Notice

DESCRIPTION CN101326126A

10 Photocatalytic reaction water generating device

[0001]

14 Technical field

[0002]

18 The present invention relates to a photocatalytic reaction water generating device. The photocatalytic reaction water generating device uses a photocatalytic reaction to effectively generate a large amount of active oxygen species in water, thereby being able to remove microorganisms that have come into contact with water containing the active oxygen species. , Parasites and protozoa are sterilized, dewormed, and repelled.

[0003]

25 Background technique

[0004]

29 In the past, water with the ability to sterilize and oxidize substances was used in places where sanitation was important, such as medical sites, food factories, public baths, and swimming pools.

[0005]

34 For example, as such water, ozone water in which ozone (O3) is dissolved in water and water treated with an ultraviolet germicidal lamp are generally widely used.

[0006]

39 However, it has been pointed out that a large amount of ozone leaks from the ozone generator that produces ozone water into the atmosphere, which will cause adverse effects on the environment. In addition, there are problems such as the diffusion of odor peculiar to ozone and the consumption of large amounts of electricity when ozone is generated. In recent years, there has been a tendency to control the use.

[0007]

46 On the other hand, it is known that the photocatalyst body is irradiated with light to excite the active oxygen species generated by the photocatalytic reaction, and the surface of the photocatalyst body has microbial sterilization and the oxidative decomposition of various organic chemical substances at the very close (usually 40nm) surface of the photocatalyst body. ability.

50 That is, it is only present in the very close vicinity of the photocatalyst body. These highly reactive active oxygen species such as superoxide anion radicals (O2-) and hydroxyl radicals (OH •) come into contact with water and dissolve in water, which can make microorganisms, Virus cell membranes, functional proteins, genes, etc. mutate, which can stop the survival and proliferation functions of microorganisms and viruses.

[0008]

57 Therefore, in order to sterilize microorganisms present in water, for example, as shown in FIGS. 17 and 18, it is proposed to provide a stirring shaft 54 in the central part of a cylindrical tank 53 having a water inflow port 51 and a discharge port 52, and in On the same stirring shaft 54, the stirring blade 56 with the net-shaped photocatalyst body 55 is arranged radially outward, and the black light lamp 57 for ultraviolet irradiation is arranged on the predetermined part of the inner wall of the tank, and the stirring shaft 54 is rotated to make the irradiation A water treatment device in which the amount of ultraviolet rays on the photocatalyst body 55 is increased (for example, refer to Patent Document 1).

[0009]

67 If this water treatment device is used, the efficiency of irradiating ultraviolet rays to the photocatalyst body 55 can be improved. In addition, since the water can be stirred by the stirring blade 56, microorganisms can be brought into contact with the active oxygen species generated on the surface of the photocatalyst material to sterilize the water. Organic matter can be decomposed.

[0010]

74 In addition, in the past, as one of the fields requiring microbial sterilization, there has been fish breeding.

[0011]

78 Generally speaking, fish farming involves setting up fishing nets in the sea to form a net cage. In this net cage, red yellowtail, perch, tiger fish and other fish are given bait to grow and grow food fish.

[0012]

83 Compared with catching fish that roam naturally in the ocean, this kind of fish farming can effectively obtain the target fish species in a planned way, and contribute to the stable supply of consumers.

[0013]

88 In addition, in recent years, the number of fish species that can be cultured has increased, and the quality is not inferior to that of natural fish. Therefore, the breeding industry is expected to develop more and more in the future.

[0014]

94 However, because fish culture is to grow fish in relatively narrow cages, there is a concern that diseased fish caused by microorganisms and parasites will infect other fish in the cages, and the chained increase of sick and dead fishes.

[0015]

100 Especially in fish farming, where efficiency and planning are one of its strengths, it is believed that the large increase in diseased and dead fish caused by parasites will cause major losses to the farmers, and in turn, bring confusion to market supply.

[0016]

106 The fish parasites that cause such fish diseases can generally be classified into external parasites represented by Benedenia and Heterodacty, intraluminal parasites such as Anisakis, and Myxosporidium and Angioflus Two types of internal parasites such as internal parasites are represented by tissues.

[0017]

112 These parasites are further differentiated and classified according to fish species, and various studies have been conducted on their host specificity.

[0018]

117 Generally speaking, the impact of parasites on the host is mainly caused by damage to the maintenance and management of body fluids caused by respiratory damage and osmotic pressure damage.

[0019]

122 Internal parasites such as Angioflus, not so much that the worm body causes problems, are more that the worm body lays eggs. When the worm eggs are discharged in large quantities, the worm eggs block the tiny blood vessels of the gills, and the fish suffers from suffocation problems.

[0020]

128 In addition, ectoparasites that parasitize fish are parasites that suck the blood of the host from their parasitic sites to obtain nutrients, and cause damage to the epithelial cells of the epithelium to which they are attached, thereby causing damage to the parasitic fish.

131 Especially when gills are infected, hypertrophic, stick-like changes caused by the peeling and inflammation of the gill respiratory epithelial cells are produced, which become irreversible changes, and thus the vegetative growth damage caused by respiratory injury occurs.

[0021]

137 In particular, it is very worried that most of the ectoparasites are parasitic on the parts of the fish that are in contact with the sea water, causing the worm bodies and eggs to float in the sea water and infect other fish bodies, which is one of the parasites that cause heavy losses to the aquaculture industry.

[0022]

143 Therefore, as prevention and treatment methods for diseases caused by external parasite infections, the following methods are known: Regarding Benedenia, in the case of marine fish, freshwater bathing has a significant effect; Regarding Heteroparasites, in cages A porous carrier impregnated with hydrogen peroxide water is dispersed inside, and parasites and microorganisms are weakened by the hydrogen peroxide effect, thereby preventing or treating parasite parasites and microbial infections (for example, refer to Patent Document 2).

[0023]

152 According to this method of using hydrogen peroxide water, the fear of death of cultured fish due to parasites and microorganisms can be alleviated.

