e., petrochemicals).

[00282] Singlet oxygen formulation concentrate, formulated by the above embodiments, was added to the raw water in varying amounts with distilled water added to maintain equivalent dilutions between samples. The approximate mass ratios of peroxyacetic acid to TOC are reported in Table 3, above, to distinguish singlet oxygen precursor doses. The singlet oxygen precursor formulation was made by mixing and reacting 1.40 mL triacetin with 16.3 mL of a 1% w/v hydrogen peroxide stock solution adjusted to pH 12.4 with NaOH. The resulting peroxyacetic acid solution concentrate was adjusted to pH 8.9 with about 2.0 mL of electrochemically generated sulfate acid concentrate of pH 1.32. The samples in Table 3, above, were prepared by mixing 37 mL of raw water with: 19.7 mL of distilled water for control sample no. 1; 19.7 mL of singlet oxygen precursor formulation for sample no. 2; 9.8 mL of singlet oxygen precursor formulation plus 9.8 mL distilled water, for sample no. 3; and 4.9 mL of singlet oxygen precursor formulation plus 14.8 mL distilled water, for sample no. 4. The samples were each contained in 100 mL glass jars at room temperature.

[00283] The initial pH was measured immediately after sample preparation. The initial pH was affected by the amount of singlet oxygen precursor formulation added to the sample. Samples containing singlet oxygen precursor formulation evolved gas rapidly enough to effervesce for 1-2 hours. Effervescence also served as an effective mixing mechanism. Within the first 30 minutes of oxidation, the color of sample nos. 2-4 had become paler, than the control sample no. 1. After 5-6 hours visible gas evolution had subsided and the oxidized samples were a significantly paler tan color than the control. Sample no. 2 was the palest in color corresponding with the greatest singlet oxygen precursor dose.

[00284] The final pH was measured at 6 hours. Higher initial singlet oxygen precursor formulation concentration led to lower final pH. Oxidized samples had a final pH of 6.7 to 7.0 demonstrating the potential to balance pH with the singlet oxygen precursor formulation and dose. The precursor formulation used in this example contained acetate and acetic acid, which can act as a pH buffer and reduce alkalinity, respectively. As oxidation proceeded, additional acetic acid (the byproduct from peroxyacetic acid reactions) and potentially partial oxidation products with carboxylic acid groups accumulated leading to a decrease in pH over time.

[00285] Nitrate was found to be an oxidation byproduct of the organic material in the hydraulic fracturing flowback water. Results of ion chromatography analysis of the samples in Table 3, above, corrected for dilution, show that byproduct nitrate content

was proportional to singlet oxygen precursor formulation concentration. Nitrogen-containing materials, such as natural organic materials, were sufficiently oxidized to liberate nitrogen as nitrate. Nitrate was not detected in the non-oxidized raw water.

[00286] In view of the many possible embodiments to which the principles of the disclosure may be applied, it should be recognized that the embodiments herein should not be taken as limiting the scope of the present disclosure.

Example 11: Electrochemical Co-Generation of Hydrogen Peroxide and Superoxide

[00287] A reactor system with an electrochemical reactor of Figure 6 and fluid process flow illustrated in Figure 7 was used in this example. A carbon fiber cathode suitable for combined hydrogen peroxide and superoxide production was installed in the reactor with an active superficial area of 255 cm². The anolyte reservoir and chamber were charged with a 2.5 L solution of about 1.5 M sodium hydroxide in distilled water. The anolyte was recirculated through the anode chamber over time. A ca. 93% oxygen gas stream generated by a pressure swing adsorption oxygen concentrator at 5 L per minute was circulated through the gas feed line and reactor by a pump at a rate of 9.0 liters per minute at 3.0 psig, while a 5 L per minute bleed stream of oxygen gas was released from the system. The catholyte was a 0.05 molar solution of sodium sulfate in distilled water adjusted to pH 11.2 with sodium hydroxide to precipitate trace magnesium in the electrolyte. The catholyte solution was fed into the catholyte feed line at a rate of 12.8 mL per minute at 1.6 psig (single pass, flow through). A DC current was applied to the reactor at either 5.0 amps or 8.0 amps (current control). The negative pole of the power supply was grounded. Hydrogen peroxide concentration was analyzed by titration using the Hach Inc. HYP-1 Hydrogen Peroxide Test and pH was measured using an Oakton pH 11 Series meter with a temperature compensated double junction pH electrode.

[00288] At 5.0 amps operating current the catholyte output reached a steady state composition of 2000 +/- 50 mg/L hydrogen peroxide and pH 12.20 +/- 0.04 at 25 to 27 °C. The current efficiency for hydrogen peroxide production was calculated to be 48.4% assuming a two electron reduction of molecular oxygen. A maximum potential concentration of superoxide anion produced was calculated to be 3400 mg/L, assuming 90% of the balance of the applied current caused the one electron reduction of molecular oxygen.

[00289] At 8.0 amps operating current, the catholyte output reached a steady state composition of 2500 +/- 50 mg/L hydrogen peroxide at 27 to 28 °C and pH 12.58 +/- 0.04 measured at a 10-fold dilution to adjust the pH to within the accurate range of the pH probe. The current efficiency for hydrogen peroxide production was calculated to be 37.8%, assuming a two electron reduction of molecular oxygen. A maximum potential concentration of superoxide anion produced was calculated to be 6800 mg/L assuming 90% of the balance of the applied current caused the one electron reduction of molecular oxygen.

Analysis of Electrochemically Generated Hydrogen Peroxide and Superoxide (Examples 7 and 11):

[00290] Catholyte outputs from Examples 7 and 11 above were analyzed by ultraviolet-visible absorption spectroscopy between 21 and 24 °C. Data was collected using an Ocean Optics USB4000-UV-VIS absorbance system (200-850 nm) with SpectraSuite software. Disposable 1 cm Plastibrand disposable macro cuvettes were used with a 220 nm cutoff. Hydrogen peroxide concentration was analyzed by titration using the Hach Inc. HYP-1 Hydrogen Peroxide Test and pH was measured using an Oakton pH 11 Series meter with a temperature compensated double junction pH electrode. All samples were diluted with distilled water to 100 mg/L hydrogen peroxide and pH adjustments were made using sodium hydroxide or pH 1.40 sodium bisulfate solution. Hydrogen peroxide UV standards were made from 3% topical hydrogen peroxide and sodium hydroxide combined in distilled water. Standards included 100 mg/L hydrogen peroxide at pH 6.7, 10.0, 11.0 and 12.0. Standards were also made with 0.10 mol/L NaOH (nominally pH 13) and 1.0 mol/L NaOH (nominally pH 14) measured by weight of sodium hydroxide dissolved in distilled water at room temperature.

[00291] The previously reported absorption band maximum for dilute aqueous superoxide generated by radiolysis of dissolved oxygen in the presence of sodium formate and ethylenediaminetetraacetic acid at pH 10.5 was 245 nm. See "Reactivity of HO_2/O_2^- Radicals in Aqueous Solution," Beilski, et al., *J. Phys. Chem. Ref. Data*, Vol. 14, No. 4, 1985. The reported absorption band maximum for dilute hydroperoxyl radical ($\text{HO}_2^\bullet$) in aqueous perchloric acid at pH 1.5 was 225 nm.

[00292] FIGs. 14A/B shows graphs 1400, 1450 that compares the UV absorbance spectra of fresh catholyte outputs, within 2 minutes of production, of the high efficiency hydrogen peroxide output 1402 in Example 7, and the co-generated hydrogen

peroxide and superoxide output 1404 in Example 11. Both outputs were produced at 5 amps.

[00293] FIG. 14A shows graph 1400 that illustrates the full spectra of samples diluted to 100 +/- 4 mg/L hydrogen peroxide and adjusted to pH 12.00 +/- 0.04 and graph 1450 of FIG. 14B shows the same spectra with hydrogen peroxide absorbance subtracted off. The co-generated hydrogen peroxide and superoxide output exhibits additional absorbance intensity on the shorter wavelength side of the hydrogen peroxide band and a weak absorbance band in the subtracted spectrum. The high efficiency hydrogen peroxide output did not exhibit a second absorbance band after subtracting off the hydrogen peroxide absorbance. Hydrogen peroxide at 100 +/- 4 mg/L and pH 12.0 has an absorbance maximum near 232 nm, while the weak absorbance band of the co-generated hydrogen peroxide and superoxide output is shifted to shorter wavelength.

[00294] The weak absorbance band of the co-generated hydrogen peroxide and superoxide output increases in intensity over time at pH 12, which is behavior not observed for alkaline hydrogen peroxide alone.

[00295] FIGs. 15A/B show graphs 1500, 1550 that illustrate the evolution of the UV absorbance spectrum over five hours for the co-generated hydrogen peroxide and superoxide output produced at 8 amps in Example 11 diluted to 100 +/- 4 mg/L hydrogen peroxide, adjusted to pH 12.00 +/- 0.04 and analyzed over time. Graph 1500 shows the full spectra of the output including hydrogen peroxide at two minutes after production 1502, three hours after production 1504 and five hours after production 1506. Graph 1550 shows the same spectra with hydrogen peroxide absorbance subtracted off at two minutes after production 1552, three hours after production 1554, and five hours after production 1556. The growing band in graph 1550 has an absorbance maximum near 224 nm at five hours, which is consistent with the reported position of the hydroperoxyl radical. The original spectrum in graph 1500 shows an 18% decrease in absorbance and a shift in the absorbance band maximum from 230 nm, to 228 nm at three hours, to 226 nm at five hours. These spectral changes were accompanied by a decrease in pH to 11.66 +/- 0.04, but there was no measurable decrease in hydrogen peroxide concentration. The aforementioned behavior is consistent with the buildup of a different species with lower molar absorptivity by a slow chemical reaction or equilibrium process and a slow loss of a non-hydrogen peroxide species in the electrochemically generated output.

[00296] For comparison, the same output produced at 8 amps in Example 11, diluted to 100 +/- 4 mg/L hydrogen peroxide and adjusted to pH 13 (0.10 mol/L NaOH)

did not exhibit any change in the 224 nm hydrogen peroxide subtracted peak intensity or hydrogen peroxide concentration over 5 hours (data not shown). The original spectra did show a 10% decline in peak intensity of the hydrogen peroxide peak near 231 nm over five hours without any wavelength shift in peak maximum position. This behavior shows a more stable output solution with a slower loss of a non-hydrogen peroxide species in the electrochemically generated output.

[00297] FIGs. 16A/B show graphs 1600, 1650 that illustrates the evolution of the UV absorbance spectrum over five hours for the co-generated hydrogen peroxide and superoxide output produced at 8 amps in Example 11 diluted to 100 +/- 8 mg/L hydrogen peroxide, adjusted to pH 11.04 +/- 0.04 and analyzed over time. Graph 1600 shows the full spectra of the output including hydrogen peroxide at two minutes after production 1602, one and a half hours after production 1604 and five hours after production 1606. Graph 1650 shows the same spectra with hydrogen peroxide absorbance subtracted off at two minutes after production 1652, one and a half hours after production 1654, and five hours after production 1656. The 221 nm band in graph 1650 increases in intensity for a period of time, then decreases in intensity. The original spectrum in graph 1600 shows a 56% decrease in absorbance and a shift in the absorbance band maximum from 225 nm to 222 nm at five hours. These spectral changes were accompanied by a decrease in pH to 9.47 +/- 0.04 and a 20% decrease in hydrogen peroxide concentration to 80 +/- 4 mg/L. Approximately 55-60% of the decrease in absorbance in graph 1600 is attributable to the decrease in pH. In graph 1650 the initial spectrum of the output shows a broad absorption shoulder in the 240 to 260 nm region, which is consistent with the absorption region for the “free” form of dilute, aqueous superoxide. This shoulder is often observed for freshly made reactor output solutions. These results show that a lower initial pH leads to a more reactive and less stable output solution including the formation of a different species with lower molar absorptivity than hydrogen peroxide; a more rapid loss of this different species involving the consumption of hydrogen peroxide; and a more rapid loss of a non-hydrogen peroxide species in the electrochemically generated output.

[00298] The UV spectra of co-generated hydrogen peroxide and superoxide outputs show that the initially generated alkaline hydrogen peroxide changes in form in the presence of superoxide, especially when the pH is near or below hydrogen peroxide's pKa of 11.6. Likewise, the “free” form of superoxide is quenched by the presence of hydrogen peroxide, especially at high concentrations. Hydrogen peroxide has been reported to behave as a stabilizing co-solvent which increases the chemical reactivity of

aqueous superoxide solutions. See "Identification of the Reactive Oxygen Species Responsible for Carbon Tetrachloride Degradation in Modified Fenton's Systems," Watts, et al., *Environmental Science & Technology*, Vol. 38, No. 20, 2004. Hydrogen peroxide is a weak acid and can potentially serve as a proton source for superoxide, which has a pKa of 4.8. Based on the UV spectra it appears that hydrogen peroxide in its fully protonated form can interact with superoxide to form a different species, such as, for example, an "adduct," in an equilibrium process and/or lead to the reactions in Equations 1 and 3. At pH 11 hydrogen peroxide is consumed more rapidly, consistent with the processes in Equations 1 and 3, which produce hydroxyl radicals. A measurable increase in the concentration of hydrogen peroxide and pH over time was never observed, indicating that the disproportionation reaction in Equation 6 was negligible for the reactor output.

[00299] The stability of the co-generated hydrogen peroxide and superoxide output solutions was significantly greater than the lifetimes cited earlier, 1.5 minutes at pH 11 and 41 minutes at pH 12.5 in aqueous solution. The lifetimes of active species at pH 12 and higher were at least five hours in the diluted reactor output solutions. The stability of the concentrated, undiluted output solutions was lower as evidenced by gas bubble evolution observed after approximately 30 minutes time. At pH 11 the degradation of active oxygen species was accelerated, but persisted for at least five hours in the diluted reactor output solutions. Enhanced oxidation activity, of these output solutions was demonstrated to persist for more than 12 hours at pH 11-12 in the example cited below.

Example 12: Advanced Oxidation of Methylene Blue with Electrochemically Co-Generated Hydrogen Peroxide and Superoxide

[00300] Catholyte output solution was generated by the method cited in Example 11 at 5 amps operating current. Output solution contained 2500 +/- 50 mg/L hydrogen peroxide and a calculated maximum potential concentration of 3050 mg/L superoxide at pH 12.1. Freshly generated output solution (2.0 mL) was added to 2.0 mL of 100 mg/L methylene blue solution acidified with bisulfate. The prepared oxidation test solution had an initial pH of 11.9 and contained 50 mg/L methylene blue, 1250 mg/L hydrogen peroxide, a maximum potential superoxide concentration of 1500 mg/L. Solution temperature was 25 °C. The methylene blue color was evaluated over time by comparison to the series of methylene blue color standards as described in Example 9. A

slight decrease in color intensity, ca. 10%, was observed after 5.6 hours had passed without a significant change in pH. The solution was colorless to the eye after 50 hours. For comparison, hydrogen peroxide alone had no visible effect on methylene blue after several days.

Example 13: Singlet Oxygen Formulation for In-Situ Chemical Oxidation

[00301] Singlet oxygen may be used for remediation and decontamination of a body of soil, a geologic formation, an excavated soil, or construction or demolition debris.

[00302] A singlet oxygen formulation is prepared from bulk chemicals, formulated using the system and methods depicted in Figs. 3 and 4, for in-situ chemical oxidation (ISCO) for remediation of soil contaminated with diesel fuel (60 mg/kg) and polycyclic aromatic hydrocarbons (PAH's, 40 mg/kg). The resulting singlet oxygen formulation can be used to oxidize 85-95% of the contaminants, oxygenate the soil and supply non-toxic, low molecular weight organic substrates to heterotrophic bacteria which may consume residual contaminants and their oxidation byproducts. The present example applies to a soil sample having soil porosity of 20%, soil pH 8.0-8.5, and soil density of 2.4 g/cm³. The soil type is clayey with low vapor permeability, the depth of contamination is up to 4 meters. The method can employ injection and recovery wells.

[00303] Chemical feeds are prepared using the system 300 of Fig. 3 and method 400 of Fig. 4. Application includes applying six soil pore volumes of oxidant formulation containing a 4:1 mass ratio of peroxyacetic acid to contaminant to set the singlet oxygen dose, and a treatment rate of 32 cubic yards per day. Chemical inputs on a 100% basis are 24.3 lb/day hydrogen peroxide, 40.7 lb/day sodium hydroxide, 9.8 lb/day hydrochloric acid, 103.9 lb/day triacetin and 7942 gal/day water. The injection concentrations of oxidant formulation constituents are about 800 mg/L peroxyacetic acid, <15 mg/L hydrogen peroxide, 664 mg/L glycerol, 912 mg/L sodium acetate, 238 mg/L sodium chloride and an initial solution pH of 8.5-9.5. Additional sodium chloride can be added to match the salinity of the soil, if necessary. Non-toxic additives including co-solvents (e.g., triacetin, glycerol), compatible surfactants (e.g., sodium dodecyl sulfate) and stabilizers (e.g., phytic acid) are optionally added to enhance performance. The prepared formulation are fed as a liquid into injection wells to infiltrate the soil at ambient temperature. A residence time of at least six hours is employed and provides singlet oxygen generation activity, provides peroxyacetic acid reaction time with

contaminants and also allows Fenton-like peroxide activation processes to occur with any reduced iron minerals present.

[00304] Recovered, spent flushing fluids have pH similar to that of the soil body treated and contain salinity, hardness (e.g., calcium/magnesium carbonate), suspended solids (e.g., iron or manganese oxides), glycerol, acetate, additives, oxidation byproducts (e.g., nitrate, low molecular weight hydrocarbons) and potentially non-oxidized contaminants and microbes. The spent flushing fluids are optionally treated on site for discharge, sent to a municipal water treatment facility, disposed of in an injection well, or are processed for water recovery and recycle back into the remediation process or other use.

Example 14: Superoxide Formulation for Ex-Situ Chemical Oxidation and Reduction for Remediation.

[00305] Superoxide formulations can be used for remediation and decontamination of a body of soil, a geologic formation, an excavated soil, or construction or demolition debris.

[00306] The following example illustrates a superoxide formulation for ex situ chemical oxidation for remediation of soil contaminated with 10 mg/kg non-aqueous phase liquids (NAPL) containing low volatility halogenated materials which can include brominated flame retardants, dioxins, and/or polychlorinated biphenyls (PCB's). The superoxide formulation is prepared using the system of FIG. 5. The resulting superoxide formulation is used to chemically oxidize more than 99% of the contaminants and flush residuals out of the soil. The soil sample of the example has a pH 7.0-7.5, average soil density is 2.4 g/cm³, and the soil type is a sand/alluvial mixture. The soil is excavated for treatment and then is returned to its origin.

[00307] In the present example, treatment includes applying the equivalent of 4 soil pore volumes (20% porosity assumed) of superoxide formulation containing a 3:1 mass ratio of hydrogen peroxide to contaminant to set the superoxide dose, and a treatment rate of 32 cubic yards per day. Chemical input and output rates are calculated based on the process described for Figures 7 and 11, using an electrochemical reactor of the type in Figure 6. Inputs into the electrochemical generator are 834 lb/day sodium sulfate, 218 gal/day water, 5600 L/day oxygen gas at STP and approximately 1070 kWh per day to operate the system. The reactor can produce 100 lb/day hydrogen peroxide at 40% current efficiency (produced as sodium peroxide), a maximum potential mass of

235 lb/day superoxide at about 50% current efficiency (produced as sodium superoxide), approximately 28 lb/day sodium hydroxide and, in a separate output stream, 711 lb/day sodium bisulfate. Sodium bisulfate may be used for pH adjustment of superoxide formulations and/or treated soil, if desired. The reactor output can be diluted with 4880 gal/day water to produce an oxidant formulation of about 90 mg/L hydrogen peroxide, up to 212 mg/L superoxide, up to 750 mg/L sodium sulfate and an initial solution pH of 10.5-11.5. A relatively low concentration of oxidants is employed to avoid the quenching of generated hydroxyl radicals, similar to an ultraviolet-hydrogen peroxide advanced oxidation process. Other additives such as surfactants and co-solvents are optionally used, but are selectively used to minimize consumption of hydroxyl radicals produced by the formulation. The prepared formulations are applied as a liquid to the excavated soil and allowed to contact the soil for a period of time at ambient temperature or elevated temperature. The soil is optionally flushed in a second step with excess co-generated acid or sodium bisulfate, to balance the pH of the soil if becomes elevated during treatment and if desired.

[00308] Recovered, spent soil washing fluids will have a pH similar to that of the soil and contain salinity, hardness (e.g., calcium/magnesium carbonate), additives and potentially oxidation or reduction byproducts or non-oxidized or reduced contaminants and microbes. The spent flushing fluids are optionally treated on site for discharge, sent to a hazardous waste facility, disposed of in an injection well, or processed for water recovery and recycle back into the remediation process or other use.

Example 15: Clean in Place (CIP) Applications for Food, Beverage, Dairy, and Biopharma Processing Equipment Cleaning.

[00309] Clean in place (CIP) applications involve preparing cleansers and sanitizer solutions and dispensing them into pipes, tanks and other processing equipment that is not disassembled for cleaning. The chemical activity of such solutions provides the cleansing and sanitizing capabilities. CIP cleansers and sanitizers are prepared in day tanks, often ranging in capacity from 50 to 500 gallons, and distributed to equipment when needed during cleaning cycles. Alkaline cleansers and oxidizing alkaline cleansers are particularly useful for removing soils and organic residues. Acids are particularly useful for removing scaling minerals. Antimicrobial sanitizers are particularly useful for disinfection. The use of non-chlorine based cleansers and sanitizers is of interest to

minimize corrosion of stainless steel processing equipment and to avoid chlorinated oxidation or disinfection byproducts.

[00310] Acid compatible sanitizers, such as peroxyacetic acid, can be used to reduce the number of system cleaning flushes needed relative to chlorine and chlorine bleach based sanitizers, which are not compatible with acid pH of less than about pH 4 due to the release of chlorine gas. Alkaline oxidizing cleansers may be more effective at removing organic soils, proteins and fat deposits than alkali detergents alone. See U.S. Pat. No. 7,754,064, Figs. 13-14, for example.

[00311] FIG. 17 shows an exemplary system and flow process for electrochemically generating a CIP cleanser, in one embodiment. An electrochemically generated CIP cleanser and sanitizer formulation is used for food, beverage, dairy and biopharma processing equipment. Alkaline oxidizing cleanser 1720 and acid sanitizer 1722 are co-generated and stored in 500 gallon day tanks 1716, 1718, respectively until use. The alkaline oxidizing cleanser 1720 is formulated to contain 0.01 M NaOH (pH 12.0) and 200 mg/L peroxyacetic acid to generate singlet oxygen, by method 500. The acid sanitizer 1722 is formulated to contain 0.02 M citric acid (pH 2.6) and 400 mg/L peroxyacetic acid, generated by, for example, using the electrochemical reactor of FIG. 6. Surfactants and stabilizers are optionally used in either a cleanser or sanitizer solution, but are not required, and not shown in FIG. 17. Cleanser solutions 1720, 1722 are heated to 55-60 °C prior to distribution as is customary for CIP processes.

[00312] The above specified formulations use two identical electrochemical reactors, for example, the electrochemical reactor discussed with reference to FIG. 6 above, with the exception of their cathode surface compositions and feed rates, in parallel to generate the required chemicals by the process outlined in FIG. 17. Electrochemical production is designed for 500 gallons each of alkaline and acid cleansers. Reactor inputs makeup water 1702, brine 1704, oxygen gas 1706, and power source 1708 and outputs 1724, 1726 are listed on a 100% basis.

[00313] Electrochemical reactor 1714 contains an activated carbon cathode surface for high efficiency hydrogen peroxide production and produces alkaline hydrogen peroxide and citric acid concentrates in two separate output streams. Inputs for reactor 1714 are 6.93 lb/day sodium citrate 1704, 230 L/day oxygen gas 1706 at STP, 15 gal/day water 1702(1) and approximately 9.9 kWh electricity 1708 to operate the system. Outputs for reactor 1714 are (i) an alkaline H₂O₂ concentrate 1724 including 1.12 lb/day hydrogen peroxide (at 84% cathode current efficiency) combined with 0.38 lb/day

sodium hydroxide and (i) an acid concentrate output 1726 including 4.53 lb/day citric acid in a separate stream. The alkaline hydrogen peroxide 1724 is reacted with 4.78 lb/day triacetin 1710 and two thirds of the resulting peroxyacetic acid solution 1724' is fed to the alkaline cleanser holding tank 1716 while the remainder is fed to the acid sanitizer holding tank 1718. Less than about 15 mg/L hydrogen peroxide is present in the peroxyacetic acid output 1724'.

[00314] Electrochemical reactor 1715 contains a nickel cathode surface for high efficiency sodium hydroxide production and produces alkaline hydrogen peroxide 1728 and citric acid 1730 concentrates in two separate output streams. Inputs for reactor 1715 are 17.7 lb/day sodium citrate 1705, 320 L/day oxygen gas 1707 at STP, 17 gal/day water 1702(2) and approximately 18.3 kWh electricity 1709 to operate the system. Outputs for reactor 1715 are 1.66 lb/day sodium hydroxide 1728 (at 98% cathode current efficiency) and 11.57 lb/day citric acid 1730 in a separate stream. The sodium hydroxide 1728 is fed to the alkaline cleanser holding tank 1716 while the citric acid 1730 is fed to the acid sanitizer holding tank 1718.

[00315] The alkaline cleanser holding tank 1716 and acid sanitizer holding tanks 1718 are filled with water 1702 during chemical production bringing their final volumes to 500 gallons each. The use of triacetin 1710 to generate the peroxyacetic acid 1724' results in about 340 mg/L glycerol plus 475 mg/L sodium acetate in the alkaline cleanser and 170 mg/L glycerol plus 235 mg/L acetic acid in the acid sanitizer 1722.

[00316] In some exemplary CIP applications milder cleansers are desirable. Singlet oxygen generation is not desirable when materials to be treated (or which may come in contact with formulation) are susceptible to degradation by singlet oxygen. Relevant examples include desalination filter membranes and polymers including polyamides, polysulfone, polyurethane, polyethylene terephthalate, epoxy resins, polyacrylonitrile-butadiene copolymer (nitrile rubber) and natural rubber. To quench singlet oxygen generation by the alkaline cleanser solution described in the above CIP example a lower amount of triacetin 1710 is used thereby leaving a hydrogen peroxide concentration, in combination with peracid solution 1724', high enough to quench singlet oxygen evolved by peroxyacetic acid. For example, the triacetin input 1710 may be decreased by 67% to about 1.63 lb/day thereby increasing the hydrogen peroxide concentration to about 100 mg/L and decreasing the peroxyacetic acid concentration to about 200 mg/L in the alkaline cleanser solution 1720. As a result the acid sanitizing solution 1722 will contain about 50 mg/L hydrogen peroxide and 100 mg/L peroxyacetic

acid. The alkali and acid concentrations remain virtually unchanged unless their production by electrochemical reactor 1715 is decreased.

