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WO-A-98/21152

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Description

BACKGROUND

[0001] This invention relates to a microporous diffuser and to a method of water remediation.

[0002] There is a well recognized need to clean-up contaminants that exist in ground and surface water. In particular, there is one type of contamination problem which widely exists, that is, the contamination of surface waters or subsurface waters which find their way to the surface such as, for example, in a contaminated spring. Such surface waters may be contaminated with various constituents including volatile hydrocarbons, such as chlorinated hydrocarbons including trichloroethene (TCE), tetrachloroethene (PCE).

[0003] There are several water remediation systems known in the art. US 5,879,108 describes an air sparging/soil vapour extraction apparatus positionable in a bore hole, which extends deep into an area of soil which is heavily contaminated by pollutants. A discharge of injected air through a pipe arrangement, forces pressurised air through the contaminated soil, whereby the air volatizes and removes contaminants from the soil.

[0004] In US 5,620,593 an in-well system is described for simultaneously treating and extracting groundwater by injecting compressed gas through the water in multiple stages as it is pumped from the well. The groundwater is forced to travel through separate concentric pathways to alter the chemical, physical, or radiological properties of the water prior to discharge from the well.

[0005] The system of US 5,967,230 treats in situ water to create environmentally neutral species from hydrocarbon contaminants. A catalyst is injected into the water site and is permitted to diffuse through the water. The subsequent introduction of an oxidising agent into the water, promotes the release of free radicals which act upon the contaminants to form neutral species.

[0006] Another water sparging method is described in US 5,425,598, where a well casing having permeable sidewalls is inserted into a well. The casing includes an injector tube, through which pressurised gas is forced out of the lower end of the tube and into the ground water collected in the well casing. The gas motion drives convective currents and promotes removal and biodegradation of contaminants.

[0007] In EP 546335, a system for aerating waste water is described, wherein gas is forced through a membrane-like wall of a gas distributor arranged below the water level. The wall includes a multiplicity of gas outlet orifices.

[0008] A bioremediation water system is described in EP 402158, where a subsurface pumping apparatus separates a phase of contaminated groundwater for off-site disposal, and feeds hazardous substance degrading micro-organisms into the system to treat the remaining water prior to eventual recirculation into the contaminated site.

[0009] A further method and apparatus for groundwater remediation is described in granted US patent 5855775 (corresponding to WO 98/21152). The apparatus consists of multiple microporous diffusers for injecting microfine bubbles, containing oxidising gas, into the contaminated water. The microfine bubbles oxidise dissolved hydrocarbon and chlorinated hydrocarbon products into harmless by-products, thereby stripping contaminants from the ambient groundwater and drawing them into the mini-atmosphere contained in each bubble.

SUMMARY

[0010] According to a first aspect of the present invention, a microporous diffuser comprises a first elongated member including at least one sidewall having a plurality of microscopic openings, said sidewall defining an interior hollow portion of said member, a second elongated member having a second sidewall having a plurality of microscopic openings, said second member being disposed through the hollow region or said first member, an end cap to seal a first end of the microporous diffuser and an inlet cap disposed at a second end of microporous diffuser, the inlet cap having a pair of openings to deliver a first fluid to the interior portions of the first member and a second fluid to interior portions of the second member.

[0011] According to a second aspect of the present invention there is provided a method of water remediation as defined in claim 18.

Particular embodiments of the invention are the subject of the respective dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The various features and advantages of the present invention will become more apparent by referring to the following detailed description and drawings in which:

FIG. 1 is a diagrammatical view of a typical surface water treatment example.
FIG. 2 is a block diagram of an apparatus used in the treatment process.
FIGS. 3A and 3B are respectively plan and elevational views somewhat schematic, of a spring box used in the
apparatus of FIG. 2.
FIGS. 3C and 3D are plan and elevational views of still alternate spring box arrangements.
FIGS. 4A and 4B are longitudinal cross-section and plan cross-sectional views of a microporous diffuser useful in the spring box of FIGS. 3A and 3B;
FIGS. 5A, 5B are longitudinal cross-section and plan cross-sectional views, respectively, of an alternative microporous diffuser useful in the spring box of FIGS. 3A and 3B.
FIGS. 6A and 6B are cross-sectional view of sidewalls of the microporous diffusers of either FIGS. 4A, 4B or 5A, 5B showing exemplary construction details.
FIGS. 7A, 7B are longitudinal cross-section and plan cross-sectional views, respectively, of a still alternative microporous diffuser useful in the spring box of FIGS. 3A-3D.
FIGS. 8A and 8B are respectively plan and elevational views somewhat schematic, of a circular spring box arrangement with a mixing feature also useful in the apparatus of FIG. 2.
FIG. 9 is a cross-sectional view showing an alternative treatment example.
FIG. 10 is a plot of removal rate of PCE for an aqueous solution equivalent to 120 ppb, over differing bubble sizes.

DETAILED DESCRIPTION

[0013] Referring now to FIG. 1, an example 10 of the use of an apparatus for treatment of surface water or in-situ removal of contaminants from water is shown. Illustrated in FIG. 1 is a site 11, having a subsurface aquifer 14 that produces surface waters 12 such as by a spring. A spring-box treatment system 20 disposed on the site 11. The spring box treatment system 20 is disposed to intercept the surface water 12 and to divert the surface water into the spring box treatment system 20 to remove contaminants such as volatile hydrocarbons and, in particular, chlorinated hydrocarbons which may exist in the water in the aquifer 14. The spring box treatment system 20 outputs a water stream 16 which is substantially free of the contaminants.

[0014] Contaminants which can be treated or removed by use of the spring box treatment system 20 include hydrocarbons and, in particular, volatile chlorinated hydrocarbons such as tetrachloroethene, trichloroethene, cis-dichloroethene, trans-dichloroethene, 1,1-dichloroethene and vinyl chloride. In particular, other materials can also be removed from the stream including chloroalkanes, including 1,1,1 trichloroethane, 1,1, dichloroethene, methylene chloride, and chloroform; benzene, toluene, ethylbenzene, O-xylene, P-xylene, naphthalene and methyltetrabutylyether (MTBE). It should be understood that the use of the spring-box treatment system 20 is not limited to flowing surface water but could be used to treat pumped or stored water.

[0015] Referring now to FIG. 2, the spring box treatment system 20 includes a spring box 30, and an air compressor 22, a compressor/pump control mechanism 24, and an ozone (O₃) generator 26. The air compressor 24 can feed a stream of air into the spring box 30 whereas, the compressor pump control 24 feeds a stream of air mixed with ozone (O₃) from the ozone generator 26 into the spring box 30 to affect substantial removal of the above-mentioned or similar types of contaminants. Optionally, or in addition thereto, the apparatus 20 can also include a pump 28 that supplies a liquid decontamination agent such as hydrogen peroxide or such as catalyst agents including iron containing compounds such as iron silicates or palladium or palladized carbon. To promote biodegradation reactions, the liquid introduced can be a nutrient mixture of nitrogen (ammonium or nitrate), phosphorus, and potassium along with oxygen as a gas to promote oxic reactions or carbon dioxide and hydrogen sulfide to promote reduction reactions.

[0016] The spring box 30 uses primarily a gas-gas reaction between contaminant vapors and ozone (described below). This reaction can be supplemented with a liquid phase reaction. A liquid decontaminator such as hydrogen peroxide can also be used. The use of hydrogen peroxide as a thin film coating on the bubbles promotes the decomposition rate by adding a secondary liquid phase reactive interface as volatile compounds enter the gaseous phase. It also expands the types of compounds that can be effectively removed. Alternatively, the pump control 28 can simply feed water.