[0024]

157 However, there is such a problem. In order to improve the efficiency of the photocatalytic reaction, a large-sized stirring blade is required in the water treatment device provided with the stirring blade. In order to generate a sufficient amount of water containing active oxygen, the device itself is enlarged.

160 In addition, since the oxidation ability is continued for an extremely short time of 10-6 seconds, the reaction situation is limited to the very close position of the photocatalyst body, and this effect can only be obtained in a very narrow area.

[0025]

166 In addition, although it is possible to reduce the size of the photocatalyst body to reduce the size of the device, the current situation is that it cannot be practical unless the inefficiency of the photocatalytic reaction is solved first.

[0026]

172 Moreover, driving the stirring shaft in a large-scale device requires a large amount of electricity only to resist the resistance of water. Therefore, it is not ideal in terms of energy efficiency.

[0027]

177 In addition, the photocatalyst body equipped with stirring blades exemplifies the photocatalyst body coated with titanium dioxide on the surface of the fibrous aluminum. However, simply applying the titanium dioxide coating on the surface of the fibrous aluminum makes the photocatalytic reaction inefficient and difficult to effectively produce Active oxygen water.

[0028]

184 In addition, in the method of treating farmed fish with the above-mentioned hydrogen peroxide water (generally called hydrogen peroxide bath), its strong hydrogen peroxide oxidation ability also affects the farmed fish itself.

187 In other words, it is not so much that the symptoms are eliminated by reducing the parasites in the cultured fish, but rather the fish that become vulnerable due to the disease and the parasites are eliminated together, and only the strong fish survive.

[0029]

193 In this way, the fragile fish that are killed by the dispersion of hydrogen peroxide water reduce the harvest of farmed fish, resulting in a decline in breeding efficiency. Obviously, if the parasite-infected fish can repel the parasites more safely, it will increase. The catch can not only reduce the circulation price, but also ensure food safety.

[0030]

200 In addition, the effective concentration of the dispersed hydrogen peroxide in the seawater needs to be a high concentration of 200-3000ppm. Although it can be diluted, it flows out, diffuses, and discards directly in the ocean like the conventional medicated bath methods such as formaldehyde bath.

203 In this way, the impact on other marine organisms other than aquaculture is not ideal in terms of environmental impact, and the impact on humans has not yet been determined.

[0031]

208 Moreover, in order to produce the insect repellent effect, a large amount of hydrogen peroxide preparations are required, and these required costs and labor for transportation impose a great burden on the operators.

[0032]

213 In the aquaculture industry with such problems, it is desired that a photocatalytic reaction water generating device and insecticidal method for repelling insects are not used, such as drugs remaining in the ocean, do not damage the cultivated fish bodies, and do not affect the environment.

[0033]

219 Therefore, the inventors of the present invention can produce water that fully contains active oxygen species, and can perform microbial sterilization and parasite deworming, and make its strong oxidation ability continuous, power saving, and compact, which can be applied to various machines. The research on the photocatalytic reaction water generating device in the present invention has been completed.

[0034]

226 Patent Document 1: Japanese Patent Application Publication No. 2001-327961

[0035]

230 Patent Document 2: Japanese Patent Laid-Open No. 03-200705

[0036]

234 Summary of the invention

[0037]

238 In order to solve the above-mentioned problems, in the photocatalytic reaction water generator according to the present invention, the active oxygen species generated by irradiating the photocatalyst body with light from the light source are diffused in water to give the water the function of the active oxygen species, and the The microorganisms of the oxidation reaction caused by the water are subjected to at least any one of sterilization, parasite repelling, and protozoan repelling.

[0038]

246 Furthermore, it is also characterized by the following aspects:

[0039]

(1) The aforementioned photocatalyst body is arranged around a light source for exciting the photocatalyst body.

[0040]

(2) The photocatalytic reaction water generator includes a photocatalytic reaction tank, a feed pump for supplying water to the photocatalytic reaction tank, and a discharge circuit for discharging the photocatalytic reaction water from the photocatalytic reaction tank, and the photocatalytic reaction tank is capable of The airtight container for storing water is equipped with a photocatalyst body for generating active oxygen in the water in the airtight container, a light source for radiating light for exciting the photocatalyst body, and a light source for generating on the surface of the photocatalyst body. The active oxygen species are configured by diffusion means for diffusing the active oxygen species in water, and the airtight container has an inner wall surface that is a mirror surface that reflects the light.

[0041]

(3) The light source for exciting the above-mentioned photocatalyst body utilizes sunlight and/or artificial light.

[0042]

(4) When sunlight is used as a light source for exciting the above-mentioned photocatalyst body, the photocatalyst body is directly irradiated in water by a reflector such as an optical fiber and a prism.

[0043]

(5) When using artificial light as a light source for exciting the photocatalyst body, an ultraviolet irradiation lamp irradiates at least 350-370 nm wavelength ultraviolet rays.

[0044]

(6) The photocatalyst body is an organic or inorganic filter body, and the surface of the photocatalyst body is covered with a titanium dioxide film.

[0045]

(7) The photocatalyst body is an aluminum-based metal filter body, the surface of which is covered with a titanium dioxide film.

[0046]

291 (8) The photocatalyst body is a metal fibrous body with an alumina coating film formed on the surface in advance, and the surface is covered with a titanium dioxide thin film.

[0047]

296 (9) The aluminum oxide film of the metal fibrous body is heated to a temperature of half the melting point of the aluminum-based metal constituting the metal fibrous body at a rate of 5° C./min or less, and then heated until it reaches the melting point of the aluminum-based metal.

[0048]

302 (10) The photocatalyst body is a fiber body made of glass, a fiber body made of ceramics, or a non-woven fabric, and the surface of the photocatalyst body is covered with a titanium dioxide film.

[0049]

307 (11) The titanium oxide constituting the above-mentioned titanium dioxide thin film includes an anatase-type or rutile-type crystal structure.

[0050]

312 (12) The diffusion means for diffusing the above-mentioned active oxygen species in water are ultrasonic waves of 100 kHz or more caused by an ultrasonic vibrator and/or water flow caused by blades in the water, which move the photocatalyst body and/or water.