Example 16: Singlet Oxygen Production Using Bulk Chemicals for Oil Production Well Flushing Applications

[00317] Well casings and pipelines are serviced to remove bacterial growth, slime buildup, mineral scale deposits, corrosion and contamination. These issues are common among oil and gas production wells and pipelines, groundwater wells, raw water and wastewater pipelines, and potable water and greywater distribution systems. Microbial control, removal of slime (the decaying remains of dead bacteria and other organic materials), microbial corrosion control and scale removal are significant maintenance issues for prolonging the production capacity and lifetime of a well. Pipelines carrying raw water, wastewater, produced water, greywater and other untreated water will encounter microbial growth and slime formation and will require cleaning. Methods for cleaning well bore casings and pipelines include chemical flushing with oxidizers and acids and mechanical cleaning such as brushing and scraping.

[00318] Compatibility of oxidants with seawater and brackish water is desirable in locations where there are no natural freshwater resources available. Flushing solution activity should persist for at least 5 hours and be effective in the range of pH 8-9. Ideally flushing solutions should be pH balanced and be safe for municipal disposal or discharge.

[00319] The following example presents an application of chemical flushing of an oil production well with a singlet oxygen formulation made from bulk chemicals. The singlet oxygen formulation is created using method 400 and system 300 discussed above. In this example, the production well is located in a coastal region where seawater is used as floodwater for enhanced oil recovery. The well depth is about 12,000 feet below surface and has an average casing diameter of 6 inches and volume of about 4,630 gallons.

[00320] Chemical inputs and outputs are stated as quantities per well volume. Chemical inputs on a 100% basis are 5.4 lb hydrogen peroxide, 8.9 lb sodium hydroxide, 2.2 lb hydrochloric acid, 22.8 lb triacetin, 9.6 lb nonionic polyether alcohol surfactant/wetting agent and 4630 gal water of which the majority (e.g., >90%) can be seawater filtered through a 1 micron rated filter. The prepared injection concentrations of oxidant formulation constituents are about 300 mg/L peroxyacetic acid, <10 mg/L

hydrogen peroxide, 250 mg/L glycerol, 340 mg/L sodium acetate, 250 mg/L surfactant/wetting agent, 90 mg/L sodium chloride (not including the salt added by seawater) and an initial pH of 8.5-9.5. An oxidant-compatible corrosion inhibitor such as tetrasodium pyrophosphate is optionally added to enhance performance.

[00321] The above prepared formulation is fed as a liquid into a well bore (or pipeline) at ambient temperature. A residence time of at least four to six hours is employed to provide singlet oxygen generation activity and oxidative breakdown of organic materials; to provide peroxyacetic acid contact time with microbes; and to allow Fenton-like peroxide activation processes to occur with catalytically active reduced iron surfaces or other metal surfaces present.

[00322] The use of seawater, with a natural bromide content of about 65 mg/L, as the primary water source for the flushing solution provides some hypobromous acid or hypobromite ion by oxidation of bromide by peroxyacetic acid. Hypobromous acid may function as an additional oxidant that can participate in the performance of the singlet oxygen flushing solution and has significant oxidation and antimicrobial activity up to about pH 8.5.

[00323] Recovered, spent flushing fluids will have a pH similar to that of seawater or groundwater and contain salinity, hardness (e.g., calcium/magnesium carbonate), suspended solids (e.g., iron or manganese oxides), suspended organic materials such as slime deposits, glycerol, acetate, surfactant and corrosion inhibitor additives, oxidation byproducts (e.g., nitrate, low molecular weight hydrocarbons) and potentially non-oxidized contaminants and microbes. The spent flushing fluids are optionally treated on site for discharge, sent to a municipal water treatment facility, disposed of in an injection well, or processed for water recovery and recycle back into well operations.

Example 17: Superoxide Formulation for Oil Sand Tailing Pond Water Treatment

[00324] Oil Sand Tailing Ponds in northern Alberta, Canada represent a very large impoundment of contaminated and toxic water created by bitumen extraction and processing. Water quality has been degraded through multiple reuse cycles to the point that it is no longer suitable for reuse. Natural biodegradation and attenuation of contaminants can be extremely slow or ineffective for remediating these waters due to the presence of recalcitrant organic contaminants such as naphthenic acids, phenols and polycyclic aromatic hydrocarbons and cold temperatures. A representative composition

of tailing pond water for application of treatment includes 2000 mg/L inorganic TDS, pH 8.3, 0.025 mg/L cyanide, 50 mg/L naphthenic acids, 10 mg/L oil and grease, 0.5 mg/L phenols, 0.01 mg/L polycyclic aromatic hydrocarbons, and several trace metals such as iron (2 mg/L), copper (0.05 mg/L), chromium (0.01 mg/L), and lead (0.1 mg/L) among others.

[00325] The general treatment strategy is to oxidize recalcitrant organic contaminants with a superoxide and hydrogen peroxide formulation to allow for more rapid treatment of smaller organic fragments downstream in a biological treatment process. Oxidation may be provided by hydroxyl radicals formed directly by superoxide and hydrogen peroxide by the reactions in Equations [4] and [6]. Hydroxyl radicals are expected to be formed during treatment by Fenton chemistry with catalytically active metals surfaces present in the tailing pond water, including iron and copper. Waste heat from equipment and bitumen processing can provide heat to support treatment operations.

[00326] A generation system from FIG. 18 is used in the present example to produce a superoxide precursor formulation by electrochemical generator, in one embodiment. Superoxide concentrate 1124 and, optionally, acid concentrate 1126 are electrochemically generated using an electrochemical reactor 1114. Electrochemical reduction of oxygen is conducted at a suitable cathode and water is oxidized at a suitable anode in an electrochemical reactor 1114 in which the anode and cathode chambers are separated by a membrane. Oxygen gas 1106 and a 2 g/L aqueous sodium sulfate solution 1104 are supplied to the cathode while a 47.5 g/L aqueous sodium sulfate solution 1104 is supplied to the anode. A direct current 1108 is applied to the electrodes thereby driving the reduction of oxygen at the cathode to produce superoxide, hydrogen peroxide and sodium hydroxide as the majority products 1124 of the cathode, while water is oxidized at the anode to produce sodium bisulfate acid and oxygen gas as the majority products 1126 of the anode.

[00327] In this example the cathode product solution 1810 has a composition of approximately 8.2 g/L superoxide (as $O_2^{\bullet-}$), 5.0 g/L hydrogen peroxide (as H_2O_2), 1.3 g/L sodium hydroxide and a pH of about 12.6 (as NaOH), assuming a 40% current efficiency for oxygen reduction to superoxide and 50% current efficiency for oxygen reduction to hydrogen peroxide. The anode product solution 1812 has a composition of approximately 30 g/L sodium bisulfate and 13 g/L sodium sulfate assuming about 90%

sodium sulfate to sodium bisulfate acid conversion. The anode to cathode product solution volume ratio is about 1.73.

[00328] The superoxide-containing cathode product solution 1810 is then diluted to its point of use concentration (i.e., 75 mg/L hydrogen peroxide, 124 mg/L superoxide, 20 mg/L NaOH) by mixing directly with raw tailing pond water 1820 in a 1:65.7 volume ratio. This mixture is held in an oxidation tank 1124 with a residence time of 6 to 24 hours after which the oxidized water is pH adjusted with the anode product solution 1126 in a 38.5:1 volume ratio. The pH-adjusted oxidized tailing pond water 1822 is then sent to a secondary treatment process. An example of a secondary treatment process is an aerobic bioreactor stage, to remove organic residuals and nitrification, followed by an anaerobic bioreactor stage, for sulfate reduction, removal of metal as sulfides and denitrification.

Example 18: Oxidative Reductive Potentials of ROS Solutions

[00329] Formulations of reactive oxygen species were produced to determine their resulting ORP readings at various pH's and concentrations. Formulations included (1) hydrogen peroxide with superoxide produced by electrochemical generation; (2) singlet oxygen-generating peroxyacetic acid produced by bulk chemical mixing (PM formulations); and (3) singlet oxygen-generating peroxyacetic acid with superoxide produced by electrochemical generation and bulk chemical mixing. A formulation containing approximately equi-molar concentrations of peroxyacetic acid and hydrogen peroxide (control A) was also made by bulk chemical mixing to determine the effect of hydrogen peroxide, which is present in "merchant" equilibrium peroxyacetic acid solutions, on the ORP of peroxyacetic acid.

[00330] Solution pH was measured using a high sodium pH electrode, Oakton model 35805-05, with Oakton pH 11 series meter and auto temperature compensation probe. The pH electrode and meter were calibrated with a standard three point calibration. ORP measurements were made using an Oakton model 35805-15 ORP electrode with Oakton pH 11 series meter and auto temperature compensation probe. Raw ORP readings were corrected to the standard hydrogen electrode (SHE) using the Thermo/Orion ORP standard 967901 (420 ± 3 mV vs SHE at 25°C). ORP measurements were made while stirring the solution until a stable reading was obtained and repeated up to four times on the same sample. Samples were kept at $25 \pm 3^\circ\text{C}$ using

a temperature regulated water bath. Hydrogen peroxide concentration was analyzed by colorimetric titration using the Hach Inc. HYP-1 Hydrogen Peroxide Test.

[00331] ORP vs pH measurements were made on formulations normalized to 1000 mg/L (29.4 mM) hydrogen peroxide concentration. Peroxyacetic acid concentration of 2170 mg/L (28.5 mM) was made to be approximately equi-molar to 1000 mg/L hydrogen peroxide assuming 97% conversion of hydrogen peroxide to peroxyacetic acid. Sample pH was adjusted to between pH 3 and 13 using concentrated sodium bisulfate and sodium hydroxide solutions and sample dilutions were made using distilled water. Sample pH was adjusted as needed during the measurement period to maintain a constant pH and was plus or minus 0.03 pH units of the set point during ORP measurements.

[00332] ORP vs concentration measurements were made on formulations normalized to 1000 mg/L (29.4 mg/L) hydrogen peroxide or 2170 mg/L (28.5 mM) peroxyacetic acid then diluted by a factor of 10, 50 and 100 times with distilled water and the pH adjusted to between pH 3 and 13 with sodium bisulfate and sodium hydroxide solutions. Sample pH was adjusted as needed during the measurement period to maintain a constant pH and was plus or minus 0.03 pH units of the set point during ORP measurements.

[00333] Solution 1: A formulation containing hydrogen peroxide and superoxide was produced by the method described in Example 11 at a reactor current of 8.0 amps. The reactor was operated for 1.75 hours to reach a steady-state cathode output containing 2500 mg/L hydrogen peroxide, a calculated maximum of about 14,000 mg/L superoxide anion, 7100 mg/L sodium sulfate, a pH of 13.3 and an ORP of 88 mV (SHE). Samples for ORP measurements were prepared by adjusting the pH of 8.0 mL of fresh cathode output with concentrated sodium bisulfate while diluting it to 20.0 mL with distilled water to make 1000 mg/L (29.4 mM) hydrogen peroxide concentration.

[00334] Solution 2: The cathode output generated as noted above was also used to produce peroxyacetic acid solutions containing superoxide and capable of producing singlet oxygen by mixing 8.0 mL of fresh cathode output with 0.10 g of triacetin (99%, Acros Organics) for approximately 3 to 4 minutes. This concentrate was diluted to 20.0 mL with distilled water, while adjusting the pH to make 2170 mg/L (28.5 mM) peroxyacetic acid concentration.

[00335] Solution 3: Peroxyacetic acid solutions capable of producing singlet oxygen were produced by mixing 2.0 mL of a 10.0 g/L hydrogen peroxide stock solution

(made from 3 wt% topical solution and adjusted to pH 12.5 with sodium hydroxide) with 0.09 g triacetin for 3 to 4 minutes. The resulting concentrate was diluted to 20.0 mL with distilled water while adjusting the pH to make 2170 mg/L (28.5 mM) peroxyacetic acid concentration.

[00336] Control solution A: To the peroxyacetic acid solution concentrate (CPA, at pH 12.5) was added 2.0 mL of 10.0 g/L hydrogen peroxide solution. The resulting concentrate was diluted to 20.0 mL with distilled water while adjusting the pH to make 2170 mg/L (28.5 mM) peroxyacetic acid and 1000 mg/L (29.4 mg/L) hydrogen peroxide concentration.

[00337] Figure 19 shows the ORP values of Solutions 1 through 3 and control A in the range of pH 3 to 13 varied by increments of one pH unit. Solution 1 (open diamonds) containing hydrogen peroxide and superoxide had the lowest ORP values overall in qualitative agreement with the presence of superoxide which has a standard potential of -0.33 V (SHE). The ORP of 1000 mg/L hydrogen peroxide alone at the same pH values (data not shown) was about midway between that of Solution 1 and Control solution (solid circles).

[00338] Solution 2 (opens squares) containing peroxyacetic acid with superoxide had a greater ORP than Control solution A, at a pH of less than 11, demonstrating that the presence of hydrogen peroxide in peroxyacetic acid lowers the observed ORP. The ORP of Solution 2 exceeded 650 mV (SHE) as the pH decreased to about pH 6 and lower. The ORP of Control solution A did not exceed 650 mV (SHE), until the pH was decreased to about pH 4 and lower.

[00339] According to the methylene blue dye oxidation activity described in Example 9 the generation of singlet oxygen by the Solution 2 formulation is necessary to provide the oxidative power to decolorize methylene blue. The pH range in which methylene blue oxidation occurs best is between pH 6 and 11.5. Outside of this pH range methylene blue is not significantly oxidized or oxidized at significantly slower rates. The presence of hydrogen peroxide in significant concentrations, as in Control Solution A, inhibits methylene blue oxidation throughout this pH range. Hydrogen peroxide alone at comparable concentrations has no visible effect on methylene blue.

[00340] Solution 2 has significantly stronger oxidative activity as shown by oxidation of MB than other hydrogen peroxide containing solutions in the range of about pH 6 to 11.5. However, there is no distinctive signature in the ORP of this enhanced activity as presented in FIG. 19. Singlet oxygen has a relatively low standard potential

of 0.65 V (SHE) compared to that of peroxyacetic acid, 1.81 V (SHE), and has a very short half life in water on the order of microseconds. For these reasons it is thought that singlet oxygen does not affect the ORP even though its chemical reactivity is significantly greater towards certain materials than peroxyacetic acid and hydrogen peroxide.

[00341] The ORP of Solution 2 increased slightly over the first 10 to 20 minutes after the initial preparation. The magnitude of increased ORP showed some pH dependence and one set of analyses showed increases of 17% at pH 9.0, 3% at pH 7.0, 1% at pH 6.0 and 0% at pH 5.0. The slightly elevated ORP was persistent for at least 4 hours at 25°C. It is also observed in methylene blue dye oxidation experiments that enhanced oxidative activity of the Solution 2 formulation can persist for 6-8 hours or more. This behavior indicates that there is a dynamic chemical process occurring in these solutions above pH 5 which involves peroxyacetic acid and singlet oxygen evolution.

[00342] The effect of diluting Solution 2 with distilled water on ORP was negligible in the range of 2170 to 22 mg/L peroxyacetic acid at pH 7.0, 6.0 and 5.0. The ORP of Solution 2 decreased by about 10% at pH 9.0 after diluting from 2170 mg/L to 22 mg/L peroxyacetic acid.

[00343] The production of other reactive oxygen species also contributes to the ORP in Solution 2. The presence of other ions, salt and catalytic impurities, such as iron, can affect the ORP value of freshly made solutions and an increase in ORP over time. The interaction of singlet oxygen and certain other ROS, such as superoxide discussed below, can produce solutions with significantly higher ORP. These ORP effects are most pronounced at alkaline pH indicating that an additional ROS that is more active or stabilized at alkaline pH is present.

[00344] The catalytic decomposition of hydroperoxides, such as hydrogen peroxide and peracetic acid, can produce other ROS such as superoxide radical, hydroxyl radical, hydroperoxyl radical and peracetyl radical. For example, at pH 9.0 the ORP of Solution 2 will increase over a period of several hours when diluted with unfiltered tap water from a groundwater source containing 16-18 grains hardness as shown in FIG. 20. In this figure, the relative effects of use of distilled water (solid squares) and tap water (solid diamonds) to dilute solution 2 is illustrates. PAA concentration in these solutions was 28.5 mM.

[00345] Solution 3 containing peroxyacetic acid and superoxide exhibited a significantly higher ORP of 825 mV to 1065 mV (SHE) in the range of about pH 6 to 11, which corresponds with the active pH range for superoxide production. The combination of superoxide with singlet oxygen in this formulation produces one or more reactive oxygen species which significantly impact the measured ORP. According to the methylene blue dye oxidation activity described in Example 9, the rate of oxidation is enhanced by the Solution 3 formulation over that of the Solution 2 formulation, in agreement with the presence of additional reactive oxygen species with higher oxidation potential reflected in the higher ORP observed.

[00346] Additional evidence for the production of one or more reactive oxygen species in the Solution 3 formulation was observed by monitoring ORP over time at pH 7 (solid triangles) or 9 (open circles), as shown in FIG. 21, . When Solution 3 was initially prepared the ORP values were greater than that of Solution 2, but steadily increased over the first 20 minutes (at both pH's). This behavior shows the buildup of at least one additional oxidizing species with a modest half life (e.g., minutes) depending on the rate of formation relative to decomposition. A maximum ORP is reached after the first 20 minutes and begins to decline after about 1 hour. The rate of ORP decline is accelerated at higher pH.

[00347] The effect of diluting Solution 3 on ORP was measured in the range of 2170 to 22 mg/L peroxyacetic acid at pH 9.0 (open circles) and 7.0 (solid triangles) with data shown in FIG. 22. Solution concentrates were prepared as described earlier containing 2170 mg/L peroxyacetic acid and allowed to equilibrate at 25°C for 30 minutes prior to diluting by 10, 50 and 100 times with distilled water and pH adjustment. The ORP of Solution 3 decreased with decreasing peroxyacetic acid and superoxide concentrations. Logarithmic curve fits are included in FIG. 22. The range of ORP over this wide range of concentration does not follow the expected behavior exhibited by Solution 2. The observed behavior indicates a dynamic chemical process is active involving a chemical reaction or re-speciation between multiple chemical species. For example, as the Solution 3 concentration is decreased the rate of reaction between multiple reactants to produce the transient reactive oxygen species responsible for the elevated ORP also decreases relative to the half life of the transient species. A lower Solution 3 concentration effectively results in reducing the equilibrium concentration of the transient reactive oxygen species responsible for the elevated ORP.

Example 19 Exemplary methods for generating formulations

A. Exemplary method for making peroxyacetic acid formulation to evolve single oxygen.

[00348] PM formulation prepared from 3% wt/wt or wt/vol H_2O_2) which produces 60.4 g/L PAA (assuming 98% HP conversion to PAA and no dilution by acid pH adjustment or other processes). Starting with 10 mL of 30 g/L (3%) H_2O_2 ; 0.353 g NaOH [1:1 molar ratio HP:NaOH]; 1.283 g (1.11 mL) triacetin (acetyl donor) [1:0.667 molar ratio HP:triacetin, which is the 1:2 molar ratio of HP to acetyl donor because triacetin provides three acetyl groups. Optional pH adjustment with H_2SO_4 (alternate acids that can be used include HCl, acetic acid, citric acid, phosphoric acid, bisulfate [NaHSO_4], or lactic acid).

[00349] Procedure conducted at room temperature, 15-25 °C is the typical range. Dissolve 0.353 g NaOH in 10.0 mL of 30.0 g/L H_2O_2 , about 1 min mixing time. The pH will be about 12.7-12.8 as H_2O_2 is converted substantially to NaOOH in this step. Preferably move to this step as quickly as possible, i.e. within 1 minute after dissolving NaOH as H_2O_2 will begin to degrade at room temperature forming oxygen gas and NaOH. Add the alkaline hydrogen peroxide to 1.283 g triacetin and mix rapidly until there are no oil droplets remaining, approx 1-3 min mixing time. The pH of the resulting mixture will be about 10.1-10.7. If necessary, add 0.1 M acid or NaOH to adjust the pH to the desired initial pH (pH 8-10 is a typical range for several applications). The volume of acid added will dilute initial prepared PAA concentration. Allow the mixture to “activate” naturally by inherent reactions by allowing concentrate to sit for up to 5 minutes. Singlet oxygen will begin to evolve. Side reactions not evolving singlet oxygen can evolve other transient reactive oxygen species and organic radicals which provide synergisms to enhance oxidative activity, antimicrobial activity and increase the ORP of the oxidant solution. Using a pH of 7 or greater allows for a more significant increase in ORP to occur over time, presumably due to a stabilization of certain reactive oxygen species as the pH increases. In an embodiment, begin use of the prepared formulation 2-5 minutes after preparation to minimize loss of initial PAA concentration. During use PAA continues to react forming singlet oxygen, molecular oxygen, (probably carbon dioxide), acetic acid and sodium acetate and the pH decreases as reaction proceeds. A desired amount of the concentrated formulation can be introduced into a target liquid stream; or applied to a surface, vessel or pipe (more generally any substrate). Alternatively, the concentrated formulation can be diluted to a

lower use concentration. Dilution of the concentrate (e.g., with water 10x or more) will extend working time in a day tank or buffer tank without significant loss of activity.

B. Exemplary method for making peroxyacetic acid formulation to evolve single oxygen.

[00350] PM formulation prepared from 1% wt/wt or wt/vol H₂O₂ which produces 21.1 g/L PAA (assuming 98% HP conversion to PAA and no dilution by acid pH adjustment or other processes) starting with 30 mL of 10 g/L (1%) H₂O₂ [use three times the volume as in A]; 0.353 g NaOH [1:1 molar ratio HP:NaOH]; and 1.283 g (1.11 mL) triacetin [1:0.667 molar ratio HP:triacetin]. The pH is optionally adjusted with H₂SO₄ (alternate acids include HCl, acetic acid, citric acid, phosphoric acid, bisulfate [NaHSO₄], or lactic acid).

[00351] Procedure is conducted at room temperature, 15-25 °C is a typical range. Dissolve 0.353 g NaOH in 30.0 mL of 10.0 g/L H₂O₂, about 1 min mixing time. pH will be about 12.5-12.6. H₂O₂ is converted substantially to NaOOH in this step. Move this step within about 4 hours, because the hydrogen peroxide will begin to degrade at room temperature. Add the alkaline hydrogen peroxide to 1.283 g triacetin and mix rapidly until there are no oil droplets remaining, approx 1-3 min mixing time. The pH will be about 9.8-10.6. If necessary, add 0.1 M acid or NaOH to adjust pH to desired initial pH (pH 8-10 is a typical range for several applications). The volume of acid added will dilute initial prepared PAA concentration. Allow the formulation to “activate” naturally by inherent reactions by allowing concentrate to sit for up to 10 minutes. Singlet oxygen will begin to evolve. Side reactions not evolving singlet oxygen can evolve other transient reactive oxygen species and organic radicals which provide synergisms to enhance oxidative activity, antimicrobial activity and increase the ORP of the oxidant solution. Again use of pH of 7 or greater allows for a more significant increase in ORP to occur over time, presumably due to a stabilization of certain reactive oxygen species as pH increases. Preferably begin use of the prepared concentrate formulation within 2-10 minutes after preparing to minimize loss of initial PAA concentration. PAA continues to react forming singlet oxygen, molecular oxygen, acetic acid and sodium acetate as the pH decreases as reaction proceeds. Dose desired amount of the concentrate into target liquid stream; or apply to a surface, vessel or pipe; or dilute to a lower use concentration. Diluting the concentrate (e.g., with water 10x or more) to extend working time in a day tank or buffer tank without significant loss of activity.

C. Third exemplary method for preparation of a peroxyacetic acid formulation for evolution of singlet oxygen. Continuous dose preparation (Dosing Skid).

[00352] Any appropriate device configuration for automated preparation including mixing apparatus, means for delivery of solutions, holding tanks and means for dispensing product can be employed. The method produces a 5% PAA (50 g/L concentration using 3% hydrogen peroxide feedstock (assuming 97% HP conversion) at a rate of 224 kg/day PAA (100% pure PAA basis). Starting with 2.34 L/min of 30 g/L (3.0%) H_2O_2 ; 111 mL/min 50 % wt/wt NaOH [1:1 molar ratio HP:NaOH]; 262 mL/min triacetin [1:0.667 molar ratio HP:triacetin]; 27.3 mL/min of 98% H_2SO_4 (example rate for pH adjustment).

[00353] Process is conducted at ambient temperature, 10-30 °C. Feed the 50% NaOH into the 3% H_2O_2 stream and pass through a static mixer. The pH will be about 12.7. It may be useful to dissipate heat released on addition. Feed triacetin into the alkaline peroxide stream and pass through a static mixer with an appropriate residence time (e.g., 1-3 min). The pH of the mixture will be around 10.1-10.7. Feed the up to 16% H_2SO_4 into the alkaline PAA stream and pass through a static mixer to adjust pH to desired initial pH (pH 8-10 is a typical range for several applications). Collect prepared oxidant solution concentrate in a buffer tank or holding tank for up to 5 minutes to allow the solution to “activate” naturally by inherent reactions. Singlet oxygen will begin to evolve. Side reactions not evolving singlet oxygen can evolve other transient reactive oxygen species and organic radicals which provide synergisms to enhance oxidative activity, antimicrobial activity and increase the ORP of the oxidant solution. Begin use of the prepared formulation concentrate 2-5 minutes after preparing to minimize loss of initial PAA concentration. PAA continues to react forming singlet oxygen, molecular oxygen, (probably carbon dioxide), acetic acid and sodium acetate and pH decreases as reaction proceeds. Dispense desired rate of above concentrate stream into target liquid stream; or apply to a surface, vessel or pipe; or dilute to a lower use concentration. Dilute concentrate (e.g., with water 10x or more) to extend working time in a day tank or buffer tank without significant loss of activity.