[0017] Referring now to FIGS. 3A and 3B, an arrangement of a spring box 30 is shown. The spring box includes a container 31 comprised of a sidewall 32 of a durable material such as concrete over which is disposed or attached a water tight lid 33 also comprised of concrete. Within the spring box 30 is provided an inlet port 42 to receive the water from the spring, as well as a plurality of partially closed chambers 40a-40d which are formed within the interior of the spring box by walls or partitions 38a-38c. Within each of the chambers 40a-40d are disposed a plurality of microporous diffusers such as those shown in conjunction with my issued U.S. Patent No. 5,855,775. Alternatively, microporous diffusers 50, 70, as described below in conjunction with FIGS. 4A, 4B or FIGS. 5A and 5B may be used.

[0018] In the arrangement shown in FIG. 3A, a first pair of microporous diffusers 50a, 50b or 70a, 70b are coupled to a common gas/liquid feed arrangement 36a which can be fed, for example, from compressor/pump 24 and compressor 28 (FIG. 2). The spring box 30 also includes a second feed arrangement 37a which in this embodiment has one of the microporous diffusers 50c, 70c being fed with a combination of air, ozone and air, ozone and liquid as above, and with the second microporous diffuser 50d, 70d being fed only by air to provide air stripping of any residual ozone before exiting of the treated water.
As shown in FIG. 3B, the microporous diffusers are arranged in elevation above the bottom of the spring box 30 within a pool 39 of water provided from the spring or other surface water source. FIGS. 3C and 3D show still alternate spring box arrangements. In the arrangement 30' of FIG. 3C, the diffusers 50 or 70 are coupled in series whereas FIG. 3D shows diffusers 50, 70 arranged to be staggered in elevation over the height of the spring box. The spring box 30 is an ozone reactor vessel in which ozone is pumped into the pool of water through the use of the microporous diffusers. The microporous diffusers are disposed in the water under treatment and transfer ozone into the water in the form of microfine or fine bubbles which promote rapid gas/gas/water reactions with volatile organic compounds particularly in the presence of a catalyst or enhancer which may participate in the gaseous phase of the reaction, instead of solely enhancing dissolved aqueous disassociation and reactions. In addition, with the optional use of the liquid port to the apparatus, the gas/gas reactions are optimized to include gas/gas reactions within the gaseous phase as well as inducing water aqueous phased reactions to achieve an overall decomposition rate within the gaseous phase and the aqueous phase from second water reactions. For example, the use of hydrogen peroxide as a laminate coating on the bubbles can enhance decomposition rates as mentioned below. The micron plastic bubbler may also be coated with or have sintered into construction an outer layer of activated carbon or activated carbon with palladium to simultaneously accumulate and promote decomposition of the chloroethenes.

The production of microbubbles and selection of appropriate size distribution are selected for optimized gas exchange through high surface area to volume ratio and long residence time within the liquid to be treated. The microbubbles are generated by using microporous materials in the microporous diffuser which acts as a bubble chamber, as shown in the embodiment 50 (FIG. 4A-4B) or, alternatively, through the embodiment 70 of the microporous diffuser of FIG. 5A-5B. The apparatus 20 promotes the continuous production of microbubbles minimizing coalescing or adhesion. The injected air/liquid combination moves as a fluid into the water to be treated; whereas, microencapsulated ozone within the microfine bubbles enhances and promotes in-situ stripping of volatile organics and simultaneously terminates normal reversible Henry's reaction.

Referring now to FIGS. 4A-4B, a microporous diffuser 50 is shown. The microporous diffuser 50 includes a first cylindrical member 56 comprised of a hydrophobic material which provides an outer cylindrical shell for the microporous diffuser. The cylindrical member 56 has a sidewall 56a which is comprised of a large plurality of micropores. A second cylindrical member 60 is coaxially disposed within the first cylindrical member 56. The second cylindrical member 60 is comprised of a hydrophobic material and has a sidewall 60a which is comprised of a large plurality of micropores. Also disposed within the confines of the first cylindrical member 56 are a plurality of cylindrical members 58, here four; which have sidewalls 58a having a large plurality of micropores and also comprised of a hydrophobic material.

A proximate end of central cylindrical member 60 is coupled to a first inlet port 52 which is provided from a first inlet cap 52 and proximate ends of the plurality of cylindrical members 58 are coupled to second inlet ports generally denoted as 52b. At the opposite end of the microporous diffuser 50 an end cap 54 covers distal ends of cylindrical members 56 and 60. Here distal ends of the plurality of cylindrical members 58 are sealed by separate caps 57 but could be terminated by the end cap 54. The end cap 54 in conjunction with cap 52 seals the distal ends of the microporous diffuser. Each of the cylindrical members 56, 58 and 60 are here cylindrical in shape and have a plurality of microscopic openings constructed through sidewalls 56a, 58a and 60a, respectively, thereof having pore sizes matched to or to create a pore size effective for inducing gas/gas reactions in the spring box 30. Sidewalls of each of the cylindrical members can have a pore diameter in a range of 1-200 microns, preferably 1-50 microns and more preferably 5-20 microns. The combination of the inlet cap 52 and end cap 54 seals the microporous diffuser 50 permitting liquid and gas to escape by the porous construction of sidewalls of the microporous diffusers.

The microporous diffuser 50 can be filled with a microporous material such as microbeads with mesh sizes from 20 to 200 mesh or sand pack or porous hydrophilic plastic to allow introducing a liquid into the pore spaces where liquid is exiting.

Referring now to FIGS. 5A and 5B, an alternate embodiment 70 of a microporous diffuser is shown. The microporous diffuser 70 includes an outer cylindrical member 76 having a sidewall 76a within which is disposed an inner cylindrical member 78 having a sidewall 78a. The inner cylindrical member 78 is spaced from the sidewall of the outer cylindrical member. The space 77 between the inner and outer cylindrical members 76, 78 is filled with a packing material comprised of glass beads or silica particles (silicon dioxide) or porous plastic which, in general, are hydrophilic in nature. This space is coupled to an input port 72b which receives liquid, and catalysts, and/or nutrients from pump 39 (FIG. 2). The microporous diffuser 70 has the inner cylindrical member 78 disposed coaxial or concentric to cylindrical member 76. Sidewalls of each of the cylindrical members can have a pore diameter in a range of 1-200 microns, preferably 1-50 microns and more preferably 5-20 microns. A proximate end of the inner cylindrical member is coupled to an inlet port 72a which is fed an air ozone mixture from pump 36. The microporous diffuser also includes an end cap 74 which in combination secures distal ends of the cylinders 76 and 78. The combination of the inlet cap 72 and end cap 74 seals the microporous diffuser permitting liquid and gas to escape by the porous construction of sidewalls of the microporous
diffusers.

[0027] Referring now to FIGS. 6A, 6B, construction details for the elongated cylindrical members for the microporous diffusers 50, 70 are shown. As shown in FIG. 6A, sidewalls of the members can be constructed from a metal or a plastic support layer 91 having large (as shown) or fine perforations 91a over which is disposed a layer of a sintered i.e., heat fused microscopic particles of plastic. The plastic can be any hydrophobic material such as polyvinylchloride, polypropylene, polyethylene, polytetrafluoroethylene, high density polyethylene (HDPE) and ABS. The support layer 91 can have fine or coarse openings and can be of other types of materials. FIG. 6B shows an alternative arrangement 94 in which sidewalls of the members are formed of a sintered i.e., heat fused microscopic particles of plastic. The plastic can be any hydrophobic material such as polyvinylchloride, polypropylene, polyethylene, polytetrafluoroethylene, high density polyethylene (HDPE) and alklybenzylsulfonate (ABS).