[0051]

318 (13) The water contacting the photocatalyst body is water whose oxygen concentration has been increased.

[0052]

322 (14) The above-mentioned water with increased oxygen concentration is produced by contacting at least any one of oxygen, air, and ozone with water.

[0053]

327 (15) At the upstream or downstream of the sterilization effect caused by the photocatalytic reaction, or at the same position, the sterilization effect caused by the ultraviolet germicidal lamp with a wavelength of 254 to 265 nm is irradiated.

[0054]

333 Description of the drawings

[0055]

337 Fig. 1 is an external view showing a photocatalytic reaction water generator according to the present invention.

[0056]

341 Fig. 2 is an external view showing the photocatalytic reaction water generator according to the present invention.

[0057]

346 Fig. 3 is an explanatory diagram showing the inside of the photocatalytic reaction water generator according to the present invention.

[0058]

351 Fig. 4 is a cross-sectional view of the photocatalytic reaction water generator according to the present invention.

[0059]

356 Fig. 5 is an explanatory diagram showing the photocatalytic reaction water generator for sterilization according to the present embodiment.

[0060]

361 Fig. 6 is an explanatory diagram showing microorganisms that form colonies on an agar medium.

[0061]

365 Fig. 7 is an explanatory diagram showing microorganisms that form colonies on an agar medium.

[0062]

369 FIG. 8 is an explanatory diagram showing the photocatalytic reaction water generator for repelling insects according to the present embodiment.

[0063]

374 Fig. 9 is an explanatory diagram showing the photocatalytic reaction water generator for repelling insects according to the present embodiment.

[0064]

379 Fig. 10 is an explanatory diagram showing the photocatalytic reaction water generator for repelling insects according to the present embodiment.

[0065]

384 FIG. 11 is an explanatory diagram showing the photocatalytic reaction water generator for repelling insects according to the present embodiment.

[0066]

389 FIG. 12 is an explanatory diagram showing the photocatalytic reaction water generator for repelling insects according to the present embodiment.

[0067]

394 FIG. 13 is an explanatory diagram showing the photocatalytic reaction water generator for repelling insects according to the present embodiment.

[0068]

399 FIG. 14 is an explanatory diagram showing the photocatalytic reaction water generator for repelling insects according to the present embodiment.

[0069]

404 FIG. 15 is an explanatory diagram showing the photocatalytic reaction water generator according to this embodiment.

[0070]

409 FIG. 16 is an explanatory diagram showing the photocatalytic reaction water generator according to this embodiment.

[0071]

414 Fig. 17 is an explanatory diagram showing the prior art.

[0072]

418 Fig. 18 is an explanatory diagram showing the prior art.

[0073]

422 detailed description

[0074]

426 The photocatalytic reaction water generator according to the present invention diffuses in water the active oxygen species generated by irradiating the photocatalyst body with light from the light source, and imparts the function of the active oxygen species to the water. The oxidation reaction caused by the water can be used Perform at least any one of microbial sterilization, parasite repelling parasites in marine organisms, and protozoan repelling.

[0075]

434 That is, the photocatalytic reaction water generator according to the present invention is a photocatalytic reaction water generator that diffuses active oxygen species generated on the surface of a photocatalyst body in water, and uses water as a medium to sterilize, sterilize, and remove protozoa. .

[0076]

440 In addition, at the same time, it is a photocatalytic reaction water generating device that diffuses the active oxygen species generated on the surface of the photocatalyst body in water, and uses water as a medium to repel parasites parasitic on the fish body.

[0077]

446 Since a titanium dioxide thin film with photocatalytic ability is formed on the surface of the photocatalyst body, by irradiating the titanium dioxide thin film with ultraviolet rays radiated from an ultraviolet lamp, the titanium dioxide thin film is excited and the photocatalyst body is activated.

[0078]

452 On the surface of the activated photocatalyst body, ultraviolet energy (hv) emitted from the ultraviolet lamp excites titanium oxide ($TiO2$) constituting the titanium dioxide thin film, and the water filled with the photocatalytic reaction water generator contacts the photocatalyst body, thereby generating active oxygen species. The reaction in which water contacts the excited photocatalyst body to generate active oxygen species is called a primary reaction.

[0079]

460 It is considered that a reaction proceeds as follows:

[0080]

464 $TiO_2 + hv \rightarrow e^- + h+VB$

[0081]

468 $H+VB \rightarrow h+tr$

[0082]

472 $O_2 + e^- \rightarrow O_2 \bullet -$

[0083]

476 $O_2 \bullet - + h+VB(h+tr) \rightarrow O_2$

[0084]

480 $OH^- + h+VB \rightarrow HO \bullet$

[0085]

484 Next, since the active oxygen species produced in the primary reaction have high reactivity, the active oxygen species react with substances and ions dissolved in water to further produce products.

486 Here, the reaction between the active oxygen species generated in the primary reaction and the substances and ions dissolved in water is called the secondary reaction.

[0086]

491 Then, in the secondary reaction, for example, it is thought that the following reaction occurs:

[0087]

495 $O_2^- + O_2^- + 2H^+ \rightarrow H_2O_2 + O_2$ (generate hydrogen peroxide water)

[0088]

499 Except for ultrapure water that does not contain other ions, water that exists in a normal environment is

considered to be water that contains trace element ions.
501 Especially the tap water is sterilized with chlorine, so it is thought that the following secondary reactions occur:

[0089]
505 $HCl+O_2\bullet^-+OH^-\rightarrow ClO_2+H_2O$ (to generate chlorous acid)

[0090]
509 $ClO_2+2OH^-\rightarrow HOCl+H_2O$ (generate hypochlorous acid)

[0091]
513 In addition, the environment where organisms such as rivers and seawater exist contains ammonia. Similarly, the following secondary reactions are thought to occur:

[0092]
518 $NH_3+OH^-\rightarrow NO^-+2H_2O$ (generate nitrogen oxide ions)

[0093]
522 In addition to the above reactions, of course, there are more secondary reactions. The secondary reactants produced in this way are the same as the primary reaction products (active oxygen species), which produce the photocatalytic reaction water sterilization effect and insect repellent effect. .