D. Exemplary method for preparing peroxyacetic acid formulation to evolve singlet oxygen in the presence of superoxide

[00354] Prepare parent oxidant solution concentrate as described in Example 18 (solution 3). Adjust the solution pH to between 5 and 12 and allow the solution to equilibrate to produce an elevated ORP solution. The solution is then used as-is or by dilution in an

application such as, for example, hard surface cleaning, clean in place sanitizing, sterilizing medical instruments, decontamination, filter cleaning, water and wastewater treatment, produce washing flumes and hydrocoolers, meat processing lines and chiller tanks, pulp and textile bleaching, cooling tower water treatment.

E. Exemplary method for preparation of peroxyacetic acid/superoxide formulation to evolve singlet oxygen.

[00355] The method is a continuous dose preparation method (dosing skid). Any appropriate device configuration for automated preparation including mixing apparatus, means for delivery of solutions, holding tanks and means for dispensing product can be employed. The method produces 7.0 g/L PAA + 10.5 g/L Superoxide as O_2^- (assuming 98% HP conversion) at a solution volume rate of 60 mL/min = 86.4 L/day and at a chemical mass rate of 0.60 kg PAA + 0.91 kg superoxide per day on a 100% chemical basis at 1:3.6 molar ratio of PAA:superoxide.

[00356] Starting with 60 mL/min of reactor cathode output, containing 5.8 g/L NaOOH, 15.8 g/L NaOH and 19.8 g/L NaO_2 in the presence of 2.8 g/L Na_2SO_4 electrolyte [the HP:NaOH: NaO_2 molar ratio is about 1:3.8:3.5]; 1.16 mL/min (1.35 g/min) triacetin [1:1 molar ratio HP:triacetin, which is a 1:3 molar ratio of HP to acetyl donor; with pH adjustment with 4.3 mL/min of 4.0 mol/L $NaHSO_4$ solution. (alternate acids include H_2SO_4 , HCl, acetic acid, citric acid, phosphoric acid, or lactic acid).

[00357] The process is conducted at ambient temperature, 10-30 °C. Feed the 1.16 mL/min triacetin into the 60 mL/min reactor cathode output stream. Mix these two streams with a suitable device such as a plug-flow static mixer and a reaction time of 1-2 minutes. Feed 4.3 mL/min of 4.0 mol/L $NaHSO_4$ solution into the above stream and mix by with a suitable device such as a plate type static mixer.

[00358] Use Case 1a: Convey the prepared oxidant concentrate directly to its point of use to minimize loss of PAA and superoxide concentrations and to utilize the synergistic enhancement of oxidative power or reactivity towards organic materials over the formulations of PAA without superoxide.

[00359] Use Case 2a: Collect prepared oxidant solution concentrate in a buffer tank or holding tank for up to 30 minutes to allow a chemical transformation to occur involving superoxide and singlet oxygen in the presence of PAA. The resulting oxidant formulation will develop a significantly higher ORP (from about pH 6 to pH 11) and exhibit less reactivity with organic materials. An elevated ORP will remain for a period of time with its maximum ORP and rate of decline dependent on the PAA:superoxide ratio, pH and concentration.

Example 20: Exemplary Embodiments of Reactive Oxygen Species Formulations

[00360] The following provides exemplary reactive oxygen species formulations in liquid form which are useful in various oxidation applications as described herein. Each formulation is particularly useful as an oxidizing biocide, a sanitizer and/or as a selective oxidant for inorganic and organic material oxidation, breakdown of polysaccharides, odor control and enhanced coagulation and microflocculation. Each exemplary formulation has a different activity and reactivity profile.

1. PAA (peroxyacetic acid) + Singlet oxygen formulation (designated PM)

[00361] PM formulations contains a peroxyacetic acid composition that produces singlet oxygen at high efficiency as the primary reactive oxygen species. Its biocidal activity is generally more rapid than oxidation of materials providing selectivity for microbial control over material oxidation at low use concentrations. PM formulations can also form other reactive oxygen species and other reactive species in addition to singlet oxygen, which provide synergistic performance enhancements. This formulation contains peroxyacetic acid prepared employing an acetyl donor (e.g., triacetin). Formulations having similar properties (designated PM*) can be prepared which contain peroxyacids other than peroxyacetic acid (or mixtures of peroxyacids). It will also be appreciated that alternate cation components of the formulation, exemplified by sodium ion, can be employed without significant detriment, as long as solubility of components is maintained.

Formulation compositions and production methods

[00362] PM is efficiently made by mixing bulk chemicals to produce a concentrate composition containing peroxyacetic acid as the parent oxidant. In a preferred embodiment a 1:1 molar ratio of hydrogen peroxide, 3 wt% solution, and sodium hydroxide, 50 wt% solution, are combined at room temperature and subsequently reacted with an acetyl donor, such as triacetin, pure liquid, in a 1:2 molar ratio of hydrogen peroxide to acetyl donor reactive groups. The resulting oxidant formulation, or concentrate, contains 5.7-5.8 wt% peroxyacetic acid, 0-0.05 wt% hydrogen peroxide, 4.6-4.7 wt% glycerol, 4.6-4.7 wt% acetic acid, 1.7-1.8 wt% sodium ion, a pH of 10.1-10.7 and has a measured ORP of 425-455 mV vs SHE. The concentrate's pH is within the activated singlet oxygen forming range of pH 6-12 and is evolving singlet oxygen at the expense of the peroxyacetic acid being consumed over time and a concomitant decrease in pH. The concentrate's pH can optionally be lowered to a pH within the activated singlet oxygen forming range by adding an acid.

[00363] PM formulations can also be made by producing an alkaline hydrogen peroxide solution with an electrochemical reactor to which the acetyl donor is added to produce a concentrate composition containing peroxyacetic acid as the parent oxidant. PM formed using electrochemical reactor output is designated PME. Again alternative formulations designated PME* can be formed using acyl donors other than acetyl donors. An exemplary reactor output stream contains 0.82 wt% sodium peroxide, 2.4 wt% sodium hydroxide and 0.28 wt% sodium sulfate. This reactor output stream is reacted with an acetyl donor, such as triacetin, pure liquid, in a 1:3 molar ratio of hydrogen peroxide to acyl donor reactive groups. The resulting oxidant formulation (PME), or concentrate, contains 1.06-1.08 wt% peroxyacetic acid, 0-0.01 wt% hydrogen peroxide, 1.30-1.31 wt% glycerol, 1.70-1.72 wt% acetic acid, about 0.18 wt% sulfate ion, 1.30-1.31 wt% sodium ion and a pH of 12.5-13. The pH of the concentrate as initially formed is greater than the desired activated singlet oxygen forming range of pH 6-12, and is can optionally be lowered to a pH within the activated singlet oxygen forming range by adding additional acid. The concentrated high pH precursor formulation (PME precursor) can optionally be stored before its activation by lowering the pH. Specifically, the pH of the precursor formulation (as formed or after a desired period of storage) can be adjusted to pH 10-11 to activate the formation of singlet oxygen by adding, for example, sulfuric acid, 98 wt%, in about a 0.36:1 molar ratio relative to the initial molar concentration of sodium hydroxide in the electrochemical reactor output. The ORP range and peroxyacetic acid consumption rates of this PME formulation are similar to those of the PM formulation formed by bulk chemical mixing. As an alternative, for PME where the pH of the reactor output is higher than about 12, acid, such as sulfuric acid, can be added to the reactor output prior to addition of acetyl donor to bring the reactor output into the pH 6-12 range and in this case a 1:2 molar ratio of hydrogen peroxide:acetyl donor groups can be used to generate PME, thereby increasing production efficiency relative to acetyl donor consumption. Triacetin is the preferred acetyl donor for PM, and PME formulations.

PM formulation Stability

[00364] The initial 5.7-5.8 wt% peroxyacetic acid concentration in the exemplary PM formulation above decreases by about 2% in about 2 minutes. The peroxyacetic acid consumption rate and singlet oxygen evolution rate can be decreased improving stability by diluting the PM formulation. For example, a diluted PM having peroxyacetic acid concentration of 0.5 wt% with pH 9.5 to 10.5 will exhibit a slower rate

of decrease of peroxyacetic acid concentration of about 2% in about 10 minutes (an about 5-fold enhancement in stability). The peroxyacetic acid consumption rate and singlet oxygen evolution rate of PM formulation can also be decreased by lowering the pH of the PM formulation to within the range pH to 5-6.5.

[00365] The thermal stability of peracids is known to be enhanced by increasing the number of carbons in the peracid molecule, thereby increasing their size and molecular weight. Stabilizers, as are known in the art, are often added to prevent impurities from catalyzing decomposition reactions of peracids. The rate of bi-molecular peracid reaction(s) leading to the formation of singlet oxygen and other reactive species can be decreased by increasing the size of the peracid molecule(s) and increasing the viscosity of the carrier medium thereby effectively reducing the diffusion rates of peracids. Increasing steric bulk of the peracids can also be used to hinder the bi-molecular peracid reaction rate. Peracids that are larger and more stable than peroxyacetic acid include peroxy-lactic acid, peroxypropionic acid, peroxybutyric acid, and long-chain aliphatic peroxy acids (C6 and greater) can be employed to enhance stability and slow the rate of single oxygen generation in formulations in PM* and PME* formulations. The peracid of the formulation is determined by the acyl donor or mixture of donors employed in preparation of the formulation.

2) HPS – Hydrogen peroxide + superoxide formulation

[00366] The formulations designated HPS contain hydrogen peroxide and superoxide. Superoxide in these formulations can be transformed at least in part to hydroperoxyl radical by pH adjustment. [see: Equation 7] HPS formulations are mild oxidants that can participate in both oxidative and reductive reaction mechanisms, have biocidal activity and serve as a precursor for more active oxidant formulations discussed below.

General Composition

[00367] HPS formulations of this invention are produced using an electrochemical reactor that reduces molecular oxygen in an aqueous stream at the cathode to simultaneously produce hydrogen peroxide anion, superoxide anion and hydroxide anions. It has been found that the superoxide component in such electrochemically-formed mixtures is stabilized and decomposes at a slower rate than similar mixtures prepared by simple mixture of bulk chemicals. In a preferred embodiment molecular oxygen reduction is conducted in the presence of water containing 0.2-0.8 wt% sodium sulfate electrolyte at an activated carbon cathode. In a

preferred embodiment the HPS formulations comprise 0.39-0.41 wt% sodium peroxide, 1.3-1.8 wt% sodium superoxide 1.2-1.6 wt% sodium hydroxide, 0.2-0.8 wt% sodium sulfate, pH 13.0-13.5 and ORP of 70-90 mV vs SHE. The concentrate's pH can optionally be lowered to a pH that transforms sodium peroxide to hydrogen peroxide (pKa 11.6) and further transforms sodium superoxide to hydroperoxyl radical (pKa 4.9). It will be appreciated that alternate cation components of the formulation, exemplified by sodium ion, can be employed without significant detriment, as long as solubility of components is maintained.

Stability

[00368] The controlled, efficient production of stabilized superoxide in aqueous solution is an advantage of the HPS formulations. Superoxide is known to be stabilized and its lifetime extended in aqueous media by the presence of high salinity, alkaline pH, alkaline hydrogen peroxide and other agents that can form stable complexes with superoxide such as cryptands and titanium complexes. Superoxide is also known to be stable for extended periods of time in non-aqueous phases such as ionic liquids and organic solvents. Stability of HPS formulations can be adjusted employing known stabilizers of superoxide.

[00369] For HPS formulations, decreasing the pH below approximately pH 11 can significantly increases the decomposition rate of superoxide as observed by ultraviolet spectroscopic analysis, by an accelerated decline in measured hydrogen peroxide concentration and/or by a visible increase in gas evolution rate. The decomposition rate of the superoxide can also be slowed by dilution of the concentrate.

[00370] Various exemplary HPS formulations: Effect of the ratio of hydrogen peroxide (HP) to superoxide

[00371] In HPS formulations, the ratio of hydrogen peroxide to superoxide to hydroxide is primarily dependent on cathode activity and current efficiency for each oxygen reduction process. The ratio of hydrogen peroxide to superoxide can also be increased by adding hydrogen peroxide, as bulk chemical or electrochemically generated solution, to an electrochemically generated HP-superoxide composition. HPS formulations include those having a ratio of superoxide to hydrogen peroxide of 3:1 or higher and those having a ratio of superoxide to hydrogen peroxide of 3:1 or lower. In one embodiment, designated High superoxide HPS (HHPS), the formulation contains superoxide and hydrogen peroxide having a molar ratio of superoxide to hydrogen peroxide in the range of 5:1-3:1. In another embodiment, in a subset of HHPS

formulations the molar ratio of superoxide to hydrogen peroxide is in the range of 5:1 to 3.5:1 or in the range of 5:1 to 4:1. In another embodiment, designated Low superoxide HPS (LHPS), the formulation contains superoxide and hydrogen peroxide having a molar ratio of superoxide to hydrogen peroxide in the range of 3.0:1 to 0.7:1. In another embodiment, in a subset of LHPS formulations the molar ratio of superoxide to hydrogen peroxide is in the range of 2.5:1 to 0.7:1 or in the range of 2:1 to 0.7:1.

3) S-PM-A – PAA + singlet oxygen + superoxide formulation – high oxidation reactivity

[00372] S-PM formulations contain superoxide and peroxyacetic acid which produces singlet oxygen and optionally other reactive species. S-PM formulations are prepared by addition of an acetyl donor. S-PM* formulations similar to S-PM formulations can be made using acyl donors other than acetyl donors. In a specific embodiment, S-PM-A, and alternatively S-PM*-A formulations, contain superoxide and a peroxyacetic acid composition that produces singlet oxygen at high efficiency. Combining superoxide with peroxyacetic acid and singlet oxygen significantly enhances the formulation's oxidation activity relative to PM or PM* formulations as shown by an enhanced rate of oxidation of organic material, exemplified by dye oxidation [e.g., methylene blue dye oxidation]. The selectivity for oxidation of chemical species relative to biocidal activity of S-PM-A or S-PM*-A formulations is increased relative to PM or PM* formulations. S-PM-A and S-PM*-A formulations are more preferred for applications involving oxidation of chemical species, rather than applications for disinfection or other antimicrobial applications.

Composition

[00373] S-PM-A is made by first producing an alkaline hydrogen peroxide-superoxide solution with an electrochemical reactor, as described for HPS formulations with the exception that the molar ratio of superoxide to hydrogen peroxide in the alkaline hydrogen peroxide-superoxide solution used ranges from 5:1 to 3:1 and more preferably is 5:1 to 3.5:1 or 5:1 to 4:1. A peroxyacetic acid concentrate containing superoxide is then formed by addition of an acetyl donor to the alkaline hydrogen peroxide-superoxide. This mixture is a precursor formulation containing peroxyacetic acid as a parent oxidant to form singlet oxygen on activation. Activation of this precursor peroxyacetic acid-superoxide formulation by adjusting the pH to 6-12 generates singlet oxygen. S-PM*-A formulations are similarly made employing an acyl donor other than an acetyl donor to prepare the precursor formulation.

[00374] For S-PM-A generation, an exemplary reactor output stream contains 0.4 wt% sodium peroxide, 1.5 wt% sodium superoxide, 1.4 wt% sodium hydroxide, 0.2 wt% sodium sulfate, pH 13.1 having an ORP of 80 mV vs SHE. It will be appreciated that alternate cation components, other than sodium ions, can be employed in the formulations without significant detriment, as long as solubility of components is maintained. The reactor output stream is reacted with an acetyl donor, such as triacetin, pure liquid, in a 1:3 molar ratio of hydrogen peroxide to acyl donor reactive groups (1:1 molar ratio of hydrogen peroxide to triacetin which has three acetyl group). The resulting precursor formulation or concentrate, contains up to 0.86 wt% superoxide anion, 0.52-0.53 wt% peroxyacetic acid, 0-0.005 wt% hydrogen peroxide, 0.64-0.65 wt% glycerol, 0.84-0.85 wt% acetic acid, about 0.13 wt% sulfate ion, 0.80-0.81 wt% sodium ion and a pH of 12.9-13.1. The pH of this precursor concentrate is greater than the activation pH range for forming singlet oxygen of pH 6-12. The pH of the precursor concentrate is adjusted to pH 10-11 to activate the formation of singlet oxygen by adding acid to form the S-PM-A formulation. For example, to the precursor described above, sulfuric acid, 98 wt%, in about a 0.40:1 molar ratio relative to the initial molar concentration of sodium hydroxide in the electrochemical reactor output is added. The higher pH precursor concentrate can be stored after production, and activated by addition of acid after storage to generate the S-PM-A formulation. S-PM-A formulations exhibit ORP of 260-400 mV vs SHE which increases over time (presumably as single oxygen and possibly other reactive species form) with a concomitant decrease in pH. The concentrate's pH can optionally be lowered to a pH within the activated singlet oxygen forming range by adding additional acid.

[00375] As noted for generation of PM formulations, S-PM-A formulations can also be produced by first adding acid to the reactor output containing superoxide and peroxide to lower the pH to the activation pH range of 6-12 and thereafter add the acetyl donor (or acyl donor for S-PM*-A formulations). In this case, singlet oxygen formation can begin on addition of the acyl donor. S-PM-A and S-PM*-A formulations can be diluted as desired.

4) S-PM-B – PAA + singlet oxygen + superoxide formulation – high ORP

[00376] S-PM-B formulations are derivatives of S-PM-A formulations having significantly higher ORP, but lower oxidative reactivity to organic materials than S-PM-A formulations as shown in ORP data (e.g., FIG. 23A) and methylene blue oxidation data (FIG. 24B) As a result, S-PM-B formulations have higher selectivity for biocidal or

disinfection activity over oxidation of chemical species compared to PM solutions. S-PM*-B formulations exhibit similar selectivity as biocides with higher ORP compared to comparable S-PM*-A formulations and PM* formulations.

Preparation and Composition

[00377] S-PM-B formulations are prepared as the A-PM-A formulations employing electrochemically generated mixtures of superoxide and hydrogen peroxide (molar ratio superoxide: hydrogen peroxide as noted for S-PM-A formulations), however it is preferred to add the acetyl donor to the reactor output to form the precursor concentrate containing peroxyacetic acid prior to addition of acid to lower the pH. Additionally, the pH of this precursor concentrate containing peroxyacetic acid is adjusted to pH 6-11 to activate the formation of singlet oxygen. Preferably the pH is initially adjusted to 10-11. After this pH adjustment, the ORP of the formulation is initially 260-400 mV vs SHE. Over 20-30 minutes the ORP increases significantly with a concomitant decrease in pH. The ORP stabilizes for a period of time at a significantly elevated ORP of about 825-875 mV vs SHE at pH 10, before the ORP starts to decline as the oxidants are consumed or decompose. The elevated ORP is characteristic of the S-PM-B formulations and persists for up to approximately 60 minutes before declining. The maximum ORP and the rate of decline depend on oxidant solution pH and concentration. [see ORP vs pH vs time data] Reducing pH within the activation pH range and reducing concentration by dilution lead to longer lifetimes of the elevated ORP state for this composition. The enhanced ORP is produced in an activated pH range of 6-11.

[00378] Thus, the S-PM-B formulations are prepared by first producing an alkaline hydrogen peroxide-superoxide solution with an electrochemical reactor and having a molar ratio of superoxide to hydrogen peroxide of 5:1 to 3:1 and forming a peroxyacetic acid concentrate containing superoxide by addition of an acetyl donor to the alkaline hydrogen peroxide-superoxide (a precursor formulation for the S-PM-A formulations). This forms a precursor formulation containing peroxyacetic acid as a parent oxidant to form singlet oxygen. Activation of this precursor peroxyacetic acid-superoxide formulation by addition of acid such that the pH is in the range of 6-11 followed by a delay of at least about 20 minutes provides the S-PM-B formulation. The S-PM-B formulation can be decreased in pH to 6-9 or diluted to extend its activity. S-PM*-B formulations are made employing an acyl donor other than an acetyl donor to prepare the precursor formulation. The change in ORP with time indicates the formation

of one or more reactive species in addition to superoxide, peroxyacetic acid and superoxide.

[00379] It will be appreciated that S-PM-A or S-PM*-A formulations with pH of 6-11 will convert to S-PM-B or S-PM*-B formulations with time. Thus, the S-PM-A or S-PM*-A formulations with pH of 6-11 can be used in dual application for initial oxidation of chemical species and later biocide and disinfection.

5) S-PM-C – PAA + singlet oxygen + superoxide formulation – Extended lifetime

[00380] S-PM-C formulations exhibit a long-lasting, elevated ORP which is intermediate to S-PM-A and S-PM-B formulations by the interaction of superoxide with singlet oxygen in the presence of peroxyacetic acid. Similar S-PM*-C formulations are prepared using an acyl donor other than an acetyl donor. S-PM-C and S-PM*-C formulations contain superoxide and a peroxyacetic acid and produce singlet oxygen at high efficiency, but the superoxide to peroxyacetic acid ratio is lower compared to the corresponding S-PM-A and S-PM-B formulations. S-PM-C and S-PM*-C formulations exhibit significantly higher ORP and comparable oxidative reactivity relative to PM formulations. An important difference for S-PM-C and S-PM*-C formulations is that the elevated ORP can persist for a period of days, instead of less than 24 hours as in S-PM-A and S-PM-B formulations. S-PM-C and S-PM*-C formulations thus provide a residual ORP level that can maintain biostatic conditions for extended periods of time.

[00381] S-PM-A is made by first producing an alkaline hydrogen peroxide-superoxide solution with an electrochemical reactor, as described for HPS formulations with the exception that the molar ratio of superoxide to hydrogen peroxide in the alkaline hydrogen peroxide-superoxide solution used ranges from 3.0:1 to 0.7:1. 2.5:1 to 0.7:1 or in the range of 2:1 to 0.7:1.

Composition

[00382] S-PM-C is made by first producing an alkaline hydrogen peroxide-superoxide solution as described for S-PM-A formulations with the exception that the molar ratio of superoxide to hydrogen peroxide in the alkaline hydrogen peroxide-superoxide solution used ranges from 3.0:1 to 0.7:1. To obtain this ratio of superoxide to hydrogen peroxide, hydrogen peroxide solution is added to electrochemical reactor output to decrease the ratio of superoxide to hydrogen peroxide. An exemplary reactor output stream contains 0.4 wt% sodium peroxide, 1.5 wt% sodium superoxide, 1.4 wt% sodium hydroxide, 0.2 wt% sodium sulfate, pH 13.1 and ORP of 80 mV vs SHE. To this

reactor output stream is added 3 wt% hydrogen peroxide such that the modified composition is 0.6 wt% sodium peroxide, 1.5 wt% sodium superoxide, 1.3 wt% sodium hydroxide, 0.2 wt% sodium sulfate and has pH 12.9-13.1. This modified hydrogen peroxide-superoxide composition is then reacted with an acetyl donor, such as triacetin, pure liquid, in a 1:2.4 molar ratio of hydrogen peroxide to acyl donor reactive groups to form a high pH precursor to the S-PM-C formulation. S-PM*-C precursor concentrates are similarly produced using an acyl donor other than an acetyl donor. It will be appreciated that alternate cation components, other than sodium ions, can be employed in the formulations without significant detriment, as long as solubility of components is maintained.

[00383] The resulting peroxyacetic acid concentrate precursor, contains up to 0.86 wt% superoxide anion, 0.78-0.80 wt% peroxyacetic acid, 0-0.007 wt% hydrogen peroxide, 0.77-0.78 wt% glycerol, 0.88-0.89 wt% acetic acid, about 0.13 wt% sulfate ion, 0.72-0.73 wt% sodium ion and a pH of 12.5-13.0. The pH of this precursor concentrate is greater than the activated singlet oxygen forming pH range of 6-12 and the elevated ORP activated pH range of 6-11. The pH of the precursor is then adjusted to pH 6-11 by addition of acid. Preferably the PH is adjusted to 7-8 to activate the formation of singlet oxygen. For example, sulfuric acid, 98 wt%, in about a 0.45:1 molar ratio relative to the initial molar concentration of sodium hydroxide in the electrochemical reactor output is added to achieve pH 7-8. The ORP of the resulting S-PM-C formulation with pH 7-8 is 680-720 mV vs SHE which then increases over about 4 hours, with a concomitant decrease in pH, to a stabilized ORP of 770-800 mV vs SHE at pH 7. The pH of the concentrate can optionally be lowered, raised or held constant within the activated singlet oxygen forming range by adding additional acid or base. The elevated ORP of the S-PM-C formulation remains nearly constant at constant pH for about 34 hours when the formulation contains 0.2-0.3 wt% peroxyacetic acid. The ORP of the formulation then continues to decline slowly with time, but can persist above 740 mV for 45 hours or more.

[00384] FIGs. 23A and B illustrate the effect on ORP as a function of time of variation of initial molar ratio of PAA: superoxide (noting that amount of PAA present in formulation is directly related to the amount of hydrogen peroxide in the precursor hydrogen peroxide + superoxide precursor employed) in S-PM formulations. In FIG. 23A ORP is shown as a function of time up to 500 minutes. In FIG. 23B ORP data is shown for the same formulation at time up to 2400 minutes (40 hours). The formulations

all contained 28.5 mM PAA at an initial pH of 7. In FIG. 23A, formulations vary by molar ratio of PAA:superoxide, with 1:4.5 (solid circles); 1:3.1 (solid diamonds); 1:2.4 (solid squares) and 1:1.9 (solid triangles). In FIG. 23B, in addition to the formulations with varying molar ratio of PAA:superoxide, the ORP of a formulation containing PAA and singlet oxygen with no superoxide pH 7 (a PM formulation, gray open circles, ORP ~ 600 mV vs. SHE) and the ORP of the reactor output containing hydrogen + superoxide at pH 9 (black open circles, increasing rapidly to ORP ~900 mV vs. SHE). The ORP of the formulation having molar ratio of PAA:superoxide of 1:3.1 (about 1:3) increases over about 7 hours to close to 800 and persists for over 40 hours above 700. The ORP of the formulation having molar ratio of PAA:superoxide of 1:4.5 increases more rapidly to OORP of about 1000, but declines to below 800 by about 7 hours.

[00385] FIG. 23 C illustrates the rate of methylene blue oxidation by S-PM formulations as a function of molar ratio of PAA:superoxide. MB oxidation rate assays are described in Example 9. Formulations have 25 mM PAA initial concentration at pH 7 and molar ratio of PAA: superoxide of 1:4.5 (solid squares); 1:2.4 (solid diamonds) and open circles is a PM formulation (no superoxide).

FIGs 24A and B illustrate the rate of methylene blue oxidation for PM formulation (FIG. 24A, solid circles), S-PM formulation (molar ratio PAA:superoxide of 1:4.5) (FIGs. 24A and B, solid squares) and an S-PM-B formulation (molar ratio PAA:superoxide of 1:4.5) (FIG. 24, solid triangles).