[0028] The fittings (i.e., the inlets in FIGS. 4A, 5A can be threaded and are attached to the inlet cap members by epoxy, heat fusion, solvent or welding with heat treatment to remove volatile solvents or other approaches. Standard threading can be used for example NPT (national pipe thread) or box thread e.g., (F480). The fittings thus are securely attached to the microporous diffusers in a manner that insures that the microporous diffusers can handle pressures that are encountered with injecting of the air/ozone and liquid.

[0029] Referring to FIGS. 7A-7B, an alternate microporous diffuser 90 is shown. The microporous diffuser 90 includes a first cylindrical member 96 comprised of a hydrophobic material which provides an outer cylindrical shell for the microporous diffuser 90. The cylindrical member 96 has a sidewall 96a that is comprised of a large plurality of micro pores. A proximate end of cylindrical member 96 is coupled to a first inlet port 92a provided from a first inlet cap 92 and a distal end of the cylindrical member 96 is coupled to an end cap 94. The end cap 94 in conjunction with cap 92 seals the ends of the microporous diffuser 90. Sidewalls of the cylindrical members 96 is provided with a film of a catalysts or reaction promoter or and absorbing material. Examples include a layer 99 of activated carbon that is abraded into the surface or sintered into the surface. Additionally palladized activated carbon could also be used. As explained above the layer 93 can aid in decomposition of the contaminants in the water. Sidewalls of each of the cylindrical members can have a pore diameter in a range of 1-200 microns, preferably 1-50 microns and more preferably 5-20 microns.

[0030] The use of catalysts supported by absorptive materials such as palladized activated carbon can be particularly effective for compounds that have an absorptive affinity to activated carbon. The compounds such as TCE are concentrated near the release location of the ozone micro bubbles, allowing more efficient reaction for water containing lower concentrations of TCE as explained above. The layer 93 can also be provided on the other embodiments 50, 70 above, e.g., on either or both cylindrical members but preferably on the members that deliver the ozone to the water.

[0031] Referring now to FIGS. 8A and 8B, an alternate arrangement of a spring box 110 is shown. The spring box 110 includes a circular container 111 comprised of a sidewall 112 of a durable material such as concrete over which is disposed or attached a water tight lid 113 also comprised of concrete. Within the spring box 110 is provided an inlet port 115a to receive the water from the spring. Within the circular container are disposed a plurality of microporous diffusers such as those shown in conjunction with my issued U.S. Patent No. 5,855,775. Alternatively, microporous diffusers 50, 70, 90, as described above in conjunction with FIGS. 4A and 4B, FIGS. 5A and 5B, or FIGS. 7A-7B may be used.

[0032] In the arrangement shown in FIG. 8A, the microporous diffusers 116 are coupled to a common rotary joint 117 that can provide a gas/ozone feed arrangement 86a which can be fed, for example, from compressor/pump 24 and pump 28 (FIG. 2). As shown in FIG. 8B, the microporous diffusers are arranged in elevation above the bottom of the spring box 110 within a pool 119 of water provided from the spring or other surface water source. The rotary joint 117 enables the microporous diffusers to be rotated in the water enabling the ozone to more effectively mix with the water. The spring box 110 can include a sand or other matrix 120 containing a reaction promoter e.g., catalyst as mentioned.

[0033] The spring box 110 is an ozone reactor vessel in which ozone is pumped into the pool of water through the use of the microporous diffusers. The microporous diffusers 116 are disposed in the water under treatment and transfer ozone into the water in the form of micro fine or fine bubbles which promote rapid gas/water reactions with volatile organic compounds particularly in the presence of a catalyst or enhancer which may participate in the gaseous phase of the reaction, instead of solely enhancing dissolved aqueous dissociation and reactions.

[0034] In addition, an optional liquid port (not shown) to the rotary joint can be provided to include gas/gas reactions within the gaseous phase as well as inducing water aqueous phased reactions to achieve an overall decomposition rate within the gaseous phase and the aqueous phase from second water reactions. For example, the use of hydrogen peroxide as a laminate coating on the bubbles can enhance decomposition rates as mentioned above.

[0035] Referring now to FIG. 9, an alternative example of the use of the microporous diffusers 50, 70 is shown. The example shows an injection well to treat subsurface waters of an aquifer. The arrangement includes a well having a casing with an inlet screen and outlet screen to promote a recirculation of water into the casing and through the surrounding ground area. The casing supports the ground about the well. Disposed through the casing are microporous diffusers e.g., 50 or 70. The injection well treatment system 140 also includes an air compressor 152, a compressor/pump control mechanism 154, and an ozone (O₃) generator 156. The air compressor 154 can feed a stream of air into the microporous
diffuser 50 whereas, the compressor pump control 154 feeds a stream of air mixed with ozone (O₃) from the ozone generator 156 into microporous diffuser to affect substantial removal of the above-mentioned or similar types of contaminants. Optionally, or in addition thereto, the treatment system 140 can also include a pump 108 that supplies a liquid decontamination agent such as hydrogen peroxide as well as nutrients such as catalyst agents including iron containing compounds such as iron silicates or palladium containing compounds such as palladized carbon. In addition, other materials such as platinum may also be used.

[0036] The treatment system 140 makes use of a gas-gas reaction of contaminant vapors and ozone (described below) that can be supplemented with a liquid phase reaction. The use of hydrogen peroxide as a thin film coating on the bubbles promotes the decomposition rate by adding a secondary liquid phase reactive interface as volatile compounds enter the gaseous phase. It also expands the types of compounds that can be effectively removed. Alternatively, the pump control 108 can simply feed water.

[0037] In particular, with the microporous diffusers 50 and 70 and use of the optional port to introduce a liquid such as hydrogen peroxide or water into the chamber, the microbubbles are produced in the microporous diffuser by bubbling air/ozone through the central cylinder of the microporous diffusers and into the surrounding outer regions of the micro porous diffusers. At the same time, a liquid is introduced into the microporous diffusers 50, 70 and laminates an outer surface of bubbles formed by the gas. The liquid forms a liquid barrier between the water to be treated and the inside gas containing air/ozone. This arrangement thus can be injected into a slurry containing a catalyst such as silicate, iron silicate, palladium, palladized carbon or titanium dioxide to produce rapid reactions to decompose contaminants within the pool of water contained in the spring box 30. The reactions can proceed as set out below.

[0038] The process uses microfine bubble injection to produce simultaneous extraction/decomposition reactions as opposed to simply creating smaller and smaller sized bubbles for the purpose of injecting into free water. The process involves generation of fine bubbles which can promote rapid gas/gas/water reactions with volatile organic compounds which a substrate (catalyst or enhancer) participates in, instead of solely enhancing dissolved (aqueous) disassociation and reactions. The production of microbubbles and selection of appropriate size distribution is provided by using microporous material and a bubble chamber for optimizing gaseous exchange through high surface area to volume ratio and long residence time within the liquid to be treated. The equipment promotes the continuous production of microbubbles while minimizing coalescing or adhesion.

[0039] The injected air/liquid combination moves as a fluid into the water to be treated. The use of microencapsulated ozone enhances and promotes in-situ stripping of volatile organics and simultaneously terminates the normal reversible Henry’s reaction. The process involves promoting simultaneous volatile organic compounds (VOC) in-situ stripping and gaseous decomposition, with moisture (water) and substrate (catalyst or enhancer). The reaction mechanism is not a dissolved aqueous reaction. In some cases, with cis- or trans-DCE, the aqueous phase reaction may assist the predominantly gas-phase reaction.