[0094]
528 In particular, when the contacted water is seawater or an aqueous solution in which a predetermined substance is dissolved, these secondary reactants can be generated in various types.

[0095]
533 However, in the conventional methods, the diffusion of the active oxygen species generated by the photocatalyst body cannot proceed sufficiently. Therefore, the active oxygen species generated on the surface of the photocatalyst body can act directly without passing through the medium, and it can only show that the active oxygen species will adhere to the surface of the photocatalyst body. The effect of sterilizing microorganisms on the surface of the photocatalyst body or not attaching parasites on the surface of the excited photocatalyst body.
539 The present invention can enjoy the sterilization, sterilization, insect repellent and repellent effects caused by active oxygen species even when away from the photocatalyst body.
541 Hereinafter, the water that functions as a medium as described above and contains active oxygen species is

referred to as photocatalytic reaction water.

[0096]

546 In addition, the concept of light here is not limited to visible light, but also includes ultraviolet rays with a shorter wavelength.

[0097]

551 In addition, the light source for exciting the photocatalyst body can utilize sunlight and/or artificial light.
552 For example, when sunlight is used, the cost for exciting the photocatalyst body can be reduced, and the photocatalyst body can be irradiated with ultraviolet energy stronger than that obtained from artificial light.
554 In addition, when light is irradiated to the photocatalyst body arranged in water, a reflector such as an optical fiber or a prism may be used to transmit sunlight or artificial light in the water and directly irradiate the photocatalyst body in the water.

[0098]

560 The photocatalyst body can be made of titanium oxide (titanium dioxide) having a rutile or anatase crystal phase.

[0099]

565 The photocatalyst body using this titanium oxide can also be made into a high-efficiency photocatalyst body with an enlarged surface area by applying a dip coating with titanium dioxide on a fibrous carrier.

[0100]

570 Here, the fibrous carrier can suitably use, for example, a metal containing aluminum (hereinafter also referred to as aluminum-based metal) such as the 1000-7000 number, and the aluminum-based metal is formed by heating the aluminum-based metal to form an alumina metal fibrous body, and titanium dioxide is coated It is densely coated on the carrier, and therefore, durability can be further improved.

[0101]

577 The alumina metal fiber body can heat the aluminum-containing metal forming the carrier to a predetermined temperature at a ratio of 5° C./min or less, and thereafter, heat it until it reaches the melting point of the metal fiber body.

[0102]

583 Here, the above-mentioned predetermined temperature can be calculated by the following calculation

formula.

[0103]

588 Specified temperature (℃) = melting point temperature of aluminum-containing metal (℃) ÷ 2

[0104]

592 In more detail, a metal fibrous body covered with alumina on the surface is used as a carrier, and if the dipping process is performed to form a titanium dioxide thin film, the titanium dioxide can be densely formed on the aluminum oxide film and can be uniformly formed Titanium dioxide film.
595 If the uniform titanium dioxide film is excited by ultraviolet light, the photocatalytic reaction can be carried out more effectively, and therefore, more active oxygen species can be generated.

[0105]

600 Here, the aluminum oxide film of the metal fibrous body is slowly heated to about half of the melting point of the aluminum metal fiber at a ratio of 5° C/min or less to oxidize the surface, and then heated until it reaches the melting point. The deep oxidation forms an artificial oxide film that fully functions as an alumina fiber.
603 In addition, the term "aluminum-based metal" means both aluminum and aluminum alloy.

[0106]

607 That is, the metal fibrous body is protected by an oxide film formed by heating the metal fibrous body to a temperature about half of the melting point of the aluminum-based metal, and the metal fibrous body is heated to the melting point to form a homogeneous aluminum oxide film.
610 It can also be heated above the melting point of the aluminum-based metal constituting the metal fibrous body, whereby the metal fibrous body forms an extremely stable oxide film.
612 Therefore, when the titanium dioxide thin film is formed on the metal fibrous body, the adhesion between the titanium dioxide thin film and the metal fibrous body can be improved.

[0107]

617 In addition, it is heated to about half of the melting point of aluminum metal to form an oxide film. The oxide film protects the metal fibrous body while heating to reach the melting point. After that, the metal fibrous body is fired beyond the melting point even if the temperature rises. The fiber shape can be maintained even near the melting point of alumina, and its ability as a fiber exhibits its function as an alumina fiber.
621 In order to form rutile-type fibers that produce rutile-type photocatalytic reactions in the photocatalyst body, the fibers need to be fired at 750° C higher than the melting point of aluminum-based metals in the dip coating process to form the homogeneous alumina film. The extremely stable aluminum oxide metal fibrous body can produce rutile-type titanium dioxide fibers with high adhesion to the titanium dioxide film while maintaining the fiber shape.

[0108]

629 In this way, by increasing the adhesion between the titanium dioxide film and the metal fibrous body, even in an ultrasonic environment, the titanium dioxide film does not peel off from the metal fibrous body, and a photocatalyst body with sufficient durability can be obtained.

[0109]

635 In this way, by heating the fibrous body formed of aluminum-containing metal to form an alumina metal fibrous body, an alumina metal fibrous body with a dense alumina coating can be made, and therefore, the durability and catalyst efficiency of the photocatalyst body can be further improved.

[0110]

641 Here, as a means for diffusing active oxygen species in water, for example, ultrasonic waves can be used.

[0111]

645 The effect of the ultrasonic vibrator used here is to make the injected air and oxygen and the water in the reflux turbid, increase the concentration of dissolved oxygen, and produce finer bubbles. On this basis, contact with the surface of the photocatalyst fiber can not only improve The generation of active oxygen species generated by the photocatalytic reaction is smoothly performed, and the electrons generated by the photocatalytic reaction caused on the photocatalyst fiber body can be easily moved away.

[0112]

653 In addition, the active oxygen species generated on the photocatalyst fiber by the electrons can be released in water because the flow velocity of the water flowing through the fiber surface is greatly increased by the high-speed movement of the fiber due to ultrasonic vibration.