6. Further Activation of formulations described in 1-5 above.

[00386] PM, HPS, and various S-PM formulations can be further activated to generate additional reactive oxygen species and/or other reactive species. Activation includes, among others:

[00387] Ultraviolet light, catalyst, ultrasound, sonic cavitation and microwave (sonic and electromagnetic energy):

[00388] Energy transfer from a material (e.g., a photo-activated dye or an activated semiconductor surface activated by light or an electrical field); or

[00389] Thermal activation (heating).

[00390] Benefits of the additionally activated formulation are demonstrated in comparative ORP measurements, oxidation experiments and biocidal data.

[00391] Further activation can be applied to each PM, HPS or various S-PM formulations after its generation by pH adjustment (to form singlet oxygen) or by mixing components (HPS formulations). Alternatively, a step of further activation can be

applied to high pH peracid containing precursors the pH or which is thereafter adjusted to activate singlet oxygen formation. Further activation can be applied to a formulation before, after or at the same time that it is dispensed into the environment in which the formulation is to be used or into contact with a substrate or environment which is to be treated with the formulation. For example, a formulation can be subject to a brief period of UV irradiation before dispensing or as it is being dispensed for use. For example, a formulation can be subject to microwave irradiation or ultrasound before dispensing or as it is being dispensed for use. For example, a formulation can be heated for a selected time before it is dispensed or can be employed in its application at a temperature higher than ambient.

Example 21: UV Activation of PM Formulations

[00392] UV light-activated PM formulations containing peroxyacetic acid exhibit an increased oxidative reactivity over PM formulations. After UV light irradiation of the formulation ceases the formulation retains an elevated activity level for a period of time (about 40 minutes in the examples below) before returning to the activity level of the peroxyacetic acid remaining in the PM formulation. The activation methods described can also be applied to PM* formulations which contain peracids other than peroxyacetic acid.

[00393] A flow-through UV irradiation device can be added to the output of an oxidant production or dosing system (such as those illustrates in the figures herein) with little impact on the process design making this activation method feasible for scaleup. A flow-through UV irradiation device can alternatively be positioned immediately upstream of the point of use of a formulation to be activated, particularly if there is a long run between the oxidant production apparatus and the point of use.

[00394] There is relatively little loss of peracid (e.g., 5-10% reduction) caused by UV irradiation, thereby not significantly increasing chemical consumption cost. The brief UV irradiation time also contributes relatively little power cost to the process cost. Clean, non-fouling formulation comes in contact with a UV lamp or window thereby minimizing cleaning and maintenance cost for the UV irradiation device.

A. Batch UV activation procedure:

[00395] Conducted at about room temperature, 15-25 °C is a typical range (PAA = peroxyacetic acid).

1. 10.4 mL of a PM formulation containing 22.7 g/L PAA was diluted to 96 mL and 2.46 g/L PAA as measured by iodometric titration (HACH method).
2. 80 mL of the diluted PM formulation was placed in a 100 mL glass beaker.
3. A UV pen lamp was immersed in the PM formulation and turned on to irradiate the formulation for 4.5 minutes. During irradiation the formulation was gently stirred with

the UV pen lamp. After irradiation the PAA concentration of the formulation had decreased by about 300 mg/L to 2.13 g/L PAA as measured by iodometric titration.

4. Immediately after irradiation the formulation was used directly, correcting for the decrease in PAA concentration, or further diluted to a point of use concentration. The UV-activated PM formulation can be dosed into a solution or applied to a surface to be treated. UV-enhanced oxidative activity of the activated PM formulation persisted for up to approximately 40 minutes in this example.

[00396] The solution pH, ORP and oxidant concentration, measured as PAA, were monitored over time in the above example:

[00397] Before UV irradiation: 2.46 g/L PAA, pH = 9.5, ORP = 423 mV (vs SHE); About 1 minute after UV irradiation ceased: 2.13 g/L PAA, pH = 9.0, ORP = 489 mV (vs SHE); 20 minutes after UV irradiation ceased: 2.02 g/L PAA, pH = 8.9, ORP = 493 mV (vs SHE); and 40 minutes after UV irradiation ceased: 2.13 g/L PAA, pH = 8.9, ORP = 497 mV (vs SHE).

[00398] The above measured decrease in PAA concentration after UV irradiation followed by at least a partial recovery of the oxidant concentration was a consistent result for freshly made PM formulations. The oxidant concentration after UV irradiation is not necessarily just due to PAA. For example, after three UV irradiation cycles on a PM formulation prepared by the same procedure the titrated oxidant molar concentration increased by a factor of 1.6 times.

[00399] The same UV irradiation process as employed for PM formulations was conducted on a “merchant” PAA solution containing 2.2 g/L PAA and 2.2 g/L hydrogen peroxide adjusted to pH 9.0. In contrast to the activation observed with irradiation with PM formulations, there was no change to the initial ORP of 358 mV (vs SHE) at pH 9.0 after 4.5 minutes of UV irradiation on irradiation of the “merchant” PAA solution.

B. Methylene Blue Dye Oxidation with UV-Activated PM Formulations- Batch Method

[00400] A PM formulation was prepared by the method described in A above. Prior to UV irradiation the pH of the formulation was adjusted to 9.3 resulting in a pH of 9.1 after 4.5 minutes of UV irradiation.

[00401] Activated PM formulation (2.0 mL) was added to 2.0 mL of a 100 mg/L methylene blue dye solution (25 mM PAA) and allowed to react at room temperature. A control PM formulation (25 mM PAA)(2.0 mL) was also added to 2.0 mL of the 100 mg/L methylene blue dye solution. The resulting test solutions initially contained 1.90 g/L PAA and 50 mg/L methylene blue at about pH 7-8. Methylene blue dye was oxidized (as assessed by the rate of dye decolorization) by UV-irradiated PM formulation and the non-irradiated PM formulation. UV-irradiated PM formulation showed a significant enhanced rate of dye oxidation compared to the control upon dosing of about 20%(data not shown). The UV-irradiated PM formulation exhibited a fast-acting bleaching activity which was not observed for any other PAA-oxidant

system examined by this method. Between 35- 60 minutes after dosing, the rate of methylene blue decolorization by the UV-activated formulation decreased to a rate similar to, or slower than that of PM formulation control.

[00402] UV irradiation of PM formulations resulted in both increased ORP and increased reactivity with methylene blue dye compared to non-irradiated PM formulations.

[00403] The UV pen lamp used in the above examples emits a mercury vapor emission wavelength of 258 nm with a fluence rating of $80 \text{ Js}^{-1}\text{cm}^{-2}$ in clear water. The immersed portion of the lamp is about 4.0 cm long and 1.3 cm in diameter providing about 8.2 cm^2 lamp area in direct contact with the solution. The 258 nm wavelength is in the range known to dissociate the oxygen-oxygen bond of peroxides into radicals. For example, hydrogen peroxide is dissociated into two hydroxyl radicals, which is the basis of the UV-hydrogen peroxide advanced oxidation process (AOP). PAA is known to be similarly dissociated on irradiation with UV light of wavelength of around 258 nm into hydroxyl and acyloxy radicals in an AOP.

[00404] Acyloxy radical is known to undergo decarboxylation forming methyl radical and carbon dioxide. Methyl radical can react with molecular oxygen to form methyl peroxy radical. All of these radical species are typically transient and short-lived. AOP applied to hydrogen peroxide or PAA is effective only during irradiation by UV light and does not result in enhanced oxidative activity in the absence of UV light. This is in contrast to the retained enhanced oxidative activity observed over a significant and useful time period after irradiation of PM formulations is ended. Continuous irradiation of the PM formulations is not required to obtain activity enhancement.

[00405] For PM formulations irradiated by UV light an elevated oxidative activity persists after UV irradiation has ceased. While not wishing to be bound by any particular theory, it is currently believed that in UV-activated PM formulations, UV-generated radical species are stabilized by other constituents present or may react with other formulation constituents to form other reactive species with longer half lives to account for the observed retention in activity after irradiation is ended. Other constituents unique to the PM formulations include singlet oxygen and glycerol. Singlet oxygen may also be directly affected by UV irradiation.

C. Continuous Dosing Apparatus and Process – UV-Activated PM formulations

[00406] In a continuous UV-activated oxidant production or dosing process PM formulations pass through a suitable flow-through UV apparatus. The total UV irradiation energy can be adjusted by oxidant solution residence time in the UV apparatus and the fluence of the UV source relative to the concentration of the oxidant solution and activity required for the application. This same approach applies to a PeroxyMax-Superoxide oxidant production and UV-activation process.

Example 22: Catalyst Activation of PM Formulations

[00407] Catalyst-activated PM formulations exhibit an increased oxidative reductive potential (ORP) compared to PM formulations. This “activation” method was initially observed when municipal tap water, which contained copper originated from contact with copper pipes was used for making formulation. Catalyst activation leading to dramatically elevated ORP’s was also observed during the treatment of produced water from oil and gas production wells which is believed to be the result of metals in the produced water.

[00408] To activate the PM formulation a suitable catalyst is added. Catalyst can be added to the output of an oxidant production or dosing apparatus with little impact on the process design. Alternatively the oxidant solution can be added to a target liquid stream, surface or environment to be treated which possesses materials or surfaces suitable to act as “activation” catalysts. In these cases the catalyst can be selectively added or may be inherently present in the target to be treated.

[00409] **A. Batch Catalyst activation procedure:**

[00410] Conducted at 25 °C.

1. 2.0 mL PM formulation containing 22.0 g/L PAA was diluted to 20.0 mL with distilled water, including pH adjustment with 0.2 mol/L NaHSO₄, to make 2.20 g/L PAA oxidant solution.
2. 2.0 mL PM formulation containing 22.0 g/L PAA was diluted to 20.0 mL with tap water, including pH adjustment with 0.2 mol/L NaHSO₄, to make 2.20 g/L PAA oxidant solution. The tap water contained 16-18 grains of hardness, about 0.18 mg/L copper, total chlorine of about 0.5 mg/L and pH 7.5.

[00411] The ORP of the above prepared solutions was monitored over time at 25°C while maintaining a constant pH of 9.0 by titrating concentrated NaOH into the samples, if necessary, before each measurement. The tap water-containing oxidant sample exhibited a higher initial ORP, which increased significantly over time, compared to the oxidant sample prepared with distilled water. Dirty glassware or equipment in contact with the oxidant solution can have a similar effect to that of the tap water-containing oxidant example.

[00412] These results show that the PM formulations can be readily activated by the presence of low levels of impurities (e.g., metals) to produce additional reactive oxygen species and other reactive species, which can be synergistic with the parent oxidant solution composition.

Example 23: Produced Water Treatment: Catalytic activation and Biocidal performance

[00413] A raw produced water sample was obtained from an undisclosed location in the Piceance Basin in western Colorado, USA. The general water characteristics included total dissolved solids near 12 g/L, total organic carbon content around 0.2-0.3 g/L, pH 6.5-6.8 and

ORP 130-185 mV (vs SHE). The water had a strong odor of volatile organic compounds, similar to fuel and aromatic hydrocarbons, but no perceptible smell of hydrogen sulfide. The water was turbid with very fine dark grey-black suspended solids, which was primarily iron sulfide produced as a result of sulfate reducing bacteria activity. A small amount of free oil phase would separate to the top of a water sample, appearing as a thin sheen, after sitting undisturbed at room temperature for 2-3 days.

A. Catalyzed Activation ORP Response in Produced Water

[00414] ORP measurements were conducted on 50 mL of solution in 100 mL glass jars with air tight lids. PM formulation was dosed 5 minutes after preparation as a 20.2 g/L concentrate into the appropriate amount of raw produced water to give a final volume of 50 mL and the desired initial oxidant dose concentration (dosage based on PAA concentration). For comparison, a “merchant” PAA formulation containing 7.78 g/L PAA, 3.47 g/L H₂O₂, and acetic acid at pH 4.4 was prepared. Oxidant concentrate was slug-dosed into the raw produced water while mixing and each sample was mixed for 2 additional minutes. The pH of each sample was adjusted to pH 7.0 and held constant by titrating in concentrated sodium hydroxide or sodium bisulfate when necessary. Sample preparations and analysis were conducted at room temperature, 22°C.

[00415] The PM formulations were dosed into raw produced water samples at 100 and 500 mg/L PAA initial concentrations. The “merchant” PAA formulation was similarly dosed at 500 mg/L PAA initial concentration. The color of all three samples rapidly turned from grey to pale yellow-orange. A light brown, small particle floc formed over several minutes and settled over several hours after measurements were completed. The solutions remaining after floc settled were clear and nearly colorless. It was also observed that conducting jar tests with PM formulations having 20 to 500 mg/L PAA doses in larger solution volumes, 1 L or more, resulted in the formation of significantly larger floc particles, which could settle within about 1.5 hours.

[00416] Samples containing PM formulations show a very rapid initial increase in ORP followed by slower changes over the next several hours. The sample dosed with PM formulation having 100 mg/L PAA showed an ORP increase to nearly 760 mV (vs SHE) and then a slow decrease in ORP as the oxidant was consumed over time. The sample dosed with PM formulation having 500 mg/L PAA showed an ORP increase after 1 hour contact time from about 890 mV to over 1000 mV (vs SHE) and the ORP remained above this value for nearly 23 hours after the initial oxidant dose (after 19.5 hours the ORP started to slowly decline). The “merchant” PAA formulation exhibited a brief, initial increase in ORP to around 670 mV, but rapidly settled in less than 8 minutes to a lower, constant potential of 470 mV (vs SHE).

[00417] For samples treated with PM formulations, the magnitude of increase in ORP and its duration correlates with the initial oxidant dose, oxidant consumption rate and

oxidant residual. At 180 minutes the residual oxidant concentration was measured in each sample by iodometric titration and reported as PAA. The samples having PM formulation dosed at 500 mg/L and 100 mg/L initial PAA doses had total oxidant residuals, as PAA, of about 160 mg/L and 30 mg/L, respectively. The “merchant” PAA 500 mg/L initial dose had a total oxidant residual, as PAA, of about 160 mg/L. The sample dosed with “merchant” PAA did not exhibit elevated ORP.

[00418] Samples dosed with PM formulation at 10 and 20 mg/L PAA initial concentration exhibited some effect on ORP, but the oxidant was consumed rapidly. These examples are reported in the biocidal efficacy tests below.

[00419] Components of the water samples functioned to catalyze oxidant activation as evidenced by the change in ORP observed in treated samples. Without wishing to be bound by any particular theory of action, component expected to be acting as catalysts in the produced water samples could include the iron sulfide suspended solids or dissolved transition metals such as copper, iron and manganese. Iron sulfide is a good catalyst candidate since the iron is in the reduced, ferrous, oxidation state, which is the preferred oxidation state for Fenton-like catalysts. The iron sulfide is oxidized by the PM formulation oxidants as evidenced by the rapid change in sample color from dark grey-black to a light brown insoluble material characteristic of ferric oxyhydroxides. Copper and manganese could also contribute significant catalyst activity.

B. Biocidal Performance in Produced Water

[00420] Biological control is one of the most critical issues in oil and gas exploration and production. Biological control is essential prior to sending water into a well as makeup water in drilling muds, hydraulic fracturing fluids and flood water. Similarly, biological control is necessary upstream of water treatment processes or prior to disposing of produced water, flowback water or other process waste water by deep well injection. Without effective biological control microorganisms from formation and surface environments, particularly sulfur-reducing, acid-forming and slime forming bacteria, will foul and degrade well casings, corrode pumps and equipment and foul the formation leading to accelerated loss of reservoir permeability and productivity. Oxidizing biocides are a fast-acting line of defense and represent a significant expense in operations. Oxidizing biocides should be very active and have a limited lifetime with no reactive residuals so that they do not interfere with non-oxidizing biocide chemicals used to provide longer-term biostatic conditions.

[00421] Biocidal efficacy tests of PM formulation with produced water samples (as in A above) were conducted on 50 mL of solution in 100 mL glass jars with air tight lids. PM formulations were dosed at 10 mg/L and 20 mg/L initial concentration of PAA. PM formulations were diluted with distilled water to 1.01 g/L five minutes after its preparation as a 20.2 g/L concentrate. Dilution allowed for a more accurately measured quantity of oxidant to be dosed on a PAA basis into the appropriate amount of raw produced water to give a final volume of 50 mL.

Similarly, a “merchant” PAA formulation containing 7.78 g/L PAA, 3.47 g/L H₂O₂, and acetic acid at pH 4.4 was prepared and diluted 20-fold with distilled water and dosed on a PAA basis. A topical hydrogen peroxide solution was diluted to 1.00 g/L H₂O₂ and a bleach solution was diluted to 1.00 g/L sodium hypochlorite (NaOCl) for more accurate dosing. A UV-activated PM formulation was prepared as described in Example XX producing an activated formulation containing 2.1 g/L PAA that was dosed into samples immediately after UV irradiation. Oxidant formulations were slug-dosed into the raw produced water while mixing and each sample was mixed for 5 additional minutes. Microbial tests were conducted after a 1 hour contact time. Sample preparations were conducted at room temperature, 21-23°C.

[00422] Microbial analysis was conducted using SaniCheck B dip slides for general bacteria counting from Biosan Laboratories, Inc. Dip slides were immersed in the sample solution for 3-5 seconds, excess liquid drained off and finally incubated for 30 hours at 28-30°C as described by the product instructions. The colony density developed on the dip slides was compared to a conversion chart scaled in 1 log increments up to 10⁷ cfu/mL bacteria concentration. Results of these assays are summarized in Table 4.

[00423] **Table 4 Antimicrobial Activity of Oxidant Formulations**

Oxidant Type	Oxidant Concentration, mg/L	Raw Water Bacteria Count, cfu/mL	Treated Water Bacteria Count, cfu/mL
None	0	10⁷	na
H₂O₂	10	10⁷	10⁶
"merchant" PAA	10	10⁷	10⁵
NaOCl	10	10⁷	10⁴
PeroxyMax PAA	10	10⁷	10³
PeroxyMax PAA	20	10⁷	10²
UV-Activated PeroxyMax PAA	10	10⁷	10⁴

[00424] PM formulation had the most effective biocidal activity in the produced water. Hydrogen peroxide exhibited very little biocidal activity and was not expected to contribute significantly to the biocidal activity of the “merchant” PAA formulation. NaOCl provided the second-best biocidal activity. UV-activated PM formulation was similar in biocidal efficacy to NaOCl. UV-activated PM formulation had been demonstrated to be a more active oxidant than PM formulation in clean water tests, but exhibited lower activity than PM formulations in these biocide assays. The lower biocide activity of UV-activated PM formulation is consistent with the elevated reactivity of UV-activated PM formulation for other organic and inorganic contaminants in the produced water which leads to less selective towards microbes. This higher oxidative activity on UV activation is expected to be useful for waste water treatment processes where the degradation and removal of chemical contaminants and volatile organic compounds is desired for water reuse or enhancing biological treatment processes.

[00425] For the oxidants tested in Table 4 at 10 mg/L and 20 mg/L oxidant doses, the greatest oxidative color change in the samples (assessed by visual comparison) for the dark suspended iron sulfide material occurred with PM formulations. The color change was only partial, even at 20 mg/L dose, indicating that much of the iron sulfide was not oxidized. Hydrogen peroxide and NaOCl had no detectable effect on the dark iron sulfide material and “merchant” PAA fell in the middle of the range by visual comparison.

Example 24: Exemplary General Water Treatment Process

FIG. 25 illustrates a exemplary water treatment process employing a reactive oxygen formulation of this invention.

[00426] Referring to FIG. 25, water to be treated enters the treatment process [2501] and treated product water exits 2520, illustrated by exemplary outputs 2520a-d of different quality. The influent can be from any source, directly from a source of production, a side-stream or slip-stream of a process, or from an impoundment or storage vessel (e.g., tank or lagoon) or may have undergone pre-processing such as grit and solids separation, gas recovery and/or pH adjustment.

[00427] Pre-treatment steps 2502 are optionally applied. For example, volatile materials (e.g., volatile organic compounds, dissolved gases, ammonia) are optionally removed by air stripping [2502a]. For example, readily oxidizable materials (e.g., dissolved or suspended metals like reduced iron and manganese) can optionally be pre-oxidized [2502b] with oxygen in air to reduce the consumption of oxidants used downstream. This step is excluded when it is beneficial to deodorize or oxidize and degrade gaseous materials in the liquid phase or if the liquid stream is susceptible to foaming. One or more steps of filtering can also be applied. Reactive oxygen species formulations are added 2503 to oxidize materials, provide a biocide, promote flocculation and/or enhance filtration and biological treatment performance. Reactive oxygen species formulations can also contain alkalinity or acid for pH adjustment, precipitants, coagulants, antiscalants and demulsifiers. A separate source of acid or base can optionally be provided 2504.

[00428] Biological treatment 2505 (aerobic and/or anaerobic) can be used to remove dissolved and suspended organic materials, metals, nutrients (e.g., nitrates, phosphates, sulfates) and reactive species oxidation byproducts. Clarification 2506 is used to remove free oil and grease, suspended solids (e.g., microflocculated solids and biological detritus), colloidal and dissolved organics and metals (e.g., Fe, Mn). Clarification methods can include coagulation and flocculation, electrocoagulation, flotation, settling, centrifugation, particle filtration (e.g., sand, dual media, micro- and ultra-filtration) and absorptive media. Forward osmosis filtration can also be used as an alternative clarification process.

[00429] ROS antimicrobial treatment 2507 can optionally be used as a final biocide prior to product water output as a biocidal pre-treatment to a water softening process 2508; and as a biocidal pre-treatment to a water softening 2508 and desalination process 2509. antimicrobial treatment 2507 can alternatively be used to increase the peroxide and concentration prior to wet peroxide and wet ROS oxidation treatment 2510.

[00430] A water softening process can be provided 2508 including methods such as lime softening, ion exchange, absorptive media, nanofiltration and electro-capacitive deionization. Desalination process 2509 can include methods such as nanofiltration, reverse osmosis, forward osmosis, membrane distillation, thermal distillation, multi-effect distillation, electro-capacitive deionization, and electrodeionization.

[00431] Additional optional treatment 2510 can be provided dependent upon water quality desired. For example, wet peroxide oxidation treatment including elevated temperature, elevated pressure, a catalyst, a catalytic surface, and combinations of such conditions can be applied to promote wet peroxide. An additional step of wet ROS oxidation of organic and inorganic materials can also be applied.

[00432] FIG. 25 illustrates a general example of a treatment process where each stage can be incorporated, excluded or moved to a different location in the exemplary sequence depending on the influent composition and product water quality required for reuse, repurposing, discharge or further processing.

What is claimed is:

1. A method for oxidative treatment of a substrate or environment with reactive oxygen species, the method comprising:
 - preparing a peracid mixture at an activated pH range of from pH 9.5 to pH 12.5 for generating reactive oxygen species comprising singlet oxygen during the oxidative treatment, the preparing comprising:
 - mixing an alkaline hydrogen peroxide solution with a molar excess of an acyl donor to hydrogen peroxide at a molar ratio of hydrogen peroxide to acyl donor in a range of from 1:1.25 to 1:4; and
 - during or after the mixing adjusting the pH to prepare the peracid mixture at a pH in the activated pH range; and
 - after the preparing, distributing the peracid mixture to a point of use and at the point of use applying the peracid mixture in the activated pH range to the substrate or environment.
2. The method of claim 1 wherein the reactive oxygen species comprise singlet oxygen and superoxide.
3. The method of either one of claim 1 or claim 2 wherein the acyl donor is an acetyl donor.
4. The method of any one of claims 1-3 wherein the alkaline hydrogen peroxide solution is generated from the combination of an alkali and a hydrogen peroxide concentrate.
5. The method of claim 4 wherein the alkaline hydrogen peroxide solution is generated using a molar ratio of H_2O_2 to alkali in the range 1:1.2 to 1:2.5.
6. The method of any one of claims 1-3 wherein the alkaline hydrogen peroxide solution is generated electrochemically.
7. The method according to claim 6, wherein the electrochemically generated alkaline hydrogen peroxide solution comprises a molar ratio of superoxide to hydrogen peroxide in a range of from 0.01:1 to 10:1 and a pH in a range of from pH 8 to pH 13.
8. The method of either one of claim 6 or claim 7 wherein the pH of the electrochemically generated alkaline hydrogen peroxide solution is in a range of from pH 12 to pH 13.

9. The method of either one of claim 6 or claim 7 wherein the alkaline hydrogen peroxide solution has a pH in the range of 12.0 to 13.0 and has a percent weight of hydrogen peroxide in the range of 0.1 to 3 wt%.
10. The method of any one of claims 1-9 further comprising the step of further activating the reactive oxygen species of the peracid mixture using activation chosen from a Fenton or Fenton-like catalyst, ultrasound, ultraviolet radiation or thermal activation.
11. The method of claim 10 wherein a reactive oxygen species formed in the further activating is hydroxyl radical.
12. The method of any one of claims 1-11 further comprising storing the alkaline hydrogen peroxide solution in a holding tank for immediate or future use in the preparing the peracid mixture.
13. The method of any one of claims 1-12 comprising after the adjusting pH, diluting the peracid mixture.
14. The method of any one of claims 1-13 wherein the peracid mixture comprises hydrogen peroxide at less than 3% of a mass concentration of peracid in the peracid mixture.
15. The method of any one of claims 1-13 wherein the peracid mixture comprises hydrogen peroxide at less than 0.5% of a mass concentration of peracid in the peracid mixture.
16. The method of any one of claims 1-13 wherein the peracid mixture comprises no detectible level of hydrogen peroxide.
17. The method of any one of claims 1-16 wherein the reactive oxygen species is distributed to the point of use in at least one form chosen from the group consisting of: the form of a liquid, an ice, a foam, an emulsion, a microemulsion and an aerosol.
18. The method of claim 17 wherein the substrate is contained in water to be treated and the applying comprises adding the peracid mixture to the water to be treated to prepare a treatment mixture for the oxidative treatment of the substrate in the water.
19. The method of claim 18 wherein the substrate comprises one or more chemical species to be oxidized in the water to be treated.