[0040] The remote process controller and monitor allows for the capability for sensor feedback and remote communication to the pump control 24 and ozone (or oxygen or both) generator 26 to achieve a certain level of gaseous content (e.g., dissolved oxygen, ozone, or other gas) and rate of mixing to promote efficient reactions. This is done by sensors 39 (FIGS. 3A, 3B) placed in the bubble chambers at certain distances from the microporous diffusers 50, 70. Oxygen content, redox potential, and dissolved VOC concentration of the water can be monitored within the treatment system. The operator can access the information, modify operations and diagnose the condition of the unit by telephone modem or satellite cell phone. This provides on-site process evaluation and adjustment without the need of on-site operator presence.

[0041] Appropriately sized microfine bubbles can be generated in a continuous or pulsing manner which allows alternating water/bubble/water/bubble fluid flow. The microfine bubbles substantially accelerate the transfer rate of volatile organic compounds like PCE from aqueous to gaseous state. Reducing the size of the bubbles to microfine sizes, e.g., 5 to 50 microns, can boost extraction rates. These sizes boost exchange rates and do not tend to retard rise time by too small a size. When an oxidizing gas (ozone) is added into the microbubbles, the rate of extraction is enhanced further by maintaining a low interior (intrabubble) concentration of PCE, while simultaneously degrading the PCE by a gas/gas/water reaction. The combination of both processes acting simultaneously provides a unique rapid removal system which is identified by a logarithmic rate of removal of PCE, and a characteristic ratio of efficiency quite different from dissolved (aqueous) ozone reactions. The compounds commonly treated are HVOCs (halogenated volatile organic compounds), PCE, TCE, DCE, vinyl chloride (VC), petroleum compounds (BTEX: benzene, toluene, ethylbenzene, xylenes).

[0042] An analysis of the reaction mechanism is set out. Gaseous exchange is proportional to available surface area. With partial pressures and mixtures of volatile gases being held constant, a halving of the radius of bubbles would quadruple (i.e., times) the exchange rate. If, in the best case, a standard well screen creates air bubbles 200 times the size of a medium sand porosity, a microporous diffuser of 5 to 20 micron size creates a bubble 1/10 the diameter and six to ten times the volume/surface ratio as shown in Table 1.
Theoretically, the microporous bubbles exhibit an exchange rate of ten times the rate of a comparable bubble from a standard ten slot well screen.

In wastewater treatment, the rate of transfer between gas and liquid phases is generally proportional to the surface area of contact and the difference between the existing concentration and the equilibrium concentration of the gas in solution. Simply stated, if the surface to volume ratio of contact is increased, the rate of exchange also increases as illustrated in Table 2. If, the gas (VOC) entering the bubble (or micropore space bounded by a liquid film), is consumed, the difference is maintained at a higher entry rate than if the VOC is allowed to reach saturation equilibrium. In the case of a halogenated volatile organic carbon compound (HVOC), PCE, gas/gas reaction of PCE to by-products of HCl, CO₂ and H₂O accomplishes this. In the case of petroleum products like BTEX (benzene, toluene, ethylbenzene, and xylenes), the benzene entering the bubbles reacts to decompose to CO₂ and H₂O. The normal equation for the two-film theory of gas transfer is:

\[ r_m = K_g A (C_g - C) \]

where:
- \( r_m \) = rate of mass transfer
- \( K_g \) = coefficient of diffusion for gas
- \( A \) = area through which gas is diffusing
- \( C_g \) = saturation concentration of gas in solution
- \( C \) = concentration of gas in solution.

The restatement of the equation to consider the inward transfer of phase change from dissolved HVOC to gaseous HVOC in the inside of the bubble would be:

\[ C_s = \text{Saturation concentration of gas phase of HVOC or VOC in bubble.} \]
\[ C = \text{Initial concentration of gaseous phase of HVOC or VOC in bubble volume.} \]

Soil vapor concentrations are related to two governing systems: water phase and (non-aqueous) product phase. Henry’s and Raoult’s Laws are commonly used to understand equilibrium-vapor concentrations governing volatilisation from liquids. When soils are moist, the relative volatility is dependent upon Henry’s Law. Under normal conditions (free from product) where volatile organic carbons (VOCs) are relatively low, an equilibrium of soil, water, and air is assumed to exist. The compound tetrachloroethene (PCE) has a high exchange capacity from dissolved form to gaseous form. If the surface/volume ratio is modified at least ten fold, the rate of removal should be accelerated substantially.

FIG. 10 shows a plot of removal rate of PCE for an aqueous solution equivalent to 120 ppb, over differing bubble sizes. The air volume and water volume is held constant. The only change is the diameter of bubbles passed through the liquid from air released from a diffuser.

Ozone is an effective oxidant used for the breakdown of organic compounds in water treatment. The major problem in effectiveness is that ozone has a short lifetime. If ozone is mixed with sewage containing water above ground, the half-life is normally minutes. Ozone reacts quantitatively with PCE to yield breakdown products of hydrochloric acid, carbon dioxide, and water.
To offset the short life span, the ozone is injected with microporous diffusers, enhancing the selectiveness of action of the ozone. By encapsulating the ozone in fine bubbles, the bubbles would preferentially extract volatile compounds like PCE from the mixtures of soluble organic compounds they encountered. With this process, volatile organics are selectively pulled into the fine air bubbles. Gas entering a small bubble of volume \((4\pi r^3)\) increases until reaching an asymptotic value of saturation. If we consider the surface of the bubble to be a membrane, a first order equation can be written for the monomolecular reaction of the first order. The reaction can be written

\[
\frac{dx}{dt} = K(Q - X)
\]

as follows: where \(X\) is the time varying concentration of the substance in the bubble, \(Q\) is the external concentration of the substance, and \(K\) is the absorption constant.

\[
X = Q (1 - e^{Kt})
\]

If at time \(t = 0\), \(X = 0\), then:

\[
K = \frac{dx/dt}{Q - X}
\]

The constant \(K\) is found to be:

\[
K = \frac{vdx/dt}{v(Q - X)}
\]

by \(V\), the volume of the bubble, we obtain which is the ratio between the amount of substance entering the given volume per unit time and quantity \(V(Q - X)\) needed to reach the asymptotic value. By analyzing the concentration change within the fine bubbles sent through a porous matrix with saturated (water filled) solution interacting with the matrix (sand), and determining the rate of decomposition of the products (TCE + ozone = CO\(_2\) + HCl) and (Benzene + ozone = CO\(_2\) + HOH), the kinetic rates of reaction can be characterized.

The rate which the quantity \(k_1QV\) of the substance flows in one unit of time from aqueous solution into the bubble is proportional to Henry’s Constant. This second rate of decomposition within the bubble can be considered as \(k_1\), a second rate of reaction \(-k_2X\), where

\[
\frac{dx}{dt} = k_1Q - k_2X
\]

and, at equilibrium, as \(dx/dt = 0\), gives

\[
X = \frac{k_1Q}{k_2}
\]

However, if the reaction to decompose is very rapid, so \(-k_2X\) goes to zero, the rate of reaction would maximize \(k_1Q\), i.e., be proportional to Henry’s Constant and maximize the rate of extraction since VOC saturation is not occurring within the bubbles.

The combination of microbubble extraction and ozone degradation can be generalized to predict the volatile
organic compounds amenable to rapid removal. The efficiency of extraction is directly proportional to Henry’s Constant. Multiplying the Henry’s Constant (the partitioning of VOCs from water to gas phase) times the reactivity rate constant of ozone for a particular VOC yields the rate of decomposition expected by the microbubble process.