656 That is, it is presumed that these ultrasonic waves promote the release of active oxygen species from the photocatalyst body, and at the same time, can enhance the reaction by mutual interference of the ultrasonic waves and ultraviolet wavelengths.

[0113]

662 In addition, an ultrasonic vibrator for atomization that generates high-frequency ultrasonic waves (generally 500 kHz or more) is used here.

664 The high-frequency ultrasonic vibration generated by the ultrasonic vibrator for atomization has a low fiber cleaning ability, but has sufficient power to shake electrons and active oxygen species generated in the photocatalytic reaction into the water.

[0114]

670 In addition, the ultrasonic waves used can also be intermediate frequency ultrasonic waves (100 to 500 kHz).

671 Use intermediate frequency ultrasound.

672 When the ultrasonic wave hits the fibrous photocatalyst body, the diffractive properties of the acoustic wave are improved, the water agitation in the airtight container can be further enhanced, and the active oxygen species can be effectively released from the photocatalyst body.

675 Moreover, by the action of the intermediate frequency ultrasound, it is also possible to produce a cleaning effect on substances with relatively large molecular weights such as dirt components attached to the fibers.

677 However, since ultrasonic waves of 100 kHz or less may deform the photocatalyst body and cause peeling damage on the catalytic reaction surface formed by the photocatalyst body, it is preferably not used.

[0115]

682 In addition, the means for diffusing the active oxygen species in water can effectively contain the active oxygen species in the water even if the photocatalyst body is moved mechanically.

[0116]

687 It is presumed that these ultrasonic waves promote the release of active oxygen species from the photocatalyst body 20 and at the same time enhance the reaction due to the mutual interference of ultrasonic waves and ultraviolet wavelengths.

[0117]

693 In the photocatalytic reaction water generator, the ultraviolet rays of 254 to 265 nm wavelength generated by the germicidal lamp can be used in combination in the upstream or downstream or the same position of the part (for example, the vicinity of the photocatalyst body) where the germicidal effect caused by the photocatalytic reaction is generated. Irradiate.

[0118]

700 That is, the water supplied to the photocatalyst body may be treated with a germicidal lamp, the water containing active oxygen obtained from the photocatalyst body may be treated with a germicidal lamp, or the treatment with a germicidal lamp may be performed near the reaction of the photocatalyst body.

[0119]

706 In other words, in the water contacting the photocatalyst body, the photocatalytic reaction water, and the water contacting the photocatalyst, ultraviolet rays with a wavelength of 254 to 265 nm are irradiated to denature the microorganisms in the respective waters of cell membrane proteins, which can improve the effect of the generated photocatalytic reaction water on the microorganisms in the water. The bactericidal

effect of bacteria and the repellent effect on parasites.

[0120]

714 Originally, the denaturation of microbial cell membranes caused by germicidal lamps is caused by mutations in microbial DNA caused by ultraviolet rays. However, due to the interruption of ultraviolet radiation, nucleic acid is repaired and regenerated, resulting in so-called light recovery, which rejuvenates bacteria.

[0121]

720 If the mechanism of action is explained in more detail, it can be seen that mutational damage of DNA particularly occurs in the base sequence of DNA, where thymine is present in two consecutive positions within the same chain.

[0122]

726 That is, the two carbons in the pyrimidine ring constituting thymine and the two carbons in the pyrimidine ring of adjacent thymine are combined separately by ultraviolet energy to form a thymine dimer forming a rectangular cyclobutyl ring. .

[0123]

732 If the thymine dimer is present, the three-dimensional structure of the DNA becomes skewed, and the progress of the replication fork is hindered during replication, and therefore errors are likely to occur in the replication of DNA.

735 In addition, when microorganisms are exposed to ultraviolet rays, such cyclobutyl rings occur in all places on the base sequence of DNA, making it difficult for microorganisms to maintain normal life activities.

737 These reactions are widely known as UV damage to DNA. These reactions are not particularly easily caused in water, but reactions that also occur in the air.

739 In addition, as an impact on the human body, it is a cause of skin cancer, and it also causes opacity of the lens and cornea of the eye.

[0124]

744 However, it is known that the cyclobutyl ring generated on the DNA of microorganisms due to ultraviolet radiation is broken by the energy of visible light by the PR enzyme (photoreactivating enzyme) possessed by the microorganisms, and the DNA is repaired, that is, so-called photorepair occurs.

747 If this photorepair occurs, the thymine dimer that forms the cyclobutyl ring is repaired to the original two thymines, and the microorganisms regenerate, survive, and continue.

[0125]

752 However, by supplying DNA-damaged bacterial cells and weakened microorganisms to the photocatalytic reaction water generator, and contacting with the active oxygen species generated by the photocatalyst body, the bacterial cells are oxidized and decomposed, causing fatal damage to the weakened microorganisms., Which can reliably sterilize the microorganisms in the water.

[0126]

759 Microbial cell membranes damaged by the combined use of germicidal lamps are subjected to oxidative denaturation caused by photocatalytic reaction water, and show strong bactericidal power even against bacteria with strong cell membranes such as entrapment, making nucleic acid damage permanent and unable to restore light. occur.

[0127]

766 In particular, in a state where a photocatalytic reaction water generator is installed in a water tank or the like to constitute a circulation system, more hygienic photocatalytic reaction water can be produced.

[0128]

771 In addition, the water supplied to the photocatalyst body is characterized in that it is produced by contacting at least any one of oxygen, air, and ozone with water.

773 In addition, the use of water in which the oxygen generating agent is brought into contact with water to increase the concentration of generated oxygen can also promote the photocatalytic reaction, so that the active oxygen species can be effectively contained in the water.

[0129]

779 In addition, the photocatalytic reaction water generating device according to the present invention exerts a great effect especially in the fields where microbial sterilization is required, the fields where fish parasite repelling is required, and the fields where protozoa such as amoeba is required to be repelled. .