20. The method of claim 18 wherein the substrate comprises microorganisms to be denatured or killed in the water to be treated.
21. The method of any one of claims 18-20 wherein the water to be treated comprises a waste water.
22. The method of any one of claims 18-20 wherein the water to be treated comprises a cooling tower water.
23. The method of any one of claims 18-20 wherein the water to be treated comprises an oil and gas produced water.
24. The method of any one of claims 18-20, wherein the water to be treated comprises hydraulic fracturing flowback water.
25. The method of any one of claims 18-24, comprising after the preparing and prior to the applying the peracid mixture to the substrate, diluting the peracid mixture to reduce the concentration of the peracid in the peracid mixture.
26. The method of any one of claims 18-24, wherein treatment mixture is at a second pH that is lower than the pH in the activated pH range, and wherein the second pH is in a second activated pH range of from pH 6.5 to pH 9.5, to continue generation of reactive oxygen species comprising singlet oxygen in the treatment mixture.
27. The method of any one of claims 18-26, wherein the substrate comprises microorganisms in the water to be treated and the adding the peracid mixture to the water to be treated is a first addition of the peracid mixture and the method further comprises after the first addition:
clarification of the water to be treated to remove free oil and suspended solids from the water to be treated; and
following the clarification, second addition of a second portion of the peracid mixture to product water from the clarification for antimicrobial treatment in the product water.
28. The method of claim 17 wherein the substrate comprises paper, pulp or textile to be bleached.

29. The method of claim 17 wherein the substrate comprises microorganisms and is to be disinfected.
30. The method of any one of claims 18-27 wherein the treatment mixture exhibits an oxidation-reduction potential (ORP) of 600 mv vs a standard hydrogen electrode (SHE) or more.
31. The method of claim 30 wherein the ORP is 700 mv vs SHE or more.
32. A peracid mixture for oxidation treatment of a substrate or environment with reactive oxygen species, the peracid mixture being in an activated pH range of from pH 9.5 to pH 12.5 and comprising hydrogen peroxide at less than 3% of a mass concentration of peracid, and
wherein the peracid mixture is prepared by a process comprising:
mixing an alkaline hydrogen peroxide solution with a molar excess of an acyl donor to hydrogen peroxide at a molar ratio of hydrogen peroxide to acyl donor in a range of from 1:1.25 to 1:4; and
during or after the mixing adjusting the pH to within the activated pH range.
33. The peracid mixture of either one of claim 32, wherein the mass concentration of the hydrogen peroxide is less than 0.5% of the mass concentration of peracid.
34. A method for oxidizing one or more environments or substrates which comprises contacting the one or more environments or substrates with a peracid mixture of claim 32 or 33.
35. The method of claim 34 which comprises processing selected from the group consisting of:
cleaning in place of pipes, tanks and other processing equipment;
removal of contaminants from wastewater, greywater, raw water, produced water or ground water;
denaturing or killing microorganisms;
soil decontamination or remediation;
hard surface cleaning or decontamination;
cleaning of membrane filtration systems;
flushing of well casings and water distribution pipes; and
in-situ chemical oxidation.

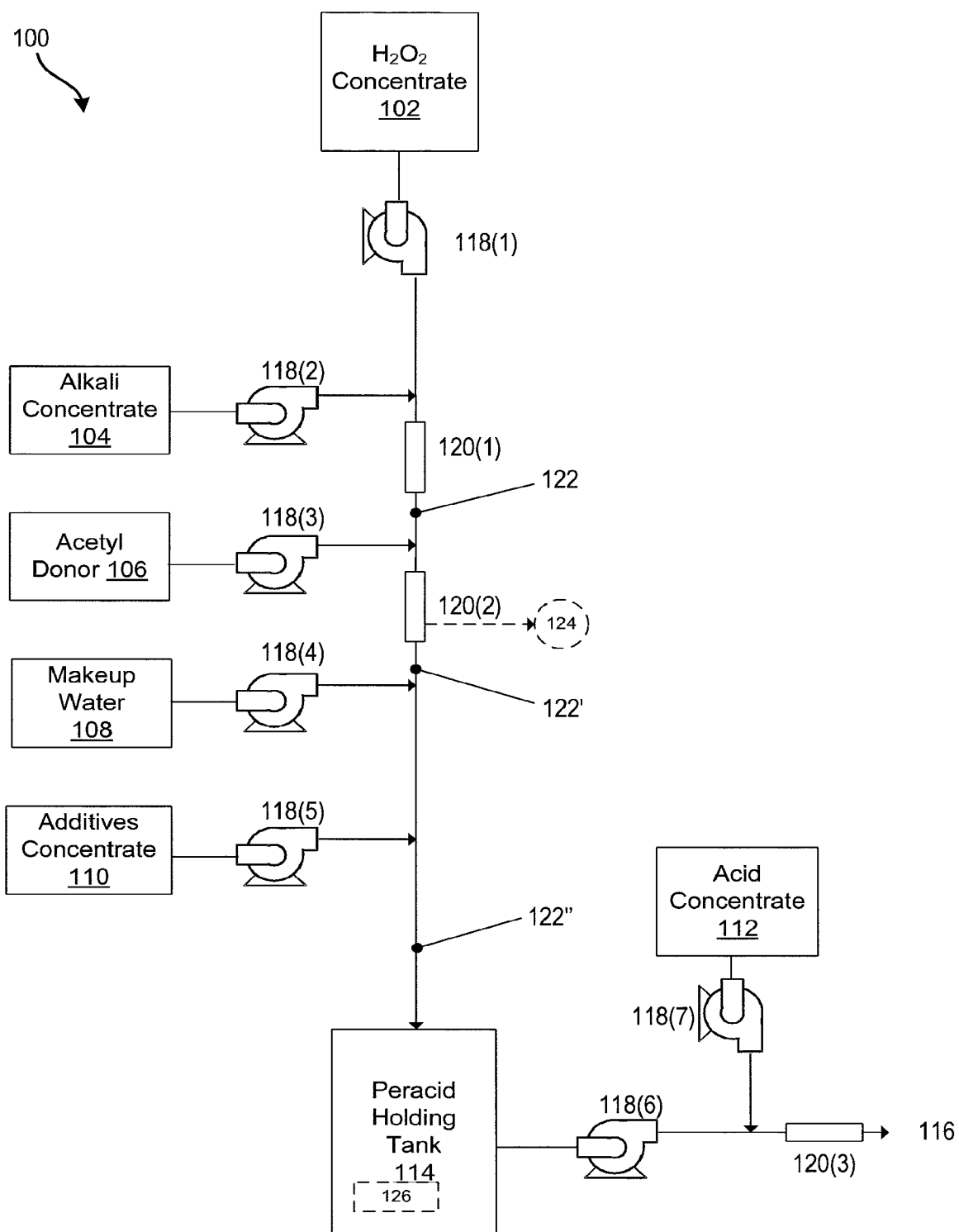
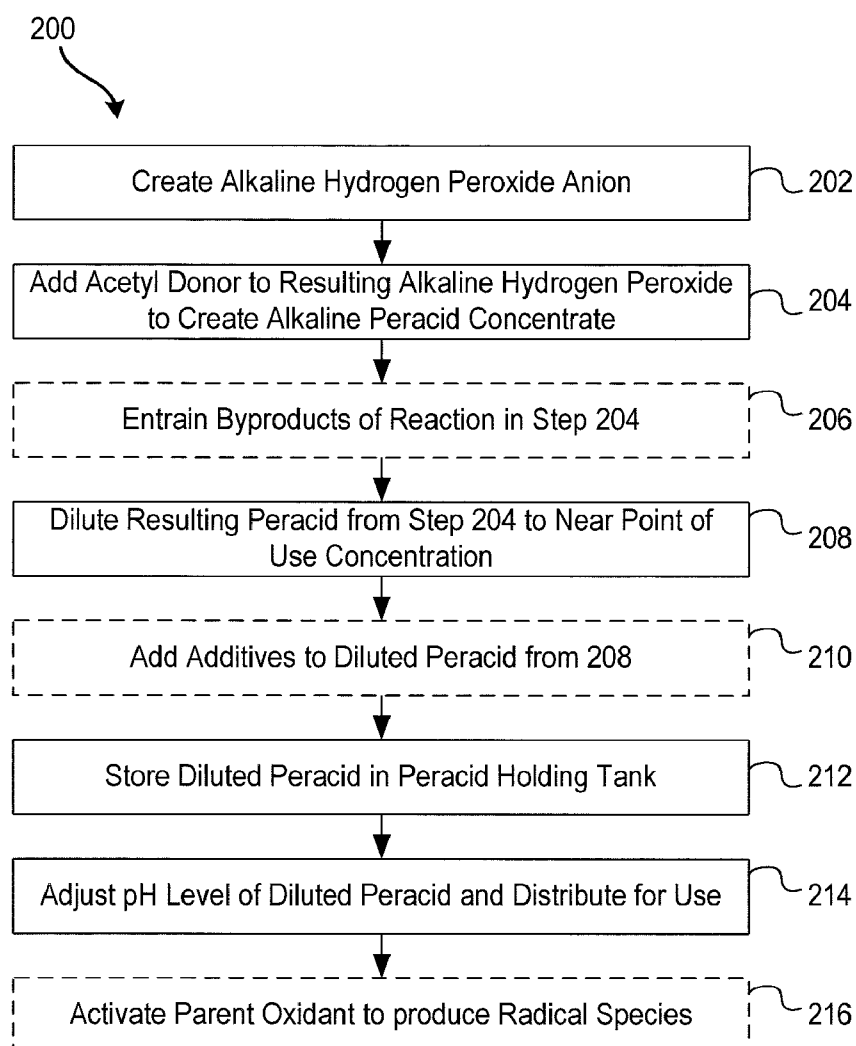


FIG. 1

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**FIG. 2**

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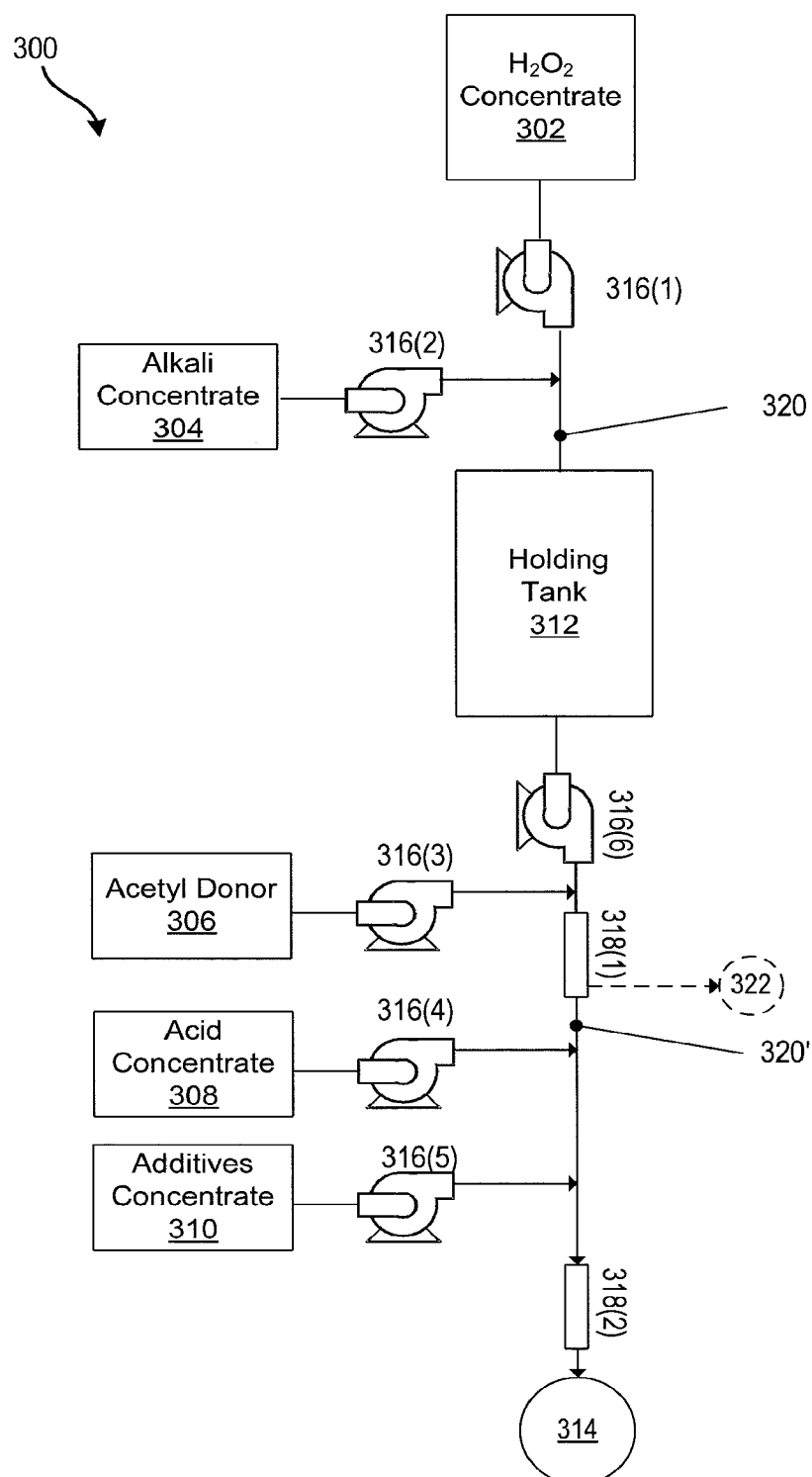
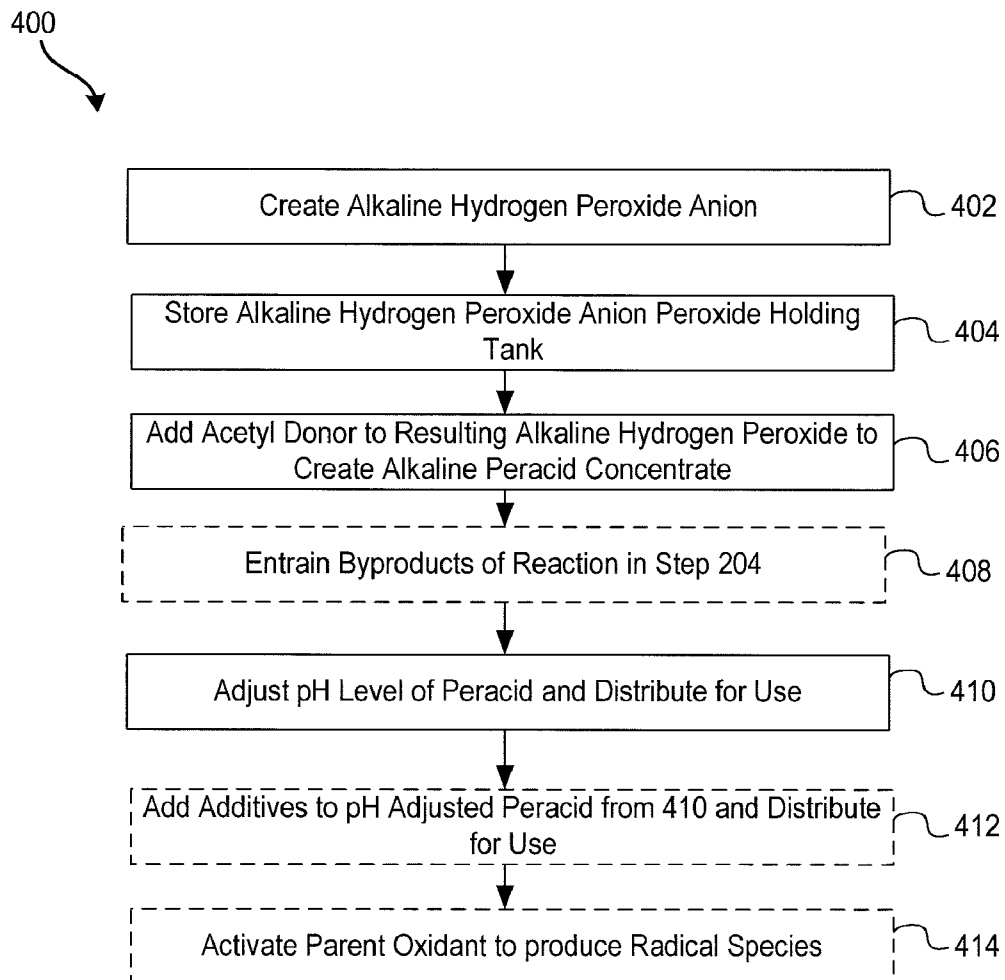


FIG. 3

**FIG. 4**

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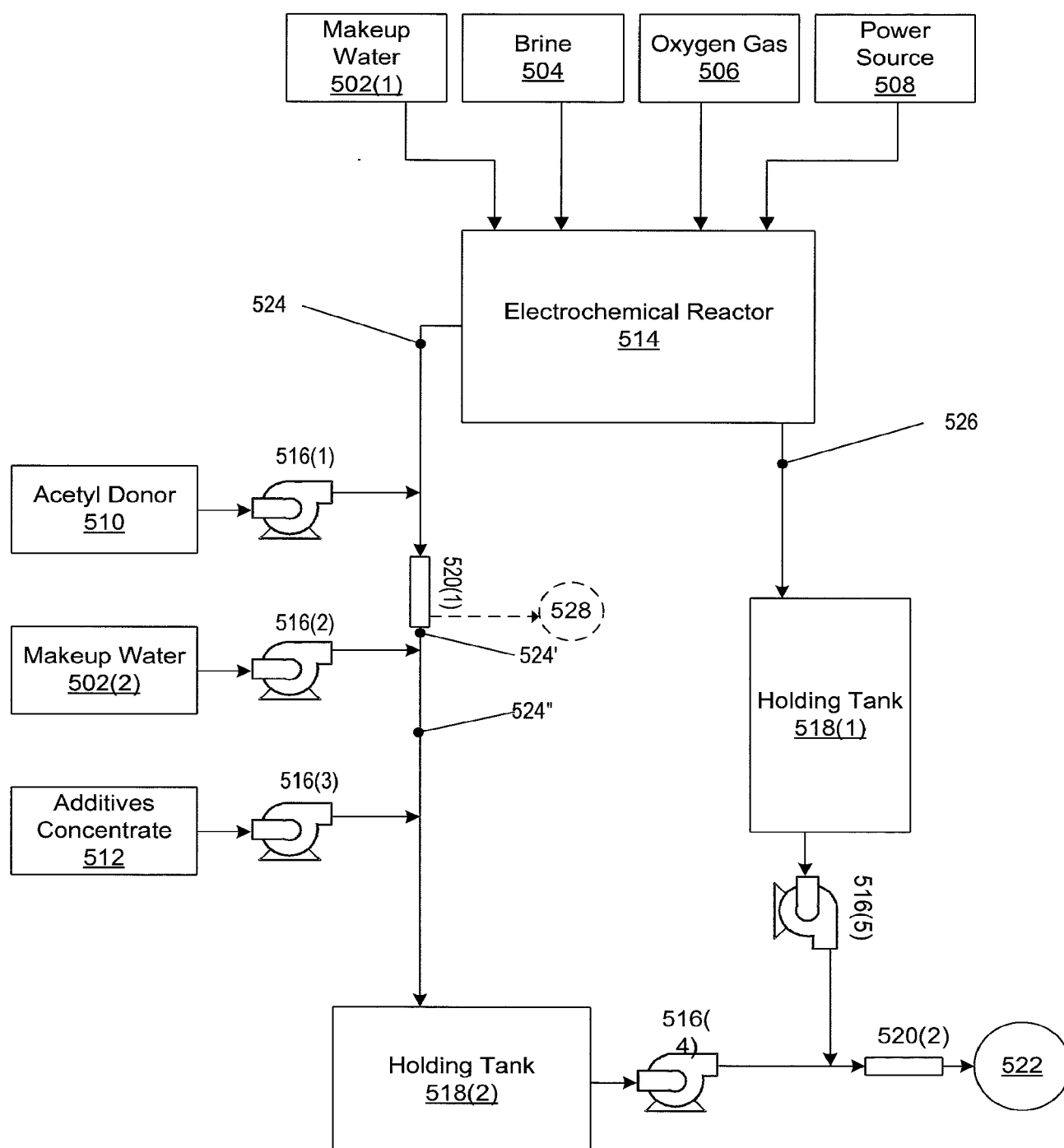
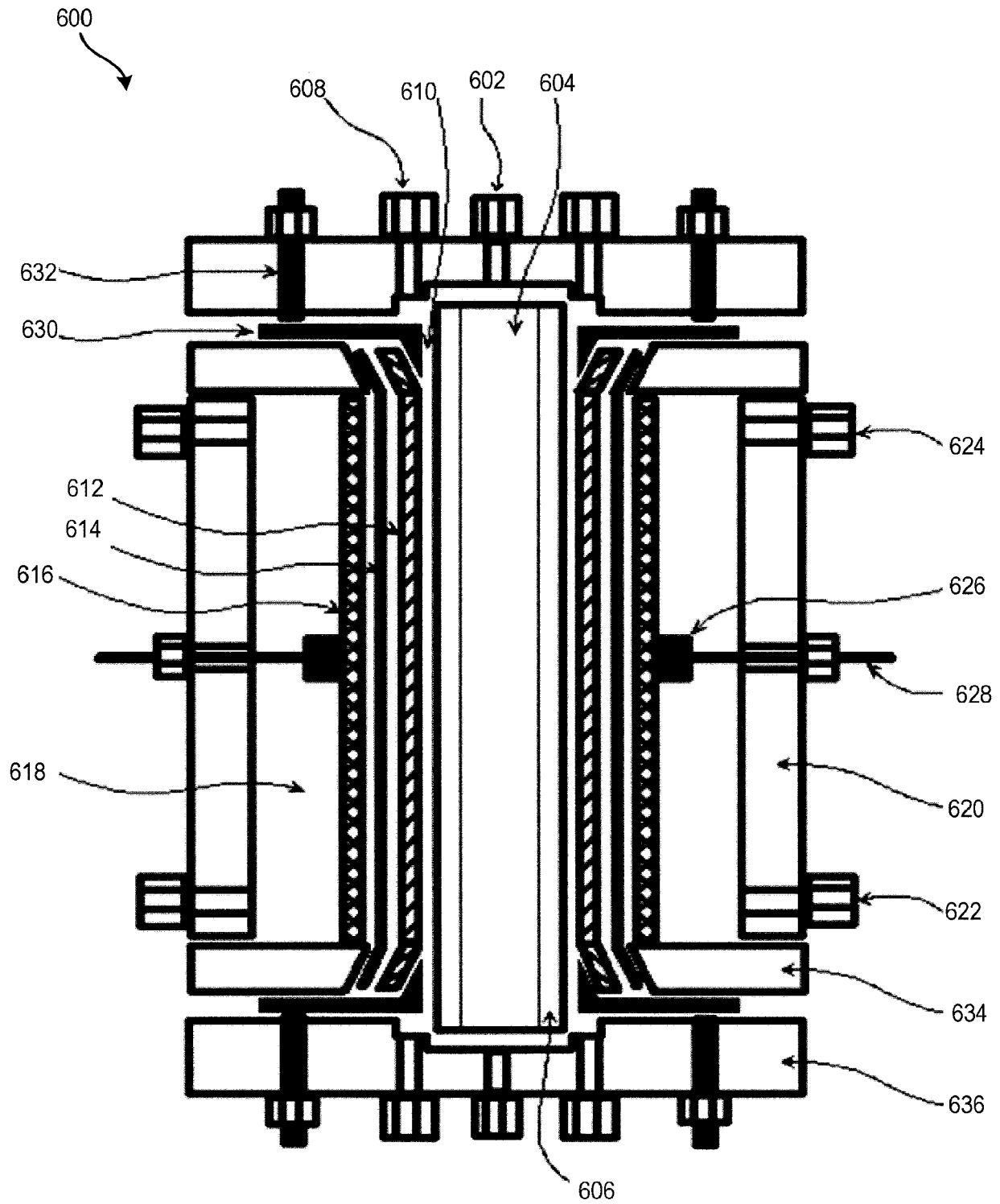
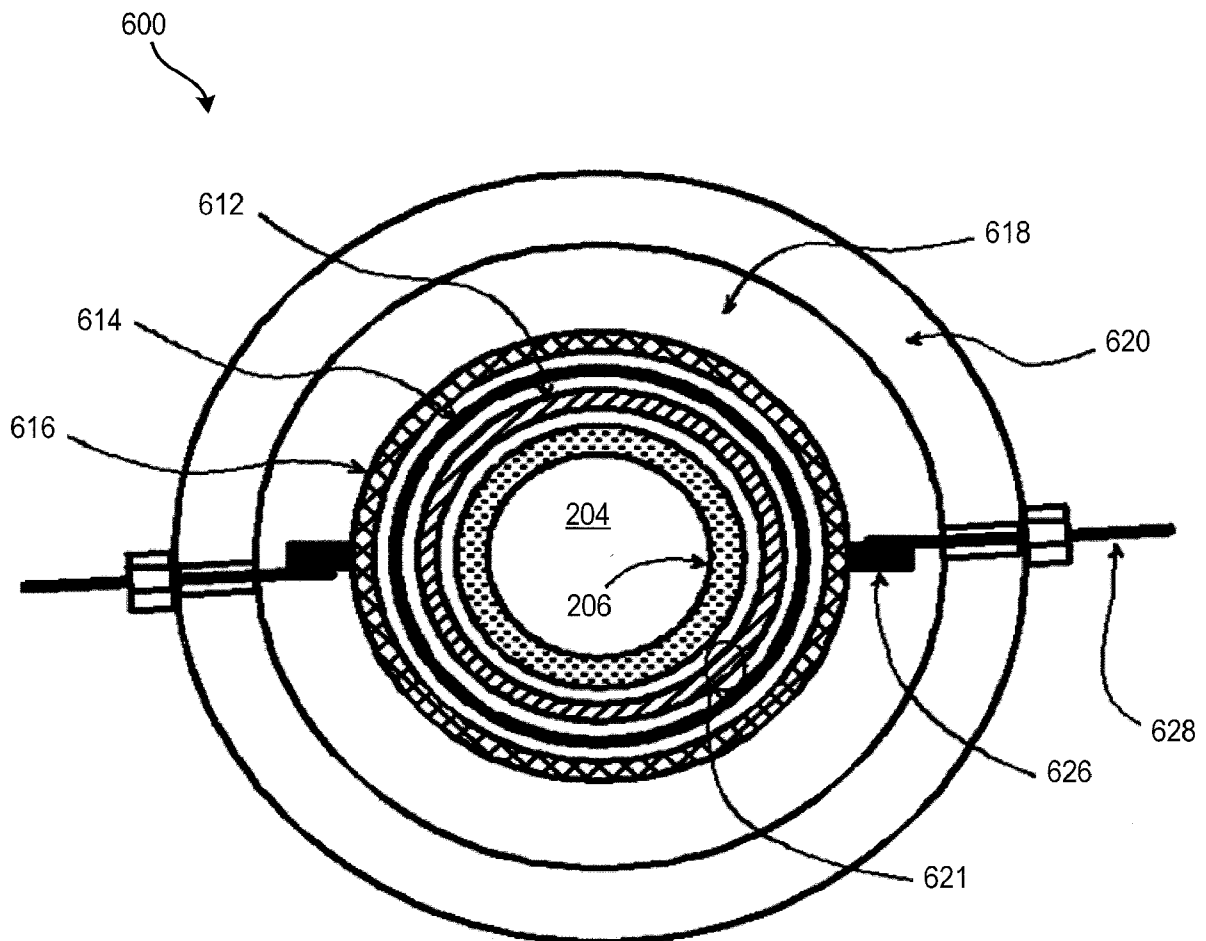