The concentration of HVOC expected in the bubble is a consequence of rate of invasion and rate of removal. In practice, the ozone concentration is adjusted to yield 0 concentration at the time of arrival

$$r_{me} = -K_L a_{me} (C - C_L)$$

at the surface.

where:

- $f_{voc}$ = rate of VOC mass transfer, $\mu g/ft^3//h$
- $(K, a)_{voc}$ = overall VOC mass transfer coefficient, $l/h$
- $C$ = concentration of VOC in liquid
- $C_L$ = saturation concentration of VOC in liquid $\mu g/ft^3 (\mu g/m^3)$

The concentration of a VOC in wastewater is a function of the partial pressure of the VOC in the atmosphere in contact with the wastewater.

$$\frac{C_g}{C_L} = H_c \text{ thus, } C_g = H_c \cdot C_L$$

$C_g$ = concentration of VOC in gas phase $\mu g/ft^3 (\mu g/m^3)$
$C_L$ = saturation concentration of VOC in liquid $\mu g/ft^3 (\mu g/m^3)$
$H_c$ = Henry’s Constant

The rate of decomposition of an organic compound $C_g$ (when present at a concentration $(C)$ by ozone can be formulated by the equation:

$$-(\frac{dC_g}{dt}) O_3 = K_{o3} (O_3) (C_g)$$

or, after integration for the case of a batch reactor:

$$-ln(\frac{C_{g, fin}} {C_g}) = K_{o3} (O_3) t \quad \text{ (equation 2)}$$

$$(C_g)_{fin} = C_g e^{-K_{o3} (O_3) t}$$

$$(C_g)_{o} = e^{-K_{o3} (O_3) t}$$

where

$(O_3)$ = concentration of ozone averaged over the reaction time $(t)$
$(C_g)_{o}$ = halocarbon initial concentration
\[(C_g)_{\text{end}} = \text{halocarbon final concentration}\]

Substituting:

\[rm = K_gA (C_g - C)\]
\[rm = K_gA ((H_gC_g)^{-1} - C)\]
\[rm = K_gZ ((H_gC_g)^{-1} - C)\]
\[rm = K_gZ ((H_cC_g)^{-1} - C - K_o (O_3) (C_g))^0\]

From Henry’s Law:

\[C_g = H_cC_g \text{ (equation 3)}\]

With ozone

\[(H_gC)^{-1} - K_o (O_3) (C_g) = 0 \text{ (equation 4)}\]

Rate of decomposition is now adjusted to equal the total HVOC entering the bubble.

\[\text{SET: } (H_cC_g) = K_o (O_3) (C_g) \text{ (equation 5)}\]

Therefore surface concentration = 0

Table 4 gives the Henry’s Constants \((H_c)\) for a selected number of organic compounds and the second rate constants \((R_2)\) for the ozone radical rate of reaction in solely aqueous reactions where superoxide and hydroxide reactions dominate. The third column presents rates of removal process.

**TABLE 4 REMOVAL RATE COEFFICIENTS**

<table>
<thead>
<tr>
<th>Organic Compound</th>
<th>Ozone Aqueous Second Order Rate Constant (a.) ((M^{-1} \text{ SEC}^{-1}))</th>
<th>Henry’s Constant (b.) ((c.))</th>
<th>Rate Removal Coefficient ((t)) ((c.))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2</td>
<td>5.59 x 10^3</td>
<td>0.06</td>
</tr>
<tr>
<td>Toluene</td>
<td>14</td>
<td>6.37 x 10^3</td>
<td>0.07</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.75</td>
<td>3.72 x 10^3</td>
<td>0.013</td>
</tr>
<tr>
<td>Dichloroethylene</td>
<td>110</td>
<td>7.60 x 10^3</td>
<td>0.035</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>17</td>
<td>9.10 x 10^3</td>
<td>0.05</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>0.1</td>
<td>25.9 x 10^3</td>
<td>0.06</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.02</td>
<td>.04 x 10^3</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

| c) See US Patent 5,855,775. |

[0061] The rapid removal rate of this process does not follow Hoigne and Bader (1983) rate constants. However, there
is a close correlation to Henry’s Constant as would be expected from equation 5. The presence of the substrate (sand) and moisture is necessary to complete the reaction. The active ingredient in the sand matrix appears to be an iron silicate. The breakdown products include CO₂ and dilute HCl.

[0062] Two sets of equations are involved in the reactions:

**Dissolved Halogenated Compounds**

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{C} = \text{C} & \quad + \quad \text{O}_3 & \quad + \quad \text{HOH} & \quad \longrightarrow & \quad 3\text{HCl} & \quad + \quad 2\text{CO}_2 \\
\text{Cl} & \quad \text{H} & \quad & & & \\
\end{align*}
\]

**Dissolved Petroleum Distillates**

\[
\begin{align*}
\text{HOH} & \\
\text{C}_6\text{H}_{12} & \quad + \quad 6\text{O}_3 & \quad \longrightarrow & \quad 6\text{CO}_2 & \quad + \quad 6\text{HOH} \\
\text{Substrate} & & & & & \\
\end{align*}
\]

Exemplary compounds are normally unsaturated (double bond), halogenated compounds like PCE, TCE, DCE, Vinyl Chloride, EDB; or aromatic ring compounds like benzene derivatives (benzene, toluene, ethylbenzene, xylenes). Also, pseudo Criegee reactions with the substrate and ozone appear effective in reducing certain saturated olefins like trichloro alkanes (1,1,-TCA), carbon tetrachloride (CCl₄), chloroform and chlorobenzene, for instance.

[0063] The following characteristics of the contaminants appear desirable for reaction:

- Henry’s Constant: \(10^{-2}\) to \(10^{-4}\) m³·atm/mol
- Solubility: 10 to 20,000 mg/l
- Vapor pressure: 1 to 3000 mmhg
- Saturation concentration: 5 to 9000 g/m³

Absorption-Destruction

[0064] Absorptive substrates like activated carbon and certain resins serve to remove dissolved volatile organic carbon compounds by absorption to the surface. The active surface of particles contain sites which the compounds attach to. The surface absorption is usually mathematically modeled by use of a Langmuir or Freundlich set of equations for particular sizes of particles or total surface area if the material is presented in cylinders or successive plates.

[0065] The derivation of the Langmuir isotherm stipulated a limited number of absorption sites on the surface of the solid. The absorption of a solute on the surface necessitates the removal of a solvent molecule. An equilibrium is then reached between the absorbed fraction and the remaining concentration in solution. If a continual gas phase of microbubbles is being released from a porous surface, can remove the absorbed molecule and decompose it, the reaction would be moved along much faster than in aqueous phase without the collecting surface.

\[
Q_i = \frac{K_{L1}C_i}{1 + K_{L1}C_i}
\]

\(Q_i\) = fractional surface coverage of solute
\(K_{L1}\) = equilibrium constant
C_{L1} = solute concentration

other Embodiments

[0066] It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims.

Claims

1. A microporous diffuser (50,70) comprising:
   a first elongated member (56,76) including at least one sidewall (56a,76a) having a plurality of microscopic openings, said sidewall defining an interior hollow portion of said member;
   a second elongated member (60,78) having a second sidewall (60a,78a) having a plurality of microscopic openings, said second member being disposed through the hollow region of said first member;
   an end cap (54,74) to seal a first end of the microporous diffuser; and
   an inlet cap (52,72) disposed at a second end of the microporous diffuser, the inlet cap having a pair of openings (52a,52b,72a,72b) to deliver a first fluid to the interior portions of the first member and a second fluid to interior portions of the second member.