782 Therefore, in the following, the general distinction is the use of sterilization, sterilization, cleaning, and the use of insect repellent, and the characteristics of each are described.

[0130]

787 First, a description will be given of a photocatalytic reaction water generator (hereinafter also referred to as a photocatalytic reaction water generator for sterilization) constructed for sterilization.

[0131]

792 According to the photocatalytic reaction water generator for sterilization, the microorganisms are brought into contact with the generated photocatalytic reaction water to perform sterilization and sterilization, and the

microorganisms can be effectively sterilized and sterilized.

[0132]

798 This sterilization method is not particularly limited as long as it can bring microorganisms into contact with the photocatalytic reaction water, and the microorganisms and water may be supplied to the photocatalytic reaction water generator together, and the microorganisms may be contacted with active oxygen species inside the device to perform sterilization.

[0133]

805 In addition, the photocatalytic reaction water generator for sterilization has a washing device configured so that the generated water can come into contact with the object to be washed, so that organic matter can be decomposed in addition to the sterilization and sterilization. There is no doubt about microbial fouling. Even visible dirt etc. can fall off.

[0134]

812 The objects to be cleaned here include, for example, dentures, medical equipment, tableware, vegetables, precision equipment, toilets, cloth, rice seeds, etc., but they are not particularly limited to these.

[0135]

817 Next, the photocatalytic reaction water generator for insect repellent (hereinafter also referred to as the photocatalytic reaction water generator for insect repellent) will be described.

[0136]

822 The photocatalytic reaction water generator according to the present invention provides an active oxygen species generated by irradiating light from a light source to a photocatalyst body by diffusion in water, imparting the function of active oxygen species to the water, and being able to utilize the water The anthelmintic repellent caused by the oxidation reaction of fish parasites is a photocatalytic reaction water generator.

[0137]

830 That is, similar to the above-mentioned photocatalytic reaction water generator for sterilization, this is a device that allows the photocatalytic reaction water to contact parasites and deworms the parasites attached to and parasitic on fish.

[0138]

836 Here, the water used in the photocatalytic reaction water generator for repelling insects is not particularly limited, and for example, it can be used regardless of fresh water, sea water, or purified water.

[0139]

841 In the photocatalytic reaction water generator for repelling fish parasites capable of repelling parasites, it is possible to equip a germicidal lamp that can produce a sterilization effect.

[0140]

846 In addition, the photocatalytic reaction water generator for repelling these fish parasites can also be equipped with a tank such as a water tank. In addition, for example, selecting a large water tank as a cage can make the entire net cage capable of repelling fish parasites. Insect repellent uses a photocatalytic reaction water generator.

[0141]

853 That is, according to the former example, for example, by attaching a photocatalytic reaction water generator for repelling parasites to fish parasites in a tank containing water and fish, the water in the tank is supplied to the photocatalytic reaction water for repelling insects. The generating device returns the water containing the active oxygen species to the water tank again, thereby bringing the water containing the active oxygen species into contact with the fish, so that the parasites of the fish can be repelled.

[0142]

861 In addition, according to the latter example, for example, a sheet-shaped photocatalyst body is floated in a net cage set up in the sea, and while the photocatalyst body is excited by sunlight, the photocatalyst body is moved by the force of a wave, as in the seawater. The structure of the active oxygen species generated by the diffusion on the photocatalyst body can repel parasites in the fish body.

[0143]

868 At this time, the shape of the photocatalyst body is not particularly limited, and it may be an endless sheet-like body, which is transferred on the driving roller and the driven roller, so that it can rotate freely and can be easily reversed. constitute.

[0144]

874 Using the photocatalytic reaction water generator for repelling parasites of fish according to the present invention, according to the method of repelling parasites on fish, it is possible to parasitize Benedenia on the skin of fish. (Lepeophtheirus salmonis, Benedenia seriolae, Benedenia skii, Neobenedenia girellae, Entobdella soleae, etc.), Heterraxine Heterocerca, Zeuxobotharium seriolae, Neobenedenia girellae, Entobdella soleae,

etc. Etc.) and other ectoparasites, so as to prevent or treat fish diseases caused by these parasites.

[0145]

882 At this time, by adjusting the water temperature to within ±5° C, preferably within ±3° C of the water temperature of the breeding environment of the target fish, the parasites can be effectively repelled without causing damage to the fish. Temperature causes burden.

[0146]

888 In addition, adjusting the dissolved oxygen concentration in the water to 12 mg/L or less, preferably 10 mg/L or less, not only prevents the depletion of the target fish due to oxygen damage, but also improves the contact efficiency between the photocatalyst body and oxygen , Which can better cause the insect repellent effect.

[0147]

894 Hereinafter, the present invention will be explained in more detail by exemplifying examples.

[0148]

898 Example 1

[0149]

902 First, FIG. 1 shows the photocatalytic reaction water generator 1 according to this embodiment that can be used for both the sterilization photocatalytic reaction water generator and the insect repellent photocatalytic reaction water generator.

905 The water tank 33 contains water 31 in advance, and the water 31 is sent to the photocatalytic reaction water generator 1 through the water supply pipe 3 by driving the water feed pump 32 immersed in the water 31.

[0150]

910 Then, the water 31 treated in the photocatalytic reaction water generator 1 becomes the photocatalytic reaction water rich in active oxygen species, and is configured to flow down from the drain port 11 through the drain pipe 10 and then return to the water tank 33.

[0151]

916 Next, a more detailed structure of the photocatalytic reaction water generator 1 will be described with reference to FIGS. 2 to 4.

[0152]

921 As shown in FIG. 2, the photocatalytic reaction water generator 1 has a closed container 6 composed of a box-shaped container body 7 having an upper opening and a closing lid 8 that seals the upper opening of the container body 7.

[0153]

927 The material constituting the airtight container 6 is not particularly limited, and may be made of metal, resin, plastic, etc. However, materials that are hard to be degraded by ultraviolet radiation and materials that have corrosion resistance that are hard to be corroded by water or seawater are preferable.