FIG. 5

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**FIG. 6A**

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**FIG. 6B**

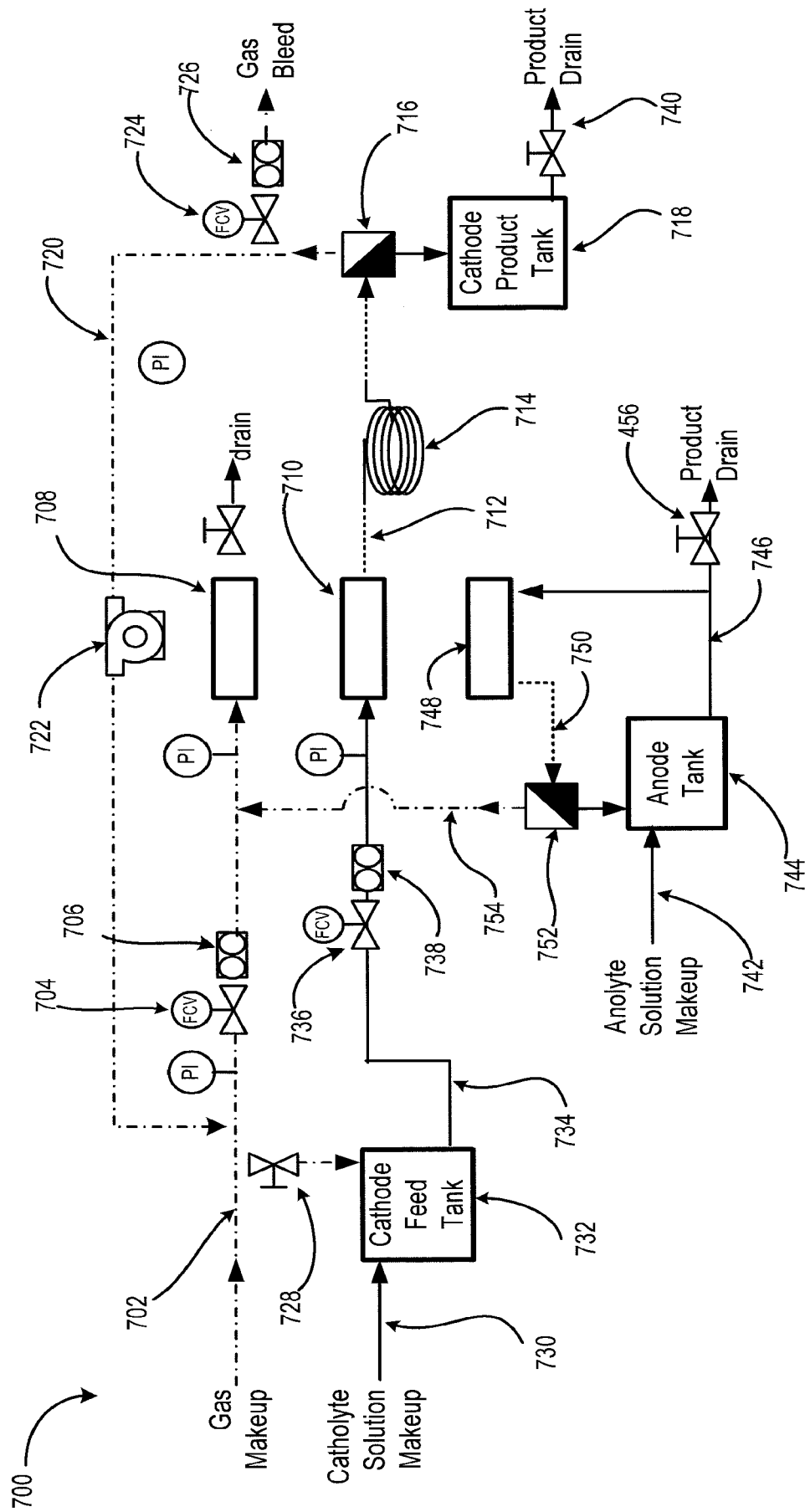
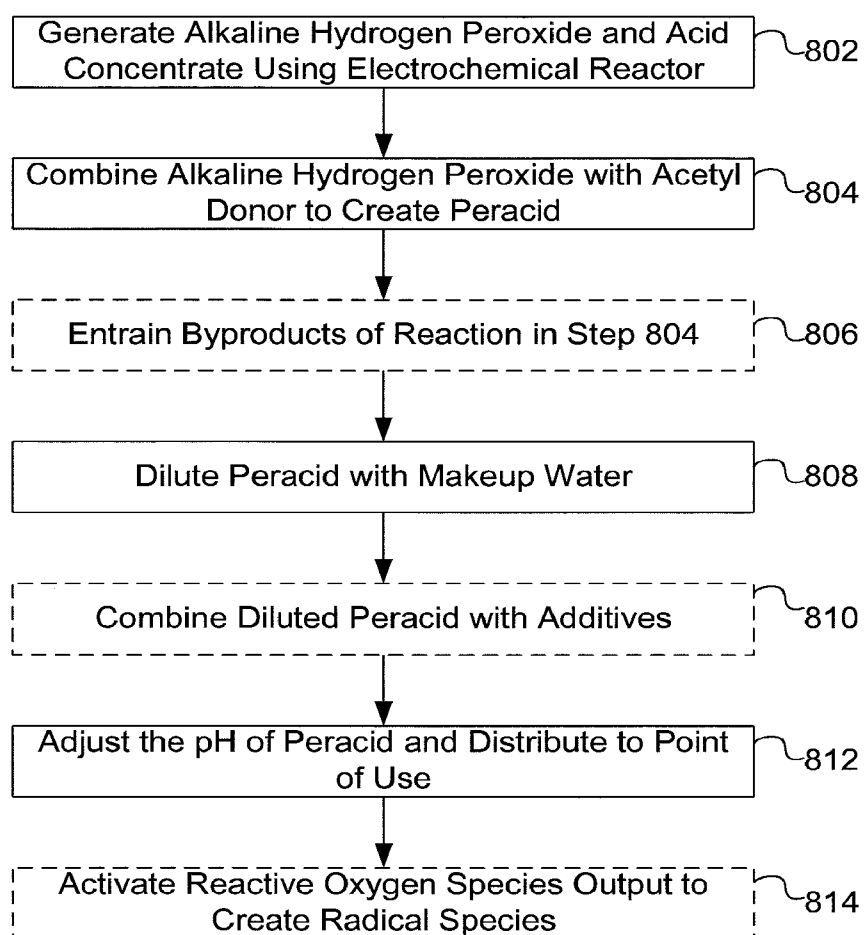


FIG. 7

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**FIG. 8**

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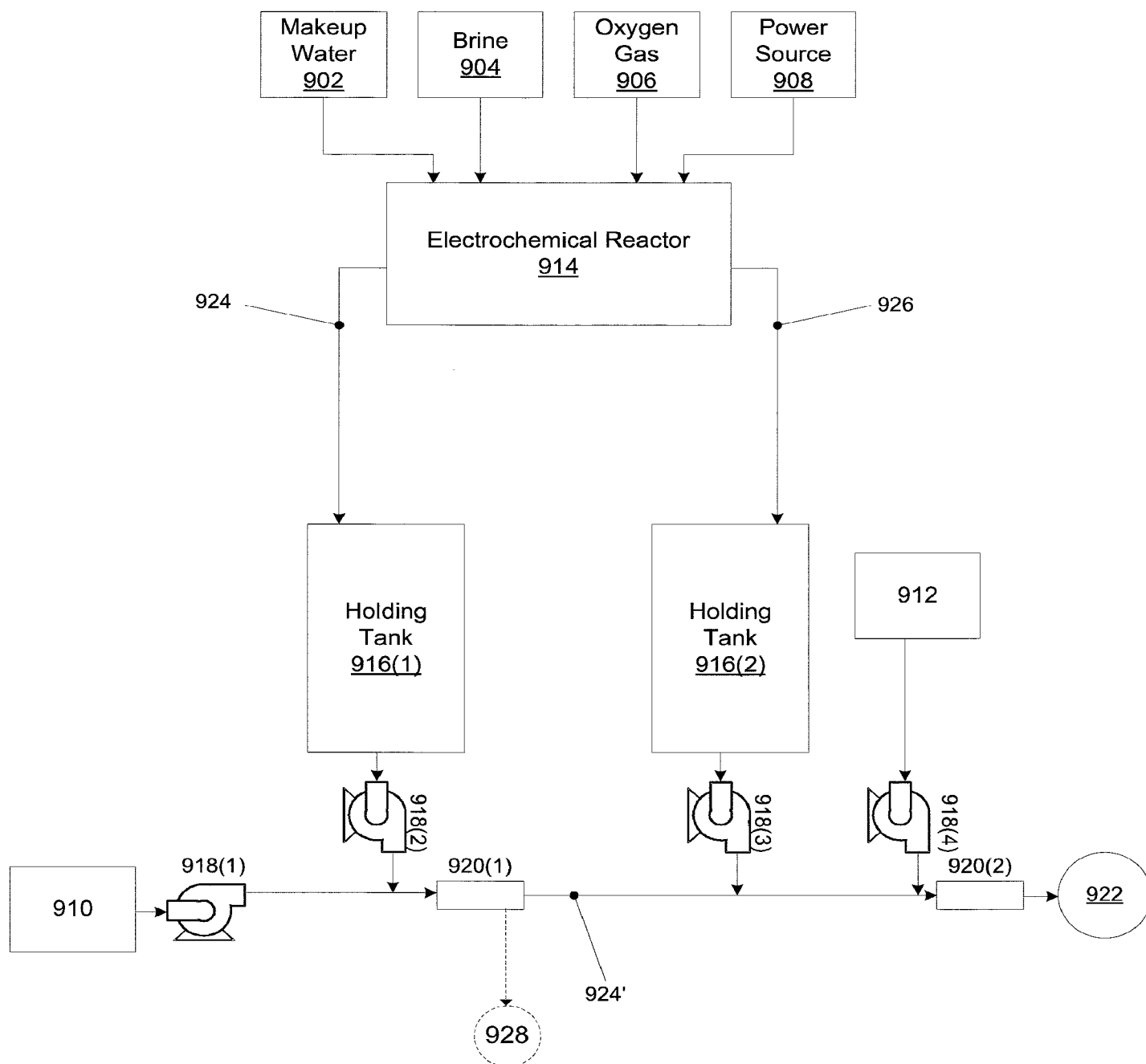
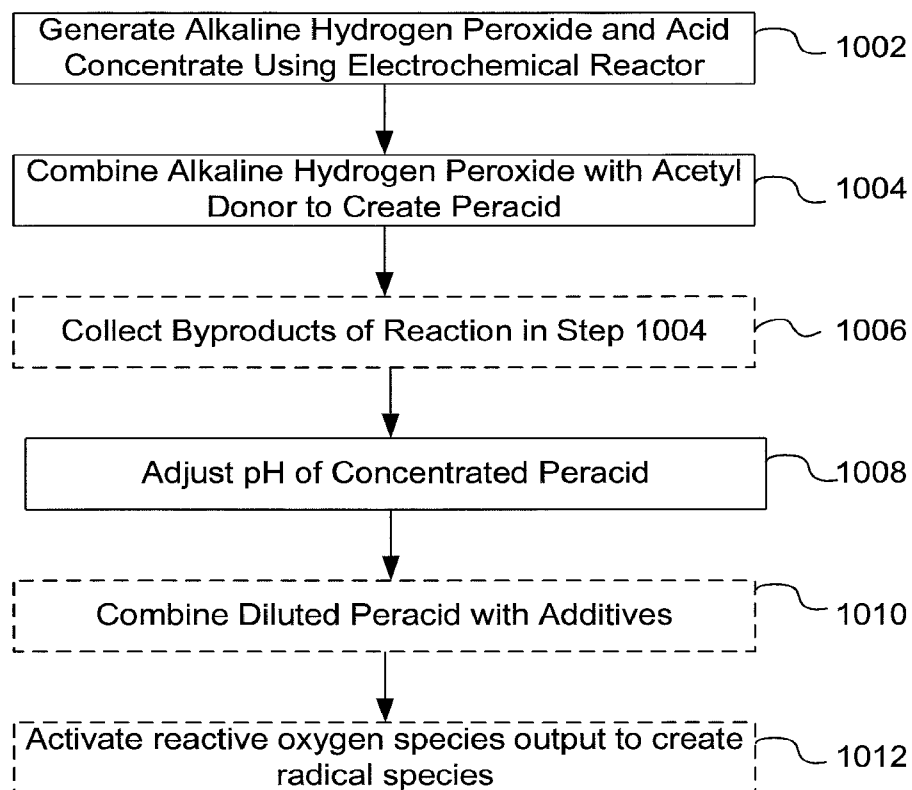


FIG. 9

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**FIG. 10**

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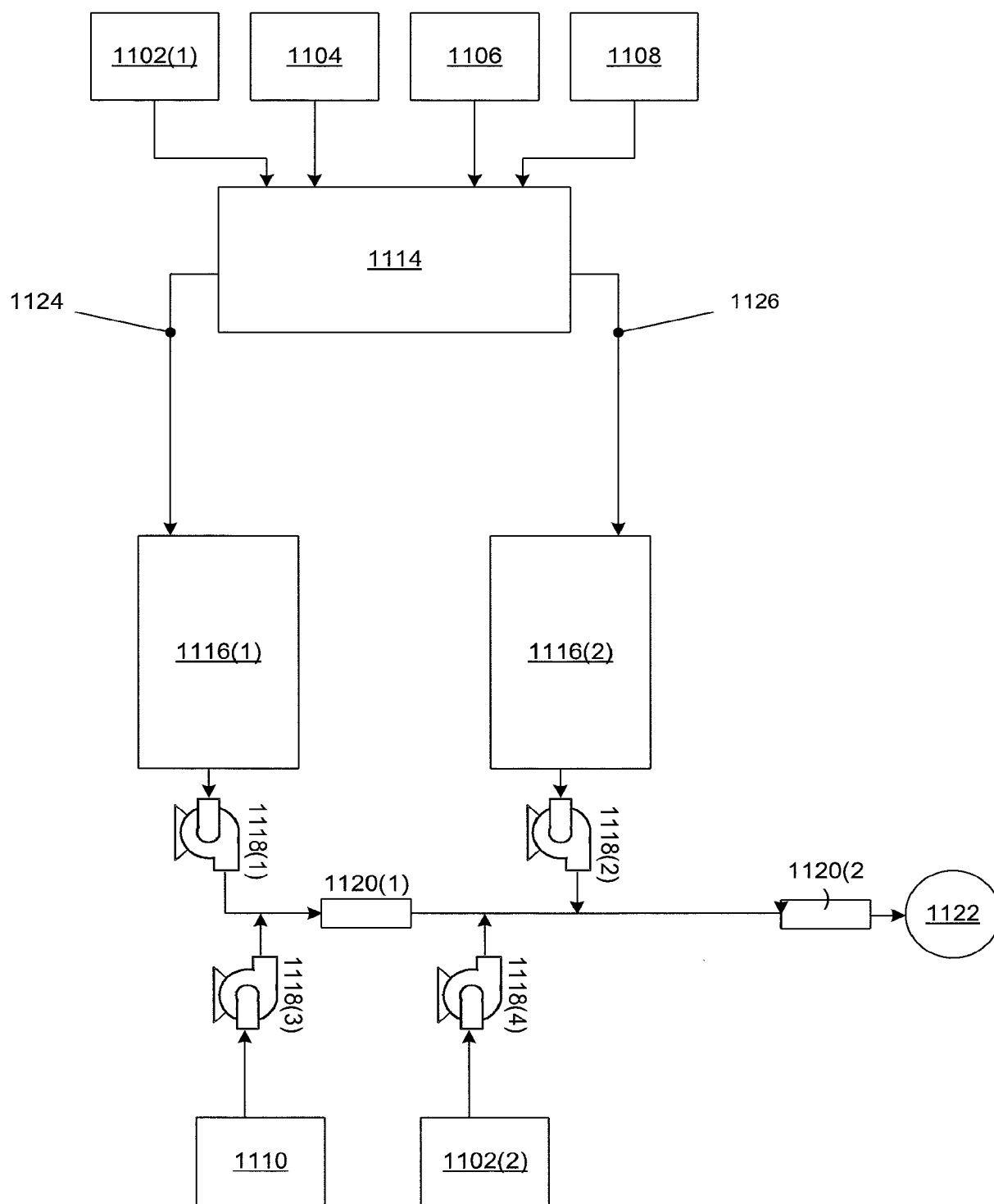
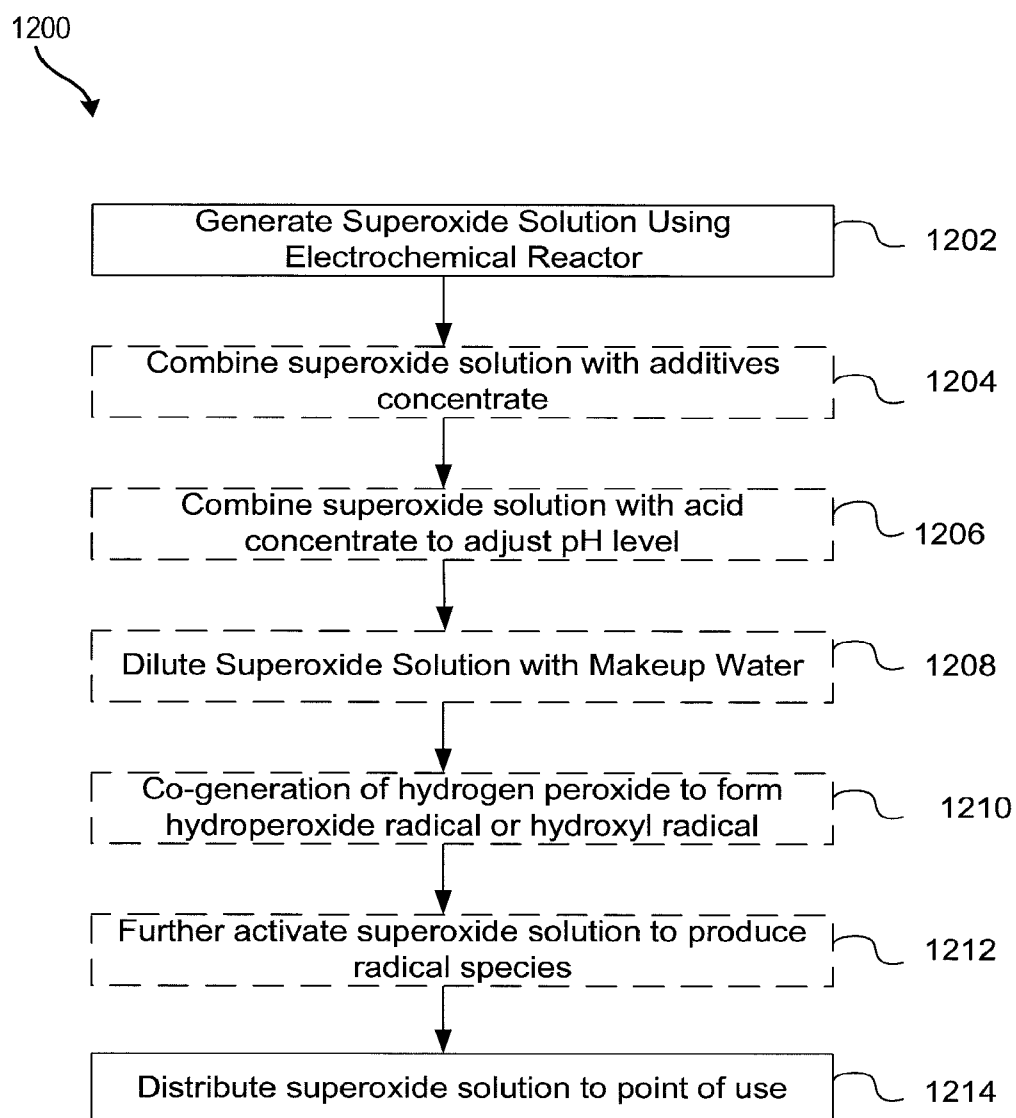


FIG. 11

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**FIG. 12**

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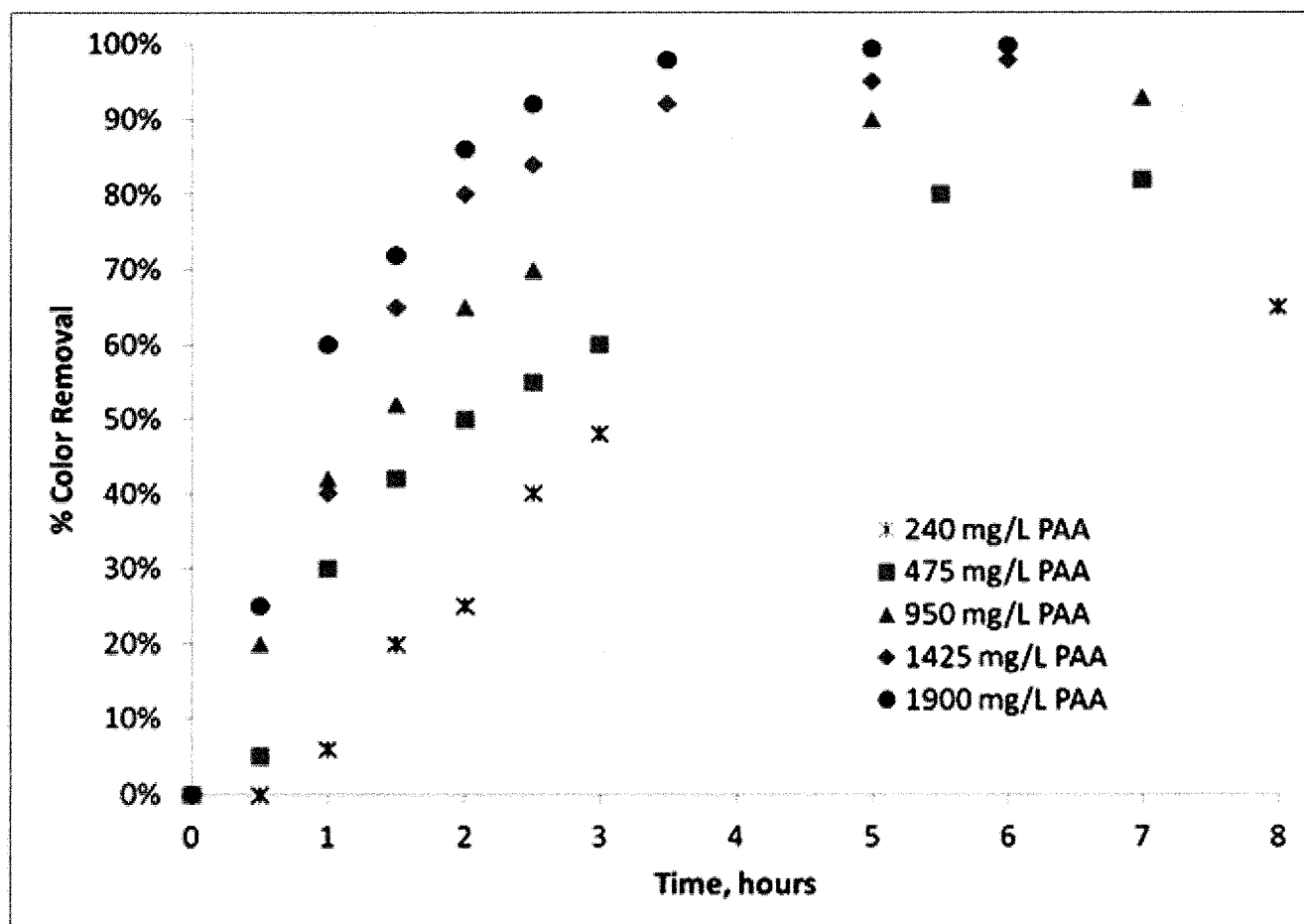
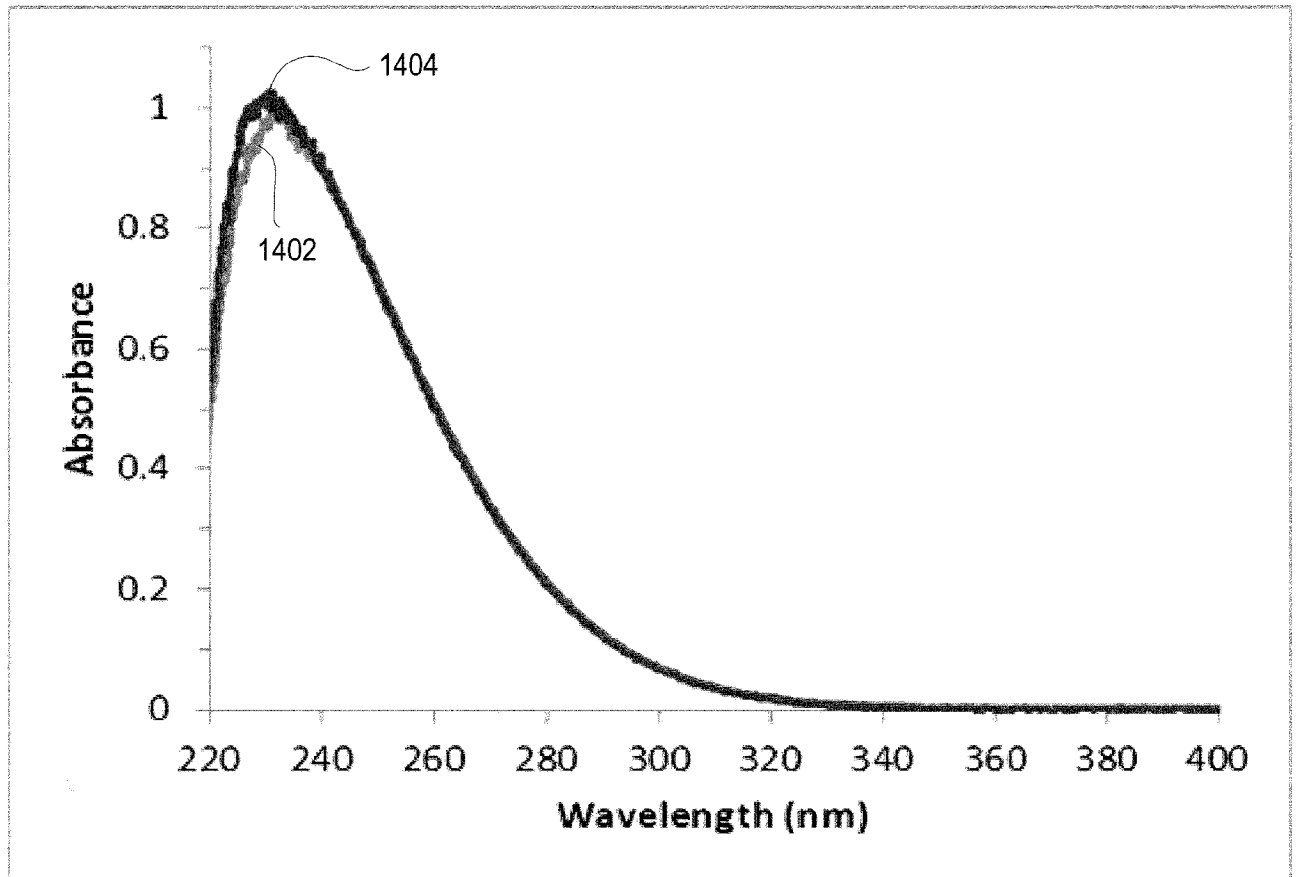