2. The microporous diffuser (50,70) of claim 1, further comprising:
   first and second fittings coupled to the pair of openings (52a,52b,72a,72b) in the inlet cap (52,72); and
   wherein a region defined between the first and second elongated members (56,76;60,78) of the microporous diffuser is filled with a catalyst suspension material and has the first and second fittings coupled to the first and second elongated members to permit delivery of the fluids.

3. The microporous diffuser (50,70) of claim 1 wherein the first and second elongated members (56,76;60,78) are cylinders and the second elongated member (60,78) is disposed concentric to the first elongated member (56,76).

4. The microporous diffuser (50,70) of claim 3 wherein a region defined between the first and second elongated members (56,76;60,78) of the microporous diffuser is filled with a catalyst suspension material and wherein the inlet cap (54,74) has a fitting coupled to the second elongated member to permit delivery of a liquid through the second member.

5. The microporous diffuser (50,70) of claim 1 wherein the end cap (54,74) seals first ends of the first and second elongated members (56,76;60,78).

6. The microporous diffuser (50) of claim 1 wherein the second elongated member (60) is one of a plurality of second elongated members (58) disposed through the first elongated member (56) and wherein the inlet cap (54) has a plurality of fittings, with each coupled to a respective one of the plurality of second elongated members to permit delivery of a liquid through the second members.

7. The microporous diffuser (50) of claim 6 wherein the plurality of second elongated members (58) are disposed through a substantial portion of a length of the first elongated member (56).

8. The microporous diffuser (50) of claim 7 further comprising:
   a plurality of caps (57) to terminate ends of the second elongated members (58) which are disposed in the hollow portion of the first elongated member.

9. The microporous diffuser (50) of claim 6 wherein a region defined between the first and second elongated members (56,76;60,78) of the microporous diffuser is filled with a catalyst suspension material.

10. The microporous diffuser (50,70) of claim 2 or claim 4 or claim 9 wherein the catalyst suspension material is glass beads or silica particles.
11. The microporous diffuser (50,70) of claim 10 wherein a catalyst is disposed in the glass beads or silica, said catalyst containing iron.

12. The microporous diffuser (50,70) of claim 11 wherein the iron is in the form of iron silicates.

13. The microporous diffuser (50,70) of any preceding claim wherein the first and second elongated members (56,76; 60,78) are comprised of heat fused microscopic plastic particles.

14. The microporous diffuser (50,70) of claim 13 wherein the first and second elongated members (56,76;60,78) are further comprised of a cylindrical support having a plurality of openings to which the heat fused microscopic plastic particles are adhered to.

15. The microporous diffuser (50,70) of claim 14 wherein the support is made from a plastic or a metal.

16. The microporous diffuser (50,70) of any of claims 13 to 15 wherein the heat fused microscopic plastic particles are comprised of a plastic selected from the group consisting of polyvinylchloride, polypropylene, polyethylene, polytetrafluoroethylene, high density polyethylene (HDPE) and ABS.

17. The microporous diffuser (50,70) of any preceding claim wherein the microscopic openings have a diameter in a range of 1 to 200 microns.

18. A method of water remediation comprising:

   treating contaminated water by introducing microfine bubbles including an oxidising gas into the water, the microfine bubbles having a coating of hydrogen peroxide over the microfine bubbles that entrap the oxidising gas.

19. The method of claim 18 wherein the microfine bubbles are introduced using a microporous diffuser (50,70).

20. The method of claim 19 wherein the treating is catalysed by a catalyst agent in the microporous diffuser (50,70).

21. The method of claim 20 wherein the treating is catalysed by a catalyst agent including any one of the following: iron containing compounds, palladium containing compounds and platinum.

22. The method of any of claims 19 to 21 wherein the microporous diffuser (50,70) has an absorptive layer over a surface of the diffuser to remove dissolved volatile organic carbon compounds by absorption to the surface.

23. The method of any of claims 19 to 22 wherein the microfine bubbles are generated using microporous materials in the microporous diffuser (50,70), the materials having a pore diameter in the range of 1 to 200 microns.

24. The method of claim 23 wherein the microporous materials have a pore diameter in the range of 1 micron to 50 microns.

25. The method of claim 24 wherein the microporous materials have a pore diameter in the range of 5 microns to 20 microns.

26. The method of any of claims 18 to 25 wherein the microfine bubbles having a coating of hydrogen peroxide also include a layer of water disposed to entrap the oxidising gas.

27. The method of claim 18 or claim 26 wherein the oxidising gas is ozone.

28. The method of claim 18 or claim 26 wherein the oxidising gas includes ozone and included in the bubbles with the ozone is air.

29. The method of claim 18 wherein treating comprises:

   introducing an air-ozone stream through a microporous diffuser (50,70) that is disposed in the contaminated water, producing microfine bubbles of water entrapping air-ozone; and introducing a liquid including hydrogen peroxide through the microporous diffuser, to coat surfaces of the mi-
crofine bubbles with a coating of the hydrogen peroxide to produce the microfine bubbles having a coating of hydrogen peroxide over the microfine bubbles that entrap the oxidising gas.

30. The method of claim 18 or claim 29 wherein the microfine bubbles are produced by diffusion from a central chamber of the microporous diffuser (50,70) through microporous materials.

31. The method of claim 30 wherein the microporous materials have a pore diameter in the range of 1 micron to 200 microns.

32. The method of claim 30 wherein the microfine bubbles diffuse from the central chamber to a second chamber where they are coated with the hydrogen peroxide to provide the coating of hydrogen peroxide and pass through second microporous materials to produce microfine bubbles having a coating of hydrogen peroxide over the microfine bubbles that entrap the oxidising gas.

**Revendications**

1. Diffuseur microporeux (50,70) comprenant :

   un premier élément allongé (56,76) comprenant au moins une paroi latérale (56a,76a) ayant une pluralité d’orifices microscopiques, ladite paroi latérale définissant une partie interne creuse dudit élément; un deuxième élément allongé (60,78) comprenant une paroi latérale (60a,78a) ayant une pluralité d’orifices microscopiques, ledit deuxième élément étant disposé dans la région creuse dudit premier élément; un embout (54,74) pour fermer une première extrémité du diffuseur microporeux; et un embout d’admission (52,72) disposé à une deuxième extrémité du diffuseur microporeux, l’embout d’admission ayant une paire d’ouvertures (52a,52b,72a,72b) pour faire entrer un premier fluide dans les parties internes du premier élément et un deuxième fluide dans les parties internes du deuxième élément.

2. Diffuseur microporeux (50,70) selon la revendication 1, comprenant en outre :

   des premier et deuxième raccords couplés à la paire d’ouvertures (52a,52b,72a,72b) située dans l’embout d’admission (52,72); et dans lequel une région définie entre les premier et deuxième éléments allongés (56,76;60,78) du diffuseur microporeux est remplie d’un matériau catalytique en suspension et a les premier et deuxième raccords couplés aux premier et deuxième éléments allongés pour permettre l’admission des fluides.

3. Diffuseur microporeux (50,70) selon la revendication 1, dans lequel les premier et deuxième éléments allongés (56,76;60,78) sont des cylindres et le deuxième élément allongé (60,78) est disposé de manière concentrique par rapport au premier élément allongé (56,76).