930 By forming the container main body 7 and the lid body 8 with such materials, the life of the photocatalytic reaction water generator 1 can be extended.

932 In the figure, a closed container 6 is formed of plastic.

[0154]

936 In addition, on the upper side surface of the container body 7, a drain hose connection portion 40 for taking out the photocatalytic reaction water generated inside the airtight container 6 is provided.

938 On the other hand, the lower side of the container body 7 is provided with a water supply pipe 3 extending outward, and the open end of the water supply pipe 3 serves as a water supply port 2 for supplying water to the inside of the airtight container 6.

941 In addition, in FIG. 1, a water supply pump 32 is connected to the water supply port 2 to send water 31 to the photocatalytic reaction water generator 1.

943 In addition, in this embodiment, the feed water pump 32 is used (e-ROKAPF-380, flow rate 6.2 L/min).

[0155]

947 Then, a hollow oxygen supply pipe 4 through which oxygen-containing gas can flow is connected to a midway portion of the water supply pipe 3, and this connection portion becomes the oxygen supply unit 5.

[0156]

952 Here, as a means of supplying oxygen to the water, the oxygen supply pipe 4 is connected to the water supply pipe 3, whereby the water flow in the water supply pipe effectively diffuses oxygen in the water, as long as the photocatalytic reaction water generator 1 can be supplied The water 31 contains oxygen and is not particularly limited. For example, the oxygen supply pipe 4 may be directly connected to the photocatalytic reaction water generator 1.

[0157]

960 In addition, the gas flowing through the oxygen supply pipe 4 may be air or ozone, or preferably a gas with a higher oxygen concentration.

962 The higher the concentration of oxygen supplied to the water, the more effectively the oxygen can be contained in the water, and the amount of active oxygen species generated from the photocatalyst body can be increased.

[0158]

968 As a method of increasing the dissolved oxygen concentration of the water 31, for example, a foaming agent or the like that foams by reacting with water to generate oxygen in the bubbles can be used.

[0159]

973 On the lower side of the container body 7, as a diffusion means for diffusing the active oxygen species in the water, an ultrasonic oscillator 12 is arranged. The ultrasonic oscillator 12 and an ultrasonic oscillator 22 (2.4MHz atomization device) arranged in the airtight container 6 Vibrator) connection.

976 In addition, an ultrasonic vibrator that generates high-frequency ultrasonic waves (generally above 500 kHz) is used here, but intermediate-frequency ultrasonic waves (100 kHz to 500 kHz) may also be used.

[0160]

981 It is presumed that these ultrasonic waves promote the release of active oxygen species from the photocatalyst body 20 and at the same time enhance the reaction by the mutual interference of ultrasonic waves and ultraviolet wavelengths.

[0161]

987 In addition, in the first embodiment, ultrasonic waves are used as a diffusion means to indirectly vibrate the photocatalyst body 20 through the water 31 to diffuse active oxygen species, but it is not limited to this. For example, the light may be directly moved in the airtight container 6 In addition, the catalyst body 20 may be provided with blades (stirring blades) that agitate the water 31 in the closed container 6 to generate a water flow, etc., to diffuse active oxygen species.

[0162]

995 In the lid body 8, as a light source for irradiating light to the inside of the airtight container 6, an ultraviolet lamp 9 (EFD15BLB produced by Toshiba Labtech Co., Ltd., peak wavelength 352nm, UV output 1.8W) is inserted so as to penetrate the lid body 8. When the lamp 9 is energized, it is possible to irradiate ultraviolet rays to the photocatalyst body 20 provided in the airtight container 6 to be described later.

999 In addition, since the energized part of the ultraviolet lamp 9 is in the air, even if the light emitting part is immersed in water, there is no fear of accidents such as electric leakage.

[0163]

1004 The ultraviolet lamp 9 can be a black light lamp or the like, but it may be an ultraviolet lamp 9 that effectively emits ultraviolet light having a wavelength of 350 to 370 nm, and more preferably an ultraviolet light having a wavelength of 364 nm. It is not particularly limited to a black light lamp, and may be an LED or LED capable of emitting ultraviolet light. Xenon lamps, etc.
1008 In addition, when sunlight is used as a light source, an optical fiber and a prism can also be used to guide the light in water and irradiate the photocatalyst body 20, so that a large amount of ultraviolet rays contained in the sunlight can be irradiated to the photocatalyst body.
1011 In addition, if the photocatalyst body 20 is a rutile (visible light responsive type) photocatalyst body, even ordinary visible light (indoor lighting) can cause a photocatalytic reaction, so it is possible to guide light in water using optical fibers and prisms., Irradiate the photocatalyst body 20.

[0164]

1017 Next, FIG. 3 shows a state where the lid 8 of the airtight container 6 is removed, and the inside is viewed from the upper opening of the container body 7, and FIG. 4 shows a cross section of the photocatalytic reaction water generator 1.

[0165]

1023 At the bottom of the inner surface side of the container body 7, an ultrasonic vibrator 22 connected to the ultrasonic oscillator 12 is arranged so as to be in contact with water, and a cylindrical photocatalyst body 20 is arranged on the upper part of the ultrasonic vibrator 22.
1026 As shown in FIG. 4, the photocatalyst body 20 is arranged so as to surround the light-emitting portion 41 of the ultraviolet lamp 9 when the container body 7 is closed with the lid body 8.
1028 Therefore, the ultraviolet rays radiated from the ultraviolet lamp 9 can be effectively used as energy for exciting the photocatalyst body 20.

[0166]

1033 However, the ultraviolet rays irradiated from the ultraviolet lamp 9 and passed through the photocatalyst body 20 are irradiated on the container body 7 and the lid body 8.

[0167]

1038 Here, the outer peripheral surfaces of the container main body 7 and the lid body 8 are covered with a reflective material 13 that can reflect light such as ultraviolet rays.

[0168]

1043 Therefore, the ultraviolet rays reaching the container body 7 and the lid body 8 are reflected by the reflective material 13 toward the inside of the container body 7 (that is, in the direction of the photocatalyst body 20) to excite the photocatalyst body 20, so that the ultraviolet rays irradiated by the ultraviolet lamp 9 can be used as light. The activation energy of the catalyst body 20 is used without waste.