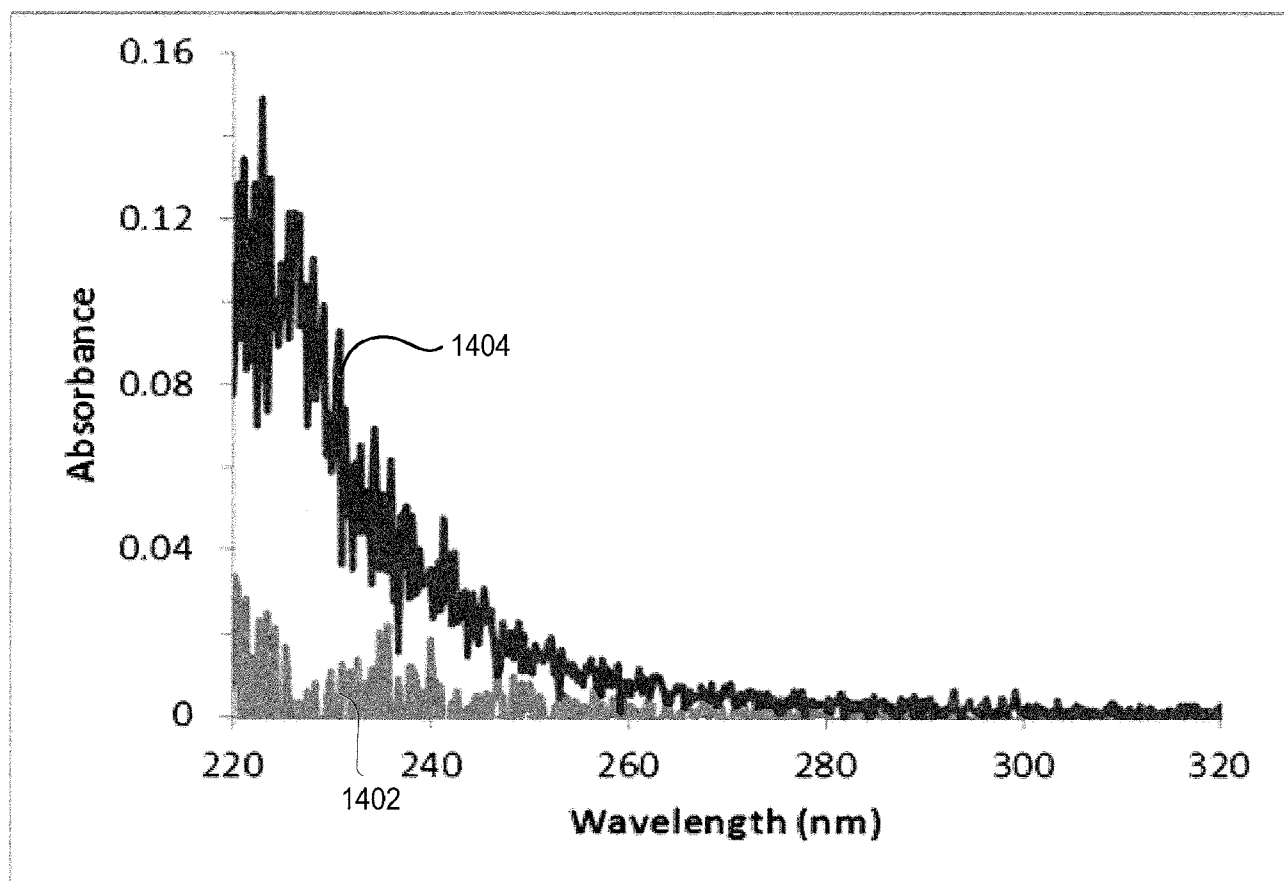
FIG. 13

1400

**FIG. 14A**

1450

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**FIG. 14B**

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1500

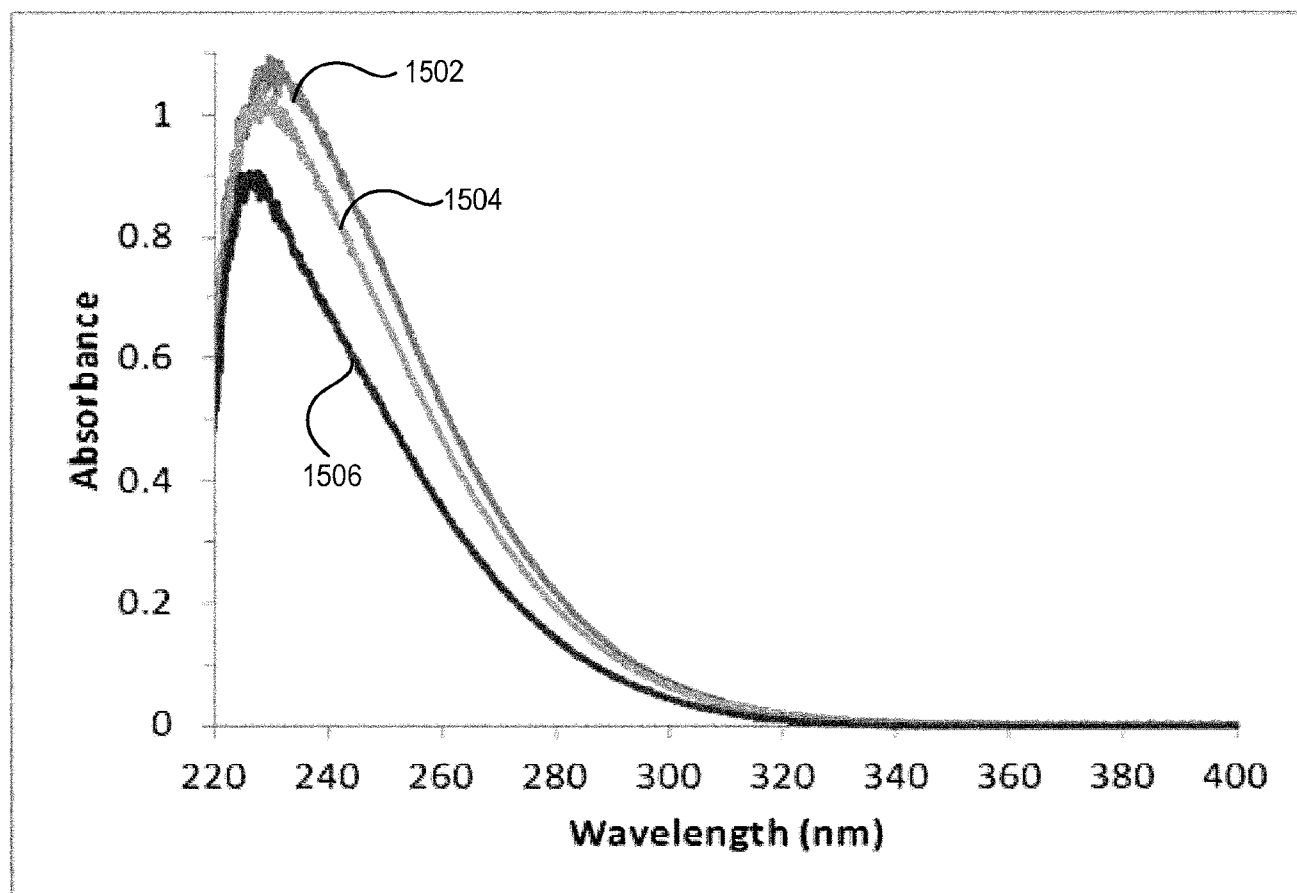
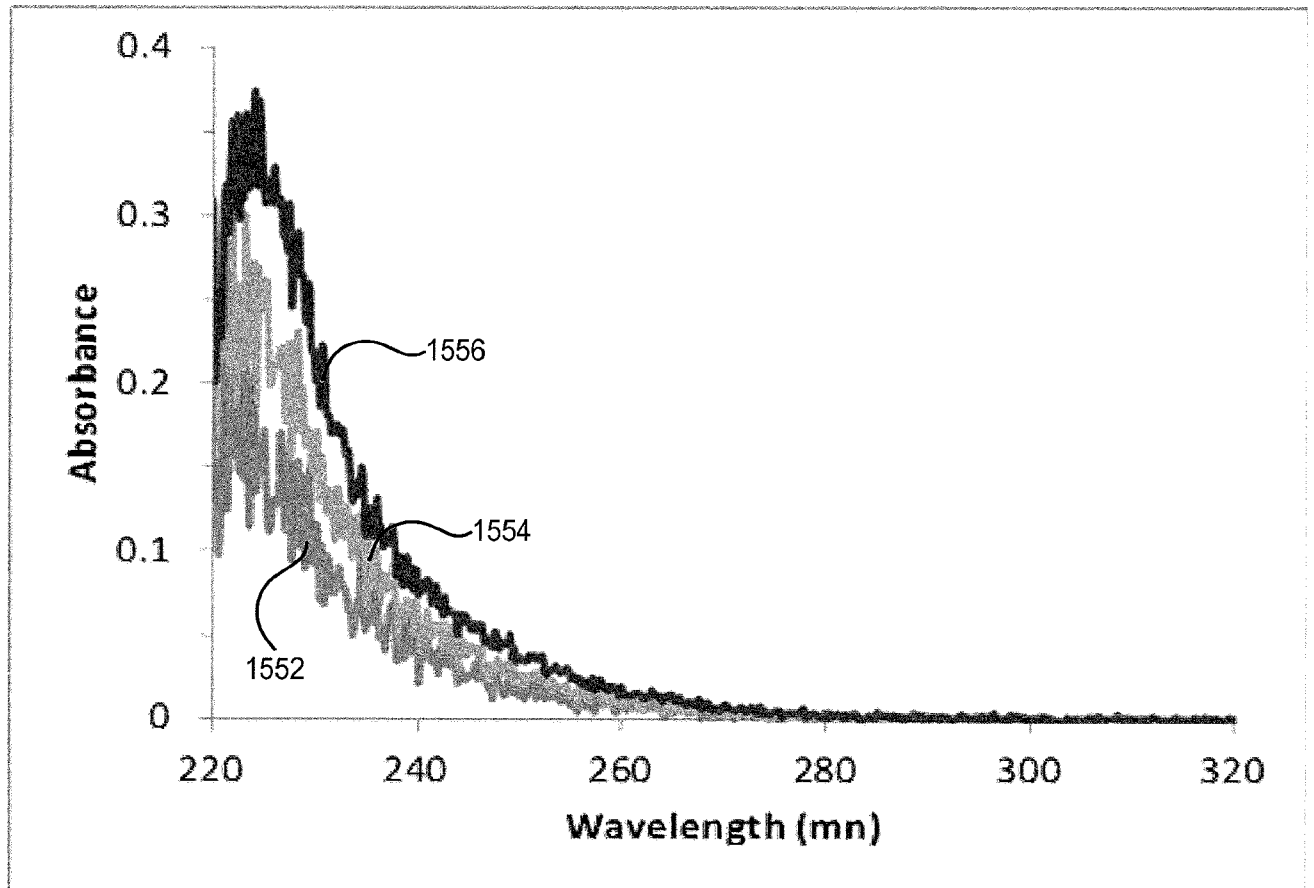


FIG. 15A

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1550

**FIG. 15B**

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1600

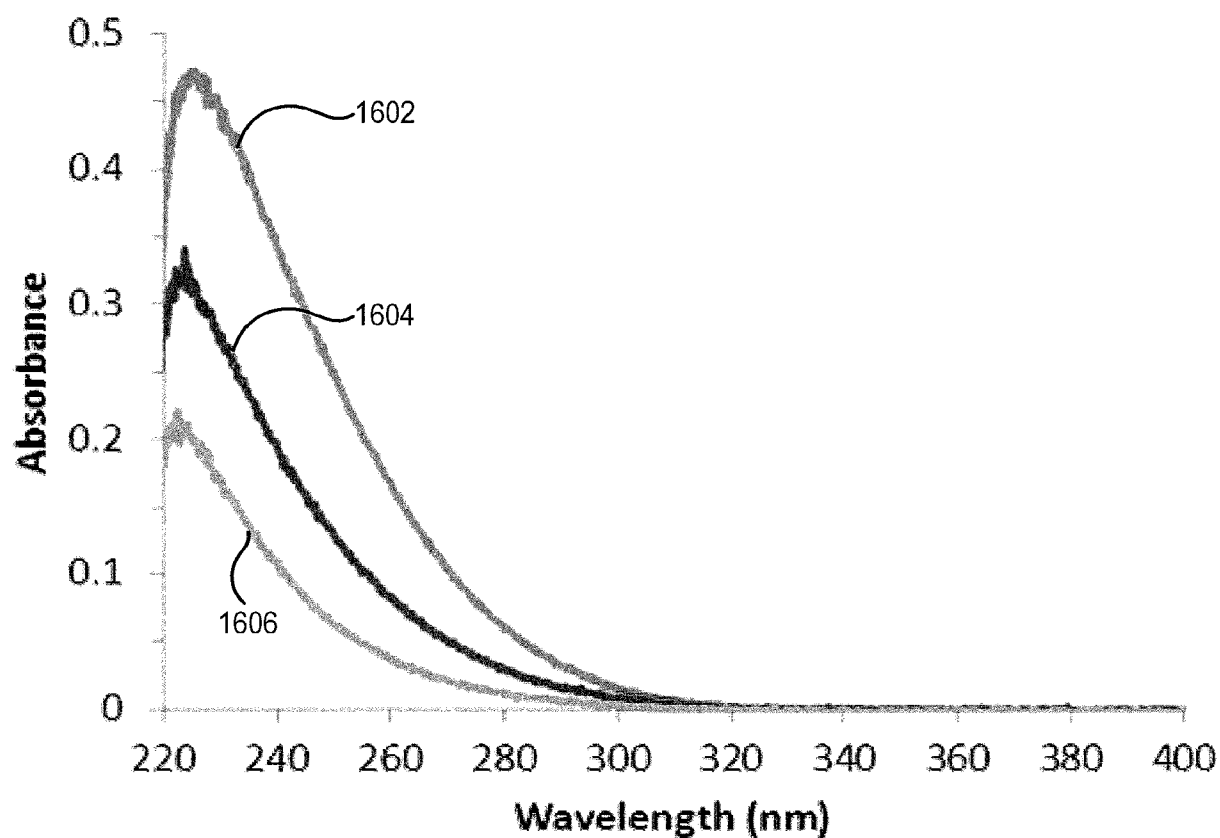


FIG. 16A

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1650

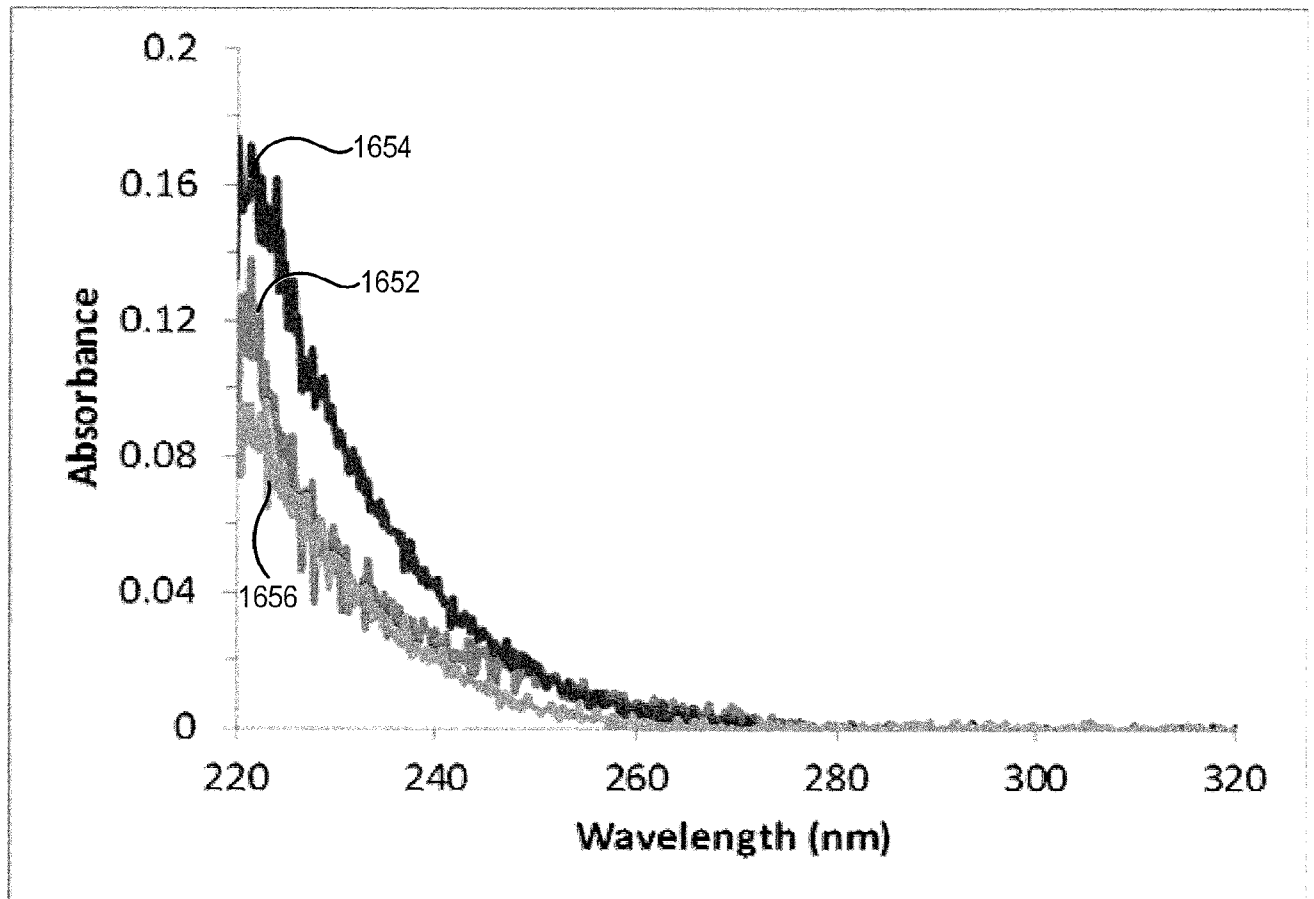


FIG. 16B

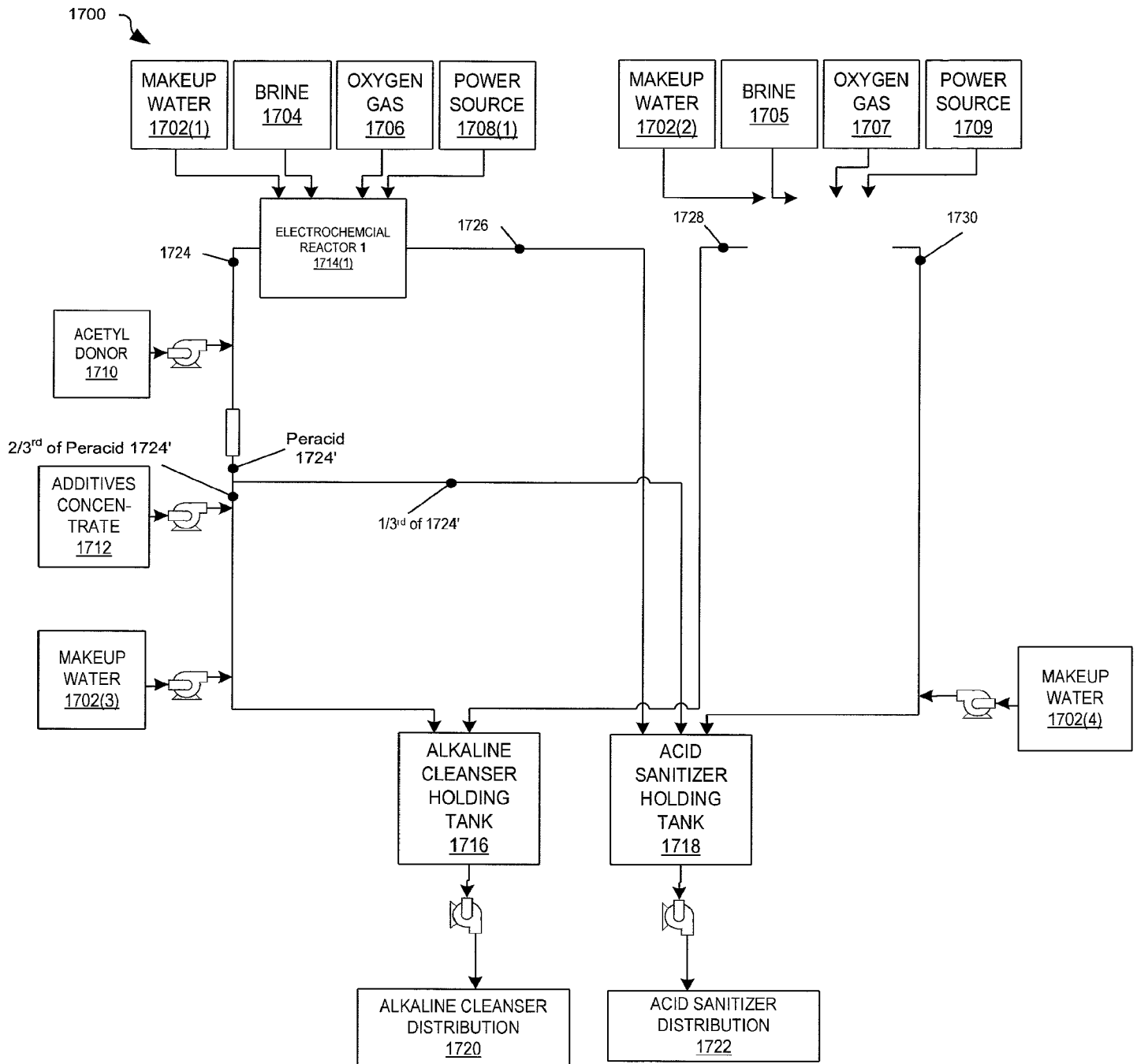


FIG. 17

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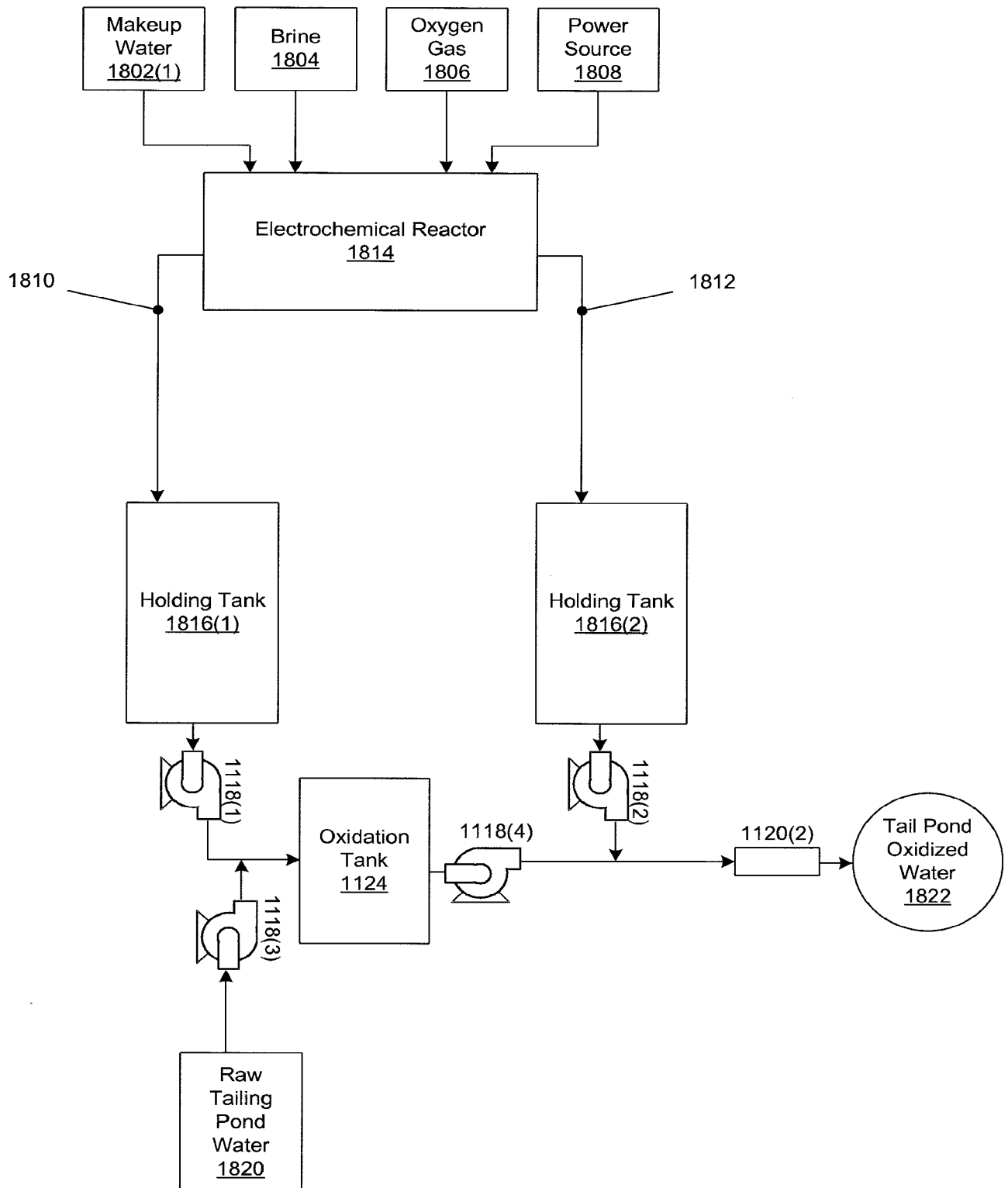