4. Diffuseur microporeux (50,70) selon la revendication 3, dans lequel une région définie entre les premier et deuxième éléments allongés (56,76;60,78) du diffuseur microporeux est remplie d’un matériau catalytique en suspension et dans lequel l’embout d’admission (54,74) a un raccord couplé au deuxième élément allongé pour permettre l’admission d’un liquide dans le deuxième élément.

5. Diffuseur microporeux (50,70) selon la revendication 1, dans lequel l’embout (54,74) ferme les premières extrémités des premier et deuxième éléments allongés (56,76;60,78).

6. Diffuseur microporeux (50) selon la revendication 1, dans lequel le deuxième élément allongé (60) fait partie d’une pluralité de deuxièmes éléments allongés (58) disposés à travers le premier élément allongé (56) et dans lequel l’embout d’admission (54) a une pluralité de raccords, chacun étant couplé à l’un respectif de la pluralité de deuxièmes éléments allongés pour permettre l’admission d’un liquide dans les deuxièmes éléments.

7. Diffuseur microporeux (50) selon la revendication 6, dans lequel la pluralité de deuxièmes éléments allongés (58) est disposée à travers une grande partie d’une longueur du premier élément allongé (56).

8. Diffuseur microporeux (50) selon la revendication 7, comprenant en outre:
une pluralité d’embouts (57) pour terminer les extrémités des deuxièmes éléments allongés (58) qui sont disposés dans la partie creuse du premier élément allongé.

9. Diffuseur microporeux (50) selon la revendication 6, dans lequel une région définie entre les premier et deuxième éléments allongés (56,76;60,78) du diffuseur microporeux est remplie d’un matériau catalytique en suspension.

10. Diffuseur microporeux (50, 70) selon la revendication 2 ou la revendication 4 ou la revendication 9, dans lequel la matériau catalytique en suspension est fait de billes de verre ou de particules de silice.

11. Diffuseur microporeux (50, 70) selon la revendication 10, dans lequel un catalyseur est disposé dans les billes de verre ou la silice, ledit catalyseur contenant du fer.

12. Diffuseur microporeux (50, 70) selon la revendication 11, dans lequel le fer est sous forme de silicates de fer.

13. Diffuseur microporeux (50, 70) selon l’une quelconque des revendications précédentes, dans lequel les premier et deuxième éléments allongés (56,76;60,78) sont composés de particules plastiques microscopiques fusionnées par voie thermique.

14. Diffuseur microporeux (50, 70) selon la revendication 13, dans lequel les premier et deuxième éléments allongés (56,76;60,78) sont composés en outre d’un support cylindrique ayant une pluralité d’ouvertures auxquelles adhèrent les particules plastiques microscopiques fusionnées par voie thermique.

15. Diffuseur microporeux (50, 70) selon la revendication 14, dans lequel le support est fait de plastique ou de métal.

16. Diffuseur microporeux (50, 70) selon l’une quelconque des revendications 13 à 15, dans lequel les particules plastiques microscopiques fusionnées par voie thermique sont constituées d’un plastique choisi dans le groupe constitué du poly(chlorure de vinyle), du polypropylène, du polyéthylène, du polytétrafluoroéthylène, du polyéthylène haute densité (HDPE) et de l’ABS.

17. Diffuseur microporeux (50, 70) selon l’une quelconque des revendications précédentes, dans lequel les orifices microscopiques ont un diamètre allant de 1 à 200 micromètres.

18. Procédé d’assainissement des eaux, comprenant :

   le traitement d’une eau contaminée en introduisant des bulles microfines contenant un gaz oxydant dans l’eau,
   les bulles microfines ayant un revêtement de peroxyde d’hydrogène sur les bulles microfines qui renferment le gaz oxydant.

19. Procédé selon la revendication 18, dans lequel les bulles microfines sont introduites au moyen d’un diffuseur microporeux (50, 70).

20. Procédé selon la revendication 19, dans lequel le traitement est catalysé par un agent catalytique contenu dans le diffuseur microporeux (50, 70).


22. Procédé selon l’une quelconque des revendications 19 à 21, dans lequel le diffuseur microporeux (50, 70) a une couche absorbante sur une surface du diffuseur pour éliminer les composés carbonés organiques volatiles dissous par absorption sur la surface.

23. Procédé selon l’une quelconque des revendications 19 à 22, dans lequel les bulles microfines sont produites au moyen de matières microporeuses contenues dans le diffuseur microporeux (50, 70), les matières ayant un diamètre de pores allant de 1 à 200 micromètres.

24. Procédé selon la revendication 23, dans lequel les matières microporeuses ont un diamètre de pores allant de 1 micromètre à 50 micromètres.
25. Procédé selon la revendication 24, dans lequel les matières microporeuses ont un diamètre de pores allant de 5 micromètres à 20 micromètres.

26. Procédé selon l’une quelconque des revendications 18 à 25, dans lequel les bulles microfines ayant un revêtement de peroxyde d’hydrogène comprennent également une couche d’eau prévue pour renfermer le gaz oxydant.

27. Procédé selon la revendication 18 ou la revendication 26, dans lequel le gaz oxydant est l’ozone.


29. Procédé selon la revendication 18, dans lequel le traitement comprend :

l’introduction d’un courant air-ozone à travers un diffuseur microporeux (30;70) qui est placé dans l’eau contaminée pour produire des bulles microfines d’eau renfermant un mélange air-ozone; et

l’introduction d’un liquide comprenant du peroxyde d’hydrogène à travers le diffuseur microporeux pour revêtir des surfaces des bulles microfines avec une couche du peroxyde d’hydrogène afin de produire les bulles microfines ayant un revêtement de peroxyde d’hydrogène sur les bulles microfines qui renferment le gaz oxydant.

30. Procédé selon la revendication 18 ou la revendication 29, dans lequel les bulles microfines sont produites par diffusion à partir d’une chambre centrale du diffuseur microporeux (50,70) à travers des matières microporeuses.

31. Procédé selon la revendication 30, dans lequel les matières microporeuses ont un diamètre de pores allant de 1 micromètre à 200 micromètres.

32. Procédé selon la revendication 30, dans lequel les bulles microfines diffusent depuis la chambre centrale vers une deuxième chambre, dans laquelle elle sont revêtues avec le peroxyde d’hydrogène pour fournir le revêtement de peroxyde d’hydrogène, et traversent des deuxièmes matières microporeuses pour produire des bulles microfines ayant un revêtement de peroxyde d’hydrogène sur les bulles microfines qui renferment le gaz oxydant.

Patentansprüche

1. Mikroporöser Diffuser (50,70), mit:

   einem ersten länglichen Element (96,76), das mindestens eine Seitenwand (56a,76a) mit mehreren mikroskopischen Öffnungen aufweist, wobei die Seitenwand einen inneren hohlen Abschnitt des Elements festlegt,

   einem zweiten länglichen Element (60,78) mit einer zweiten Seitenwand (60a,78a) mit mehreren mikroskopischen Öffnungen, wobei das zweite Element durch den hohlen Bereich des ersten Elements hindurch angeordnet ist,

   einer Endabdeckung (54,74) zum Abdichten eines ersten Endes des mikroporösen Diffusers, und
einer Einlassabdeckung (52,72), die an einem zweiten Ende des mikroporösen Diffusers angeordnet ist, wobei die Einlassabdeckung ein Paar Öffnungen (52a,52b,72a,72b) zum Überführen eines ersten Fluids zu den inneren Abschnitten des ersten Elements und eines zweiten Fluids zu den inneren Abschnitten des zweiten Elements aufweist.