FIG. 18

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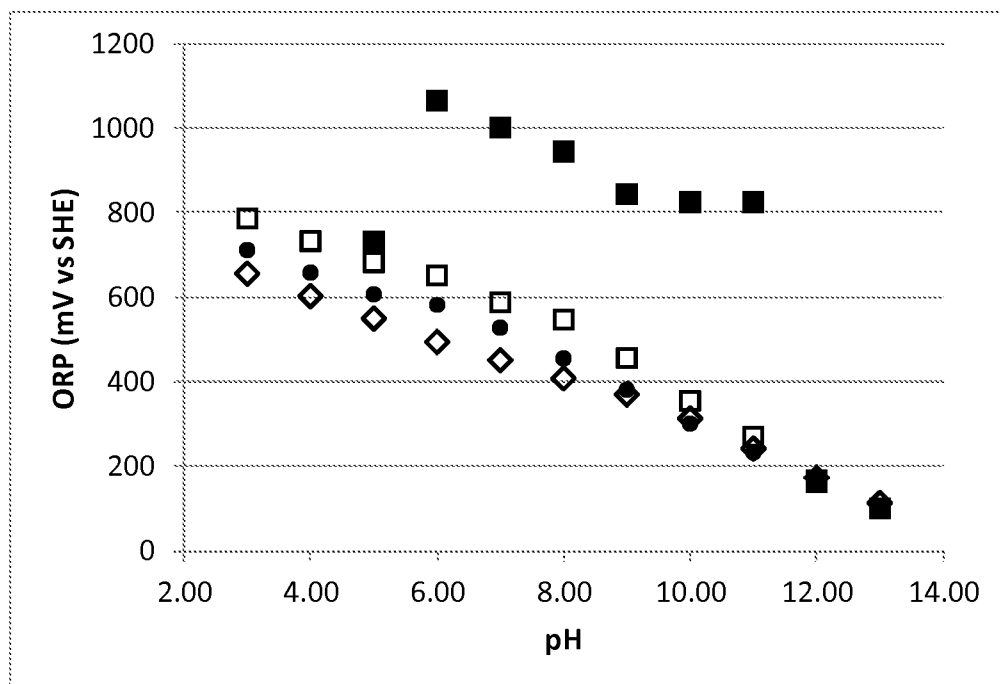


FIG. 19

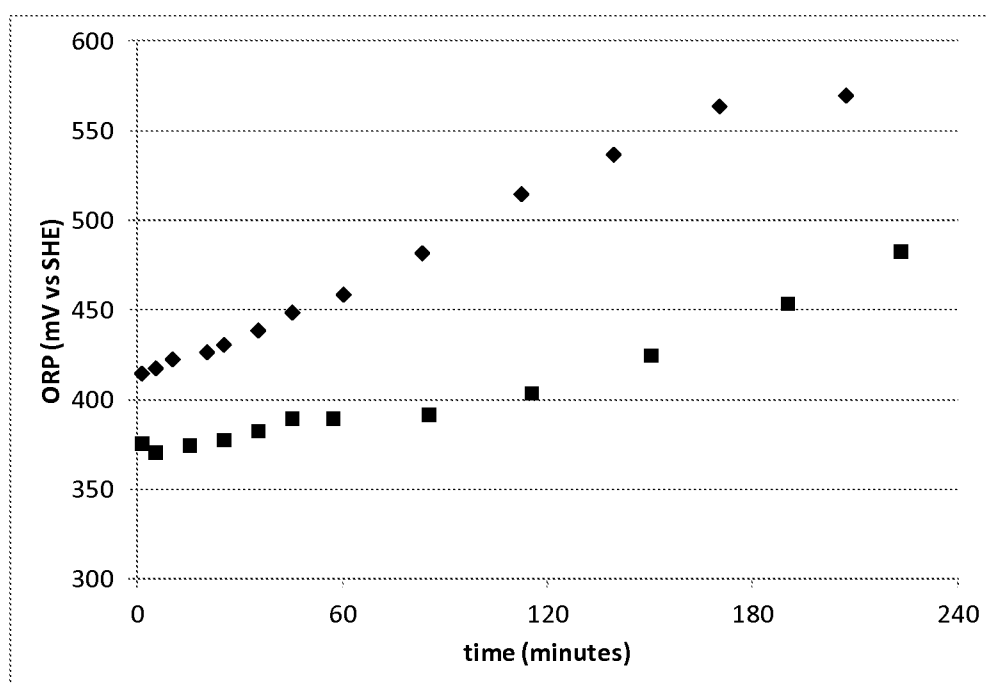


FIG. 20

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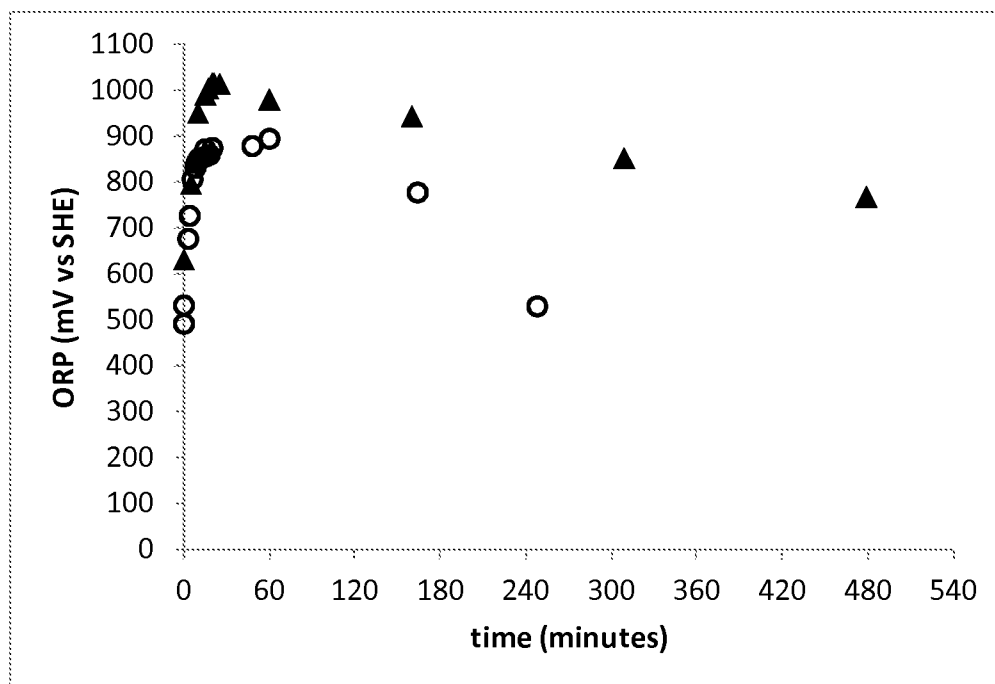


FIG. 21

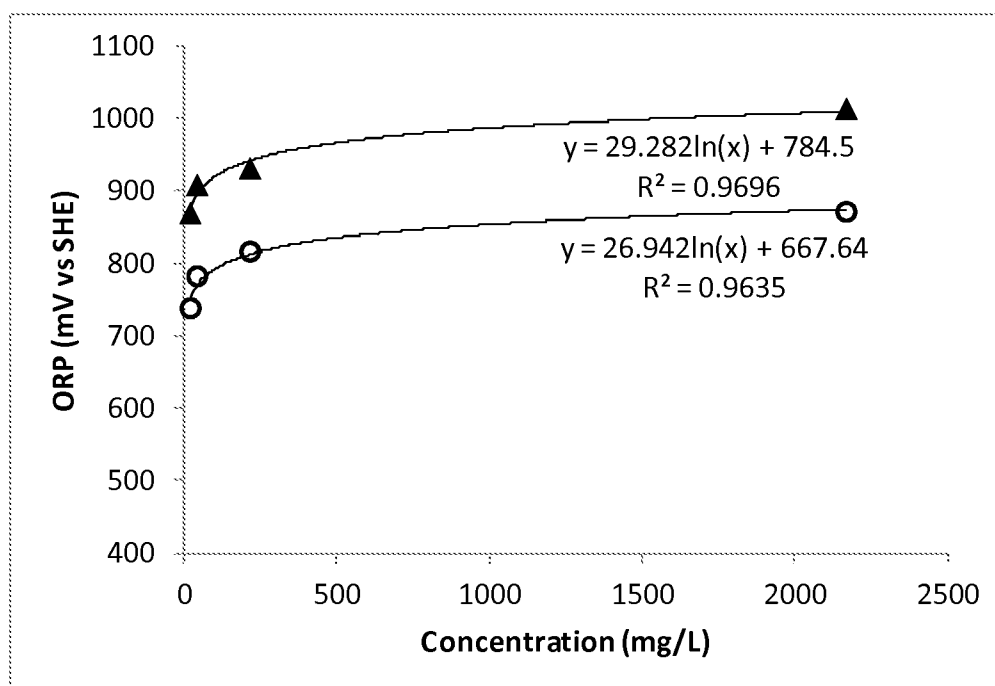


FIG. 22

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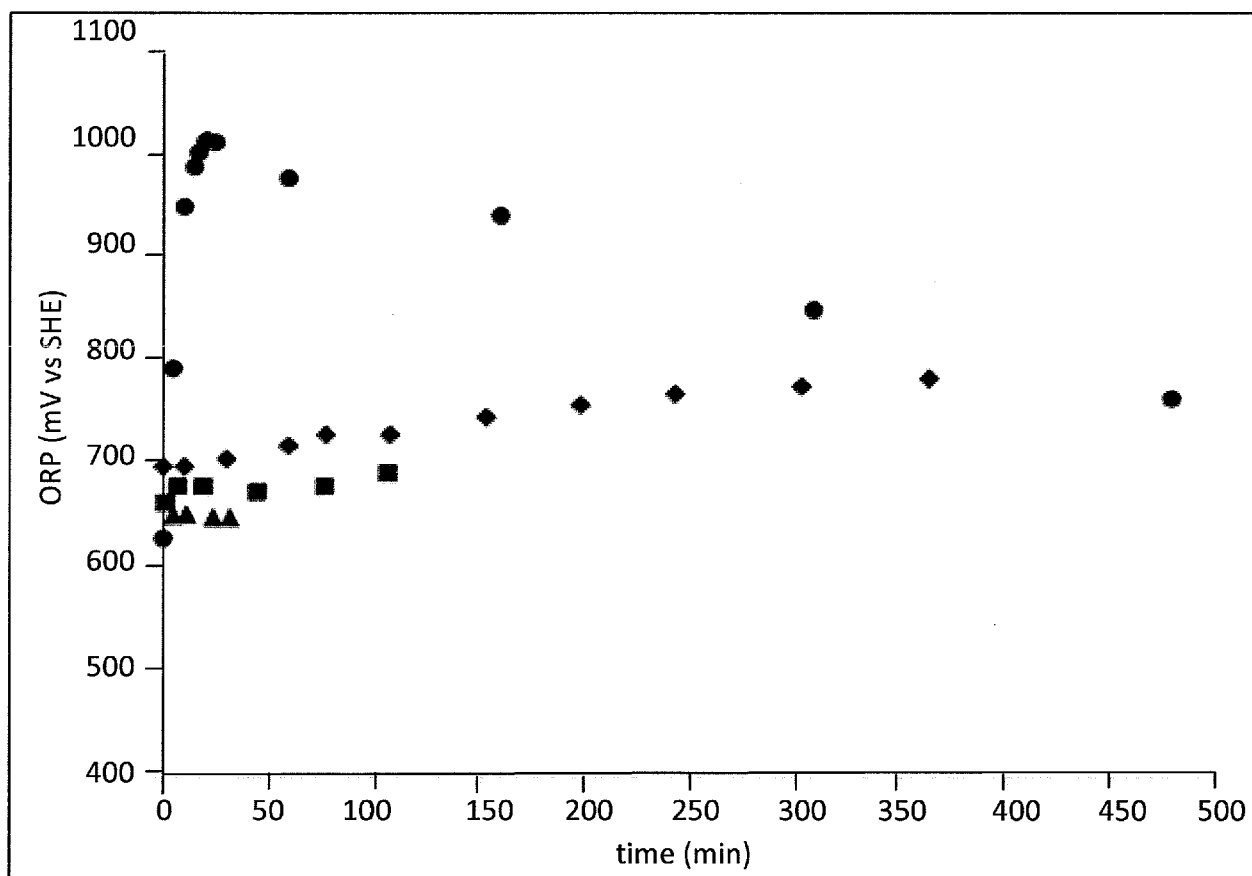
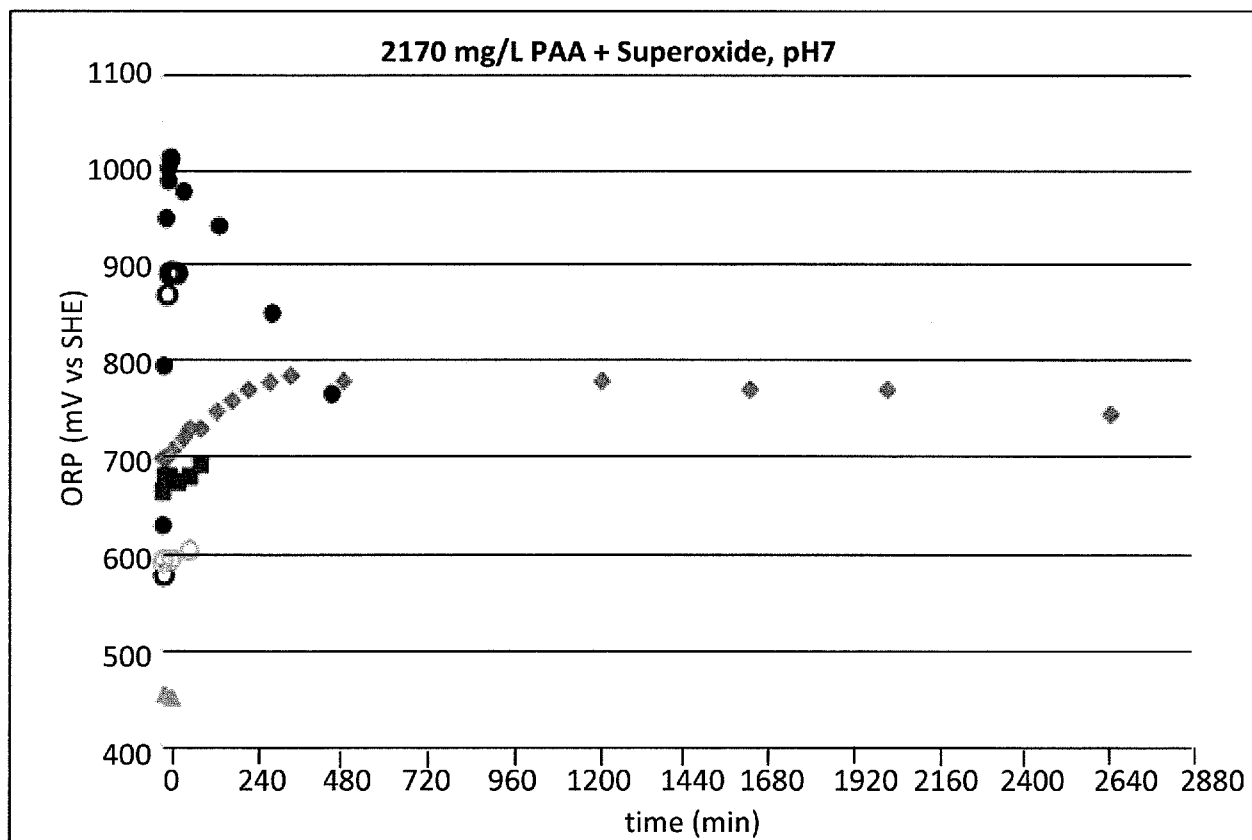
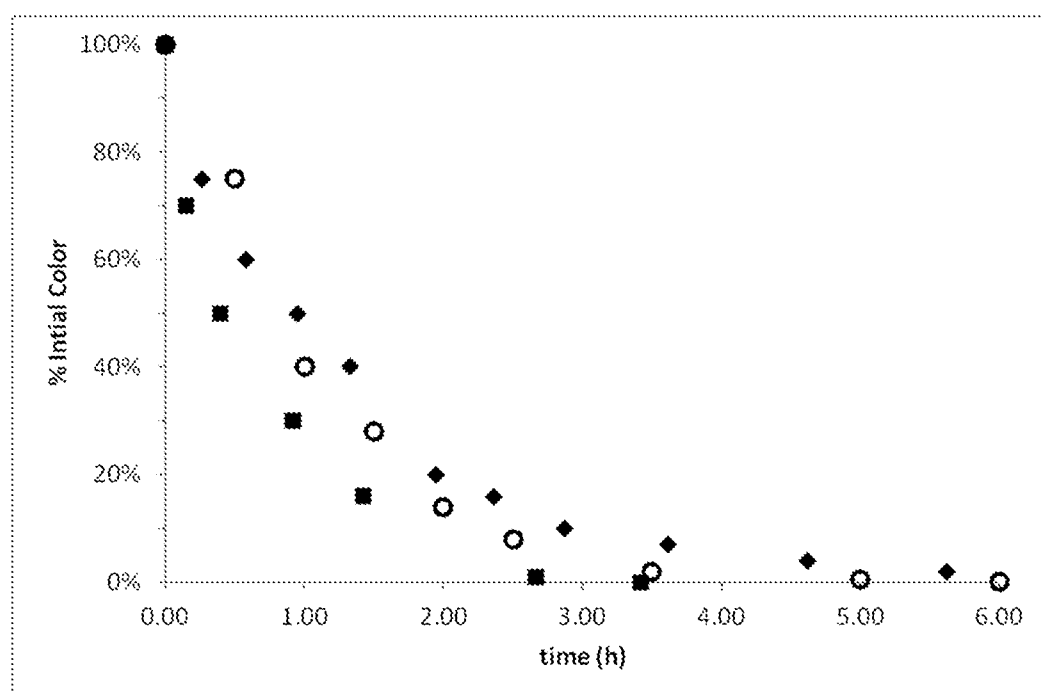


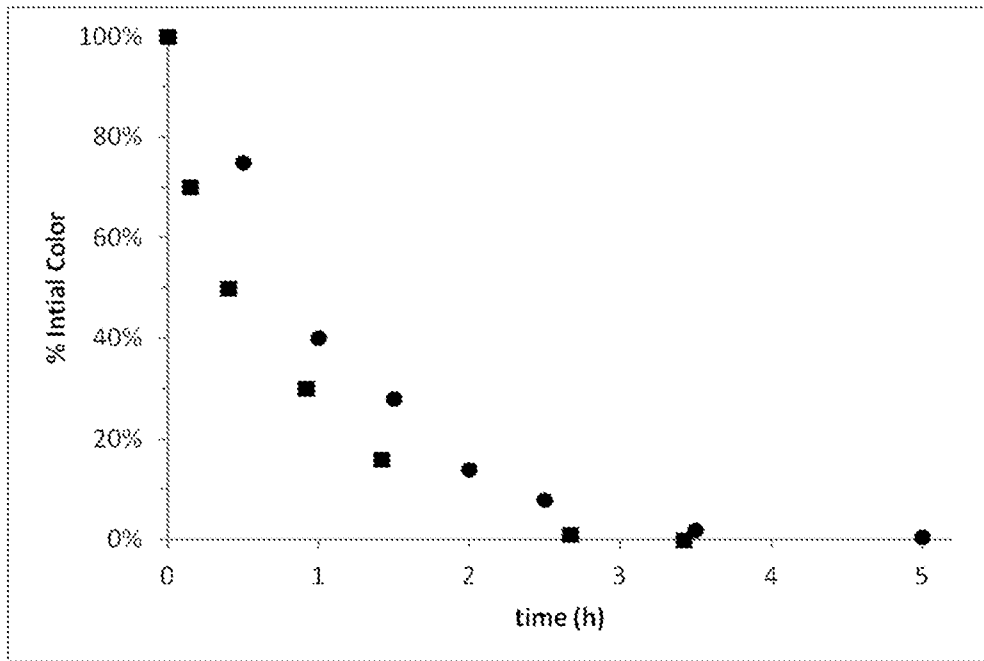
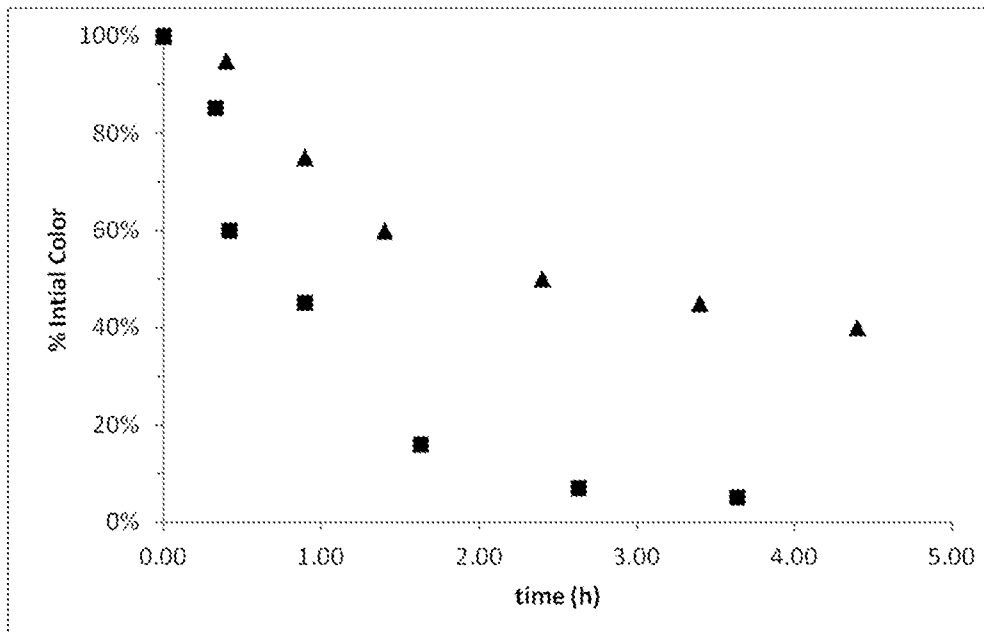
FIG. 23A



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**FIG. 23C**

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**FIG. 24A****FIG. 24B**

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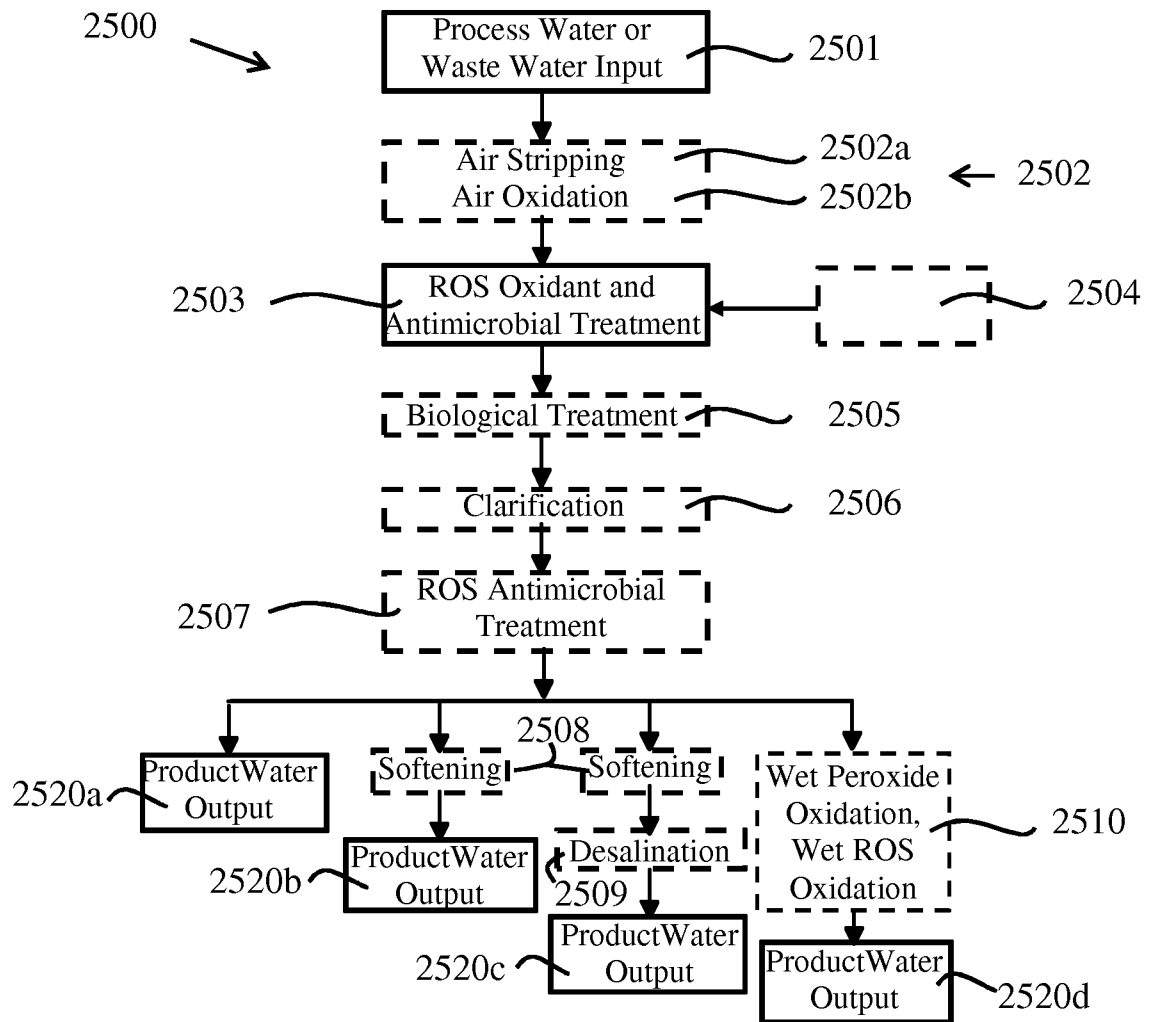


FIG. 25