2. Mikroporöser Diffuser (50,70) nach Anspruch 1, ferner mit:

   ersten und zweiten Fittings, die mit dem Paar Öffnungen (52a,52b,72a,72b) in der Einlassabdeckung (52,72) gekoppelt sind, und

   wobei ein zwischen den ersten und zweiten länglichen Elementen (56,76;60,78) des mikroporösen Diffusers festgelegter Bereich mit einem Katalysator-suspensionsmaterial gefüllt ist, und die ersten und zweiten Fittings mit den ersten und zweiten länglichen Elementen gekoppelt sind, um eine Überführung der Fluide zu ermöglichen.

3. Mikroporöser Diffuser (50,70) nach Anspruch 1, wobei die ersten und zweiten länglichen Elemente (56,76;60,78) Zylinder sind und das zweite längliche Element (60,78) konzentrisch zu dem ersten länglichen Element (56,76) angeordnet ist.
4. Mikroporöser Diffuser (50,70) nach Anspruch 3, wobei ein zwischen den ersten und zweiten länglichen Elementen (56,76;60,78) des mikroporösen Diffusers festgelegter Bereich mit einem Katalysator-Suspensionsmaterial gefüllt ist, und wobei die Einlassabdeckung (54,74) ein mit dem zweiten länglichen Element gekoppeltes Fitting hat, um die Überführung einer Flüssigkeit durch das zweite Element zu ermöglichen.

5. Mikroporöser Diffuser (50,70) nach Anspruch 1, wobei die Endabdeckung (54,74) erste Enden der ersten und zweiten länglichen Elemente (56,76;60,78) abdichtet.

6. Mikroporöser Diffuser (50) nach Anspruch 1, wobei das zweite lange Element (60) eines von mehreren zweiten länglichen Elementen (58) ist, die durch das erste lange Element (56) hindurch angeordnet sind, und wobei die Einlassabdeckung (54) mehrere Fittings aufweist, von denen jedes mit einem entsprechenden der mehreren zweiten länglichen Elemente gekoppelt ist, um das Überführen einer Flüssigkeit durch die zweiten Elemente zu ermöglichen.

7. Mikroporöser Diffuser (50) nach Anspruch 6, wobei die mehreren zweiten länglichen Elemente (58) über einen wesentlichen Teil einer Länge des ersten länglichen Elements (56) angeordnet sind.

8. Mikroporöser Diffuser (50) nach Anspruch 7, ferner mit:

   mehreren Abdeckungen (57), um Enden der zweiten länglichen Elemente (58), die in dem hohlen Abschnitt des sten länglichen Elements angeordnet sind, abzuschließen.

9. Mikroporöser Diffuser (50) nach Anspruch 6, wobei ein zwischen den ersten und zweiten länglichen Elementen (56,76;60,78) des mikroporösen Diffusers festgelegter Bereich mit einem Katalysator-Suspensionsmaterial gefüllt ist.

10. Mikroporöser Diffuser (50,70) nach Anspruch 2 oder Anspruch 4 oder Anspruch 9, wobei das Katalysator-Suspensionsmaterial Glaskügelchen oder Silikapartikel ist.


12. Mikroporöser Diffuser (50,70) nach Anspruch 11, wobei das Eisen die Form von Eisensilikaten hat.

13. Mikroporöser Diffuser (50,70) nach einem der vorangehenden Ansprüche, wobei die ersten und zweiten länglichen Elemente (56,76;60,78) aus durch Hitze ge- bzw. verschmolzenen mikroskopischen Kunststoffteilchen bestehen.

14. Mikroporöser Diffuser (50,70) nach Anspruch 13, wobei die ersten und zweiten länglichen Elemente (56,76;60,78) ferner aus einer zylindrischen Halterung mit mehreren Öffnungen bestehen, an denen die bei Hitze ge- bzw. verschmolzenen mikroskopischen Kunststoffteilchen anhaften.

15. Mikroporöser Diffuser (50,70) nach Anspruch 14, wobei die Halterung aus einem Kunststoff oder einem Metall hergestellt ist.


17. Mikroporöser Diffuser (50,70) nach einem der vorangehenden Ansprüche, wobei die mikroskopischen Öffnungen einen Durchmesser im Bereich von 1 bis 200 µm (Mikron) aufweisen.

18. Verfahren zur Wasserwiederaufbereitung, umfassend:

   Behandeln von verunreinigtem Wasser durch Einleiten mikrofeiner Bläschen mit einem Oxidationsgas in das Wasser, wobei die mikrofeinen Bläschen eine Beschichtung von Wasserstoffperoxid über den mikrofeinen Bläschen, die das Oxidationsgas enthalten, aufweisen.

19. Verfahren nach Anspruch 18, wobei die mikrofeinen Bläschen mittels eines mikroporösen Diffusers (50,70) einge-
leitet werden.

20. Verfahren nach Anspruch 19, wobei die Behandlung durch ein Katalysiermittel in dem mikroporösen Diffuser (50,70) katalysiert wird.

21. Verfahren nach Anspruch 20, wobei die Behandlung durch ein Katalysiermittel katalysiert wird, das eines aus den folgenden umfasst:

   Eisen enthaltende Verbindungen, Palladium enthaltende Verbindungen sowie Platin.

22. Verfahren nach einem der Ansprüche 19 bis 21, wobei der mikroporöse Diffuser (50,70) eine Absorptionsschicht über einer Oberfläche des Diffusers aufweist, um aufgelöste flüchtige organische Kohlenstoffverbindungen durch Absorption an der Oberfläche zu entfernen.

23. Verfahren nach einem der Ansprüche 19 bis 22, wobei die mikrofeinen Bläschen mittels mikroporöser Materialien in dem mikroporösen Diffuser (50,70) erzeugt werden, wobei die Materialien einen Porendurchmesser im Bereich von 1 bis 200 μm (Mikron) aufweisen.

24. Verfahren nach Anspruch 23, wobei die mikroporösen Materialien einen Porendurchmesser im Bereich von 1 bis 50 μm (Mikron) aufweisen.

25. Verfahren nach Anspruch 24, wobei die mikroporösen Materialien einen Porendurchmesser im Bereich von 5 bis 20 μm (Mikron) aufweisen.

26. Verfahren nach einem der Ansprüche 18 bis 25, wobei die mikrofeinen Bläschen, die eine Beschichtung von Wasserstoffperoxid haben, auch eine Wasserschicht aufweisen, die zum Umschließen des Oxidationsgases angeordnet ist.

27. Verfahren nach Anspruch 18 oder Anspruch 26, wobei das Oxidationsgas Ozon ist.


29. Verfahren nach Anspruch 18, wobei die Behandlung umfasst:


30. Verfahren nach Anspruch 18 oder Anspruch 29, wobei die mikrofeinen Bläschen durch Diffusion von einer zentralen Kammer des mikroporösen Diffusers (50,70) durch mikroporöse Materialien erzeugt werden.

31. Verfahren nach Anspruch 30, wobei die mikroporösen Materialien einen Porendurchmesser im Bereich von 1 μm (Mikron) bis 200 μm (Mikron) aufweisen.

32. Verfahren nach Anspruch 30, wobei die mikrofeinen Bläschen von der zentralen Kammer zu einer zweiten Kammer diffundieren, in der sie mit dem Wasserstoffperoxid beschichtet werden, um die Beschichtung mit Wasserstoffperoxid zu erzeugen, und durch zweite mikroporöse Materialien passieren, um mikrofeine Bläschen mit einer Beschichtung von Wasserstoffperoxid über den mikrofeinen Bläschen, welche das Oxidationsgas einschließt, zu erzeugen.
FIG. 9