[0169]

1050 The reflective material 13 is a material that can reflect light, and a material that can reflect ultraviolet rays is particularly preferable. For example, aluminum foil can be used.

[0170]

1055 In addition, in this embodiment, the reflective material 13 is attached to the outer peripheral surface of the container body 7 and the lid 8, but it can also be attached to the inner peripheral surface, and a material with the same function as the reflective material 13 can also be used to form a closed container. Ontology.

1058 Especially when the airtight container 6 is made of plastic or resin, providing the reflective material 13 on the inner wall of the airtight container 6 can reduce the amount of ultraviolet rays received by the airtight container 6, thereby preventing deterioration and denaturation of the plastic or resin caused by ultraviolet rays.

[0171]

1065 In addition, the photocatalyst body 20 uses a material that covers substantially the entire surface of the alumina metal fiber body with a titanium dioxide thin film, and the titanium dioxide thin film can be excited by receiving ultraviolet rays radiated from the ultraviolet lamp 9.

[0172]

1071 In addition, in this Example 1, a metal fibrous body was used as a photocatalyst (titanium dioxide) support, but it is not limited to this. A porous body made of organic and/or inorganic materials can be used. For example, it can also be made of glass The surface of the fibrous body, ceramic fibrous body, and non-woven fabric is formed with a titanium dioxide thin film to form the photocatalyst body 20.

1075 Here, the term "porous body" refers to the concept of a woolen article that also includes a collection of fibrous bodies.

[0173]

1080 Next, the flow of water supplied from the water supply port 2 containing active oxygen species from the drain port 11 to being taken out will be described below.

[0174]

1085 That is, the water 31 supplied from the water supply port 2 flows through the water supply pipe 3 to the oxygen supply unit 5.

1087 The oxygen supply part 5 is connected to the oxygen supply pipe 4 so that the water 31 reaching the oxygen supply part 5 and the oxygen sent in from the oxygen supply pipe 4 are mixed.

[0175]

1092 In this way, the oxygen mixed with the water 31 is dissolved in the water 31 to increase the concentration of dissolved oxygen in the water and become fine bubbles, which are sent into the airtight container 6.

1094 The bubbles that reach the inside of the airtight container 6 are turned into smaller bubbles by ultrasonic vibration, which further increases the dissolved oxygen concentration in the water 31. In addition, the remaining minute bubbles collide and rebound on the photocatalyst body 20, generating high-frequency ultrasonic waves. .

1098 This ultrasonic wave directly and indirectly vibrates the photocatalyst body 20 and contributes to promoting the release of active oxygen species.

[0176]

1103 The water 31 with the increased dissolved oxygen concentration reaches the inside of the airtight container 6 and fills the airtight container 6.

[0177]

1108 On the other hand, ultraviolet light having a wavelength of 350 to 370 nm is emitted from the energized ultraviolet lamp 9, and the emitted ultraviolet light is irradiated on the photocatalyst body 20 surrounding the ultraviolet lamp 9.

[0178]

1114 Since a titanium dioxide thin film with photocatalytic ability is formed on the surface of the photocatalyst body 20, ultraviolet rays radiated from the ultraviolet lamp 9 are irradiated on the titanium dioxide thin film to excite the titanium dioxide thin film, thereby activating the photocatalyst body 20.

[0179]

1120 On the surface of the activated photocatalyst body 20, the ultraviolet energy (hv) emitted from the ultraviolet lamp 9 excites titanium oxide (TiO2) constituting the titanium dioxide thin film. Therefore, the water 31 filled with the airtight container 6 contacts the activated photocatalyst body 20, thereby Produce reactive oxygen species.

[0180]

1127 In addition, in the water 31 filled with the airtight container 6, oxygen is mixed in through the oxygen supply unit 5 and the dissolved oxygen concentration is high. Therefore, the electrons (e-) generated on the photocatalyst body 20 and the amount of electrons (e-) generated in the photocatalyst body 20 can be increased. The contact efficiency of the contained oxygen.

[0181]

1134 Therefore, the water 31 containing a large amount of oxygen contacts the activated photocatalyst body 20, causing a violent photocatalytic reaction, and more active oxygen species are generated on the surface of the photocatalyst body 20.

[0182]

1140 In addition, the fine air bubbles generated when oxygen is mixed in collide with the metal fiber body to burst the bubbles, generate ultrasonic waves, vibrate the metal fiber body, and make the active oxygen species generated on the metal fiber body easy to be released from the metal fiber body.

[0183]

1146 On the other hand, the energized ultrasonic oscillator 12 vibrates the ultrasonic vibrator 22 arranged inside the airtight container 6 to generate ultrasonic waves.

[0184]

1151 Here, the generated ultrasonic waves vibrate the water 31 and the photocatalyst body 20. In particular, the photocatalyst body 20 included in the photocatalytic reaction water generator 1 according to the present invention is formed by coating the surface of a metal fiber with a photocatalyst (For example, titanium dioxide) is made into a metal fibrous body of wool-like aggregates.

[0185]

1158 Therefore, active oxygen species are generated from the surface of the metal fiber body having a large surface area that gathers the surface area of each metal fiber. At the same time, the generated active oxygen species are quickly removed from the surface of the photocatalyst body 20 due to the ultrasonic vibration. Being shaken off, a lot of free in the water 31.

[0186]

1165 Then, new active oxygen species are instantly generated on the surface of the photocatalyst body 20, and are again harmonized with the vibration of the ultrasonic wave to be shaken off, and free in the water 31.

[0187]

1170 Since this is repeated many times in an instant, the active oxygen species can be contained in the water 31 extremely effectively.

[0188]

1175 In addition, the photocatalyst body 20, for example, compared with a plate-shaped photocatalyst, is more likely to be tuned to the fine vibration of ultrasonic waves to cause vibration, and the active oxygen species can be released from the surface of the photocatalyst body 20 more easily.

[0189]

1181 In addition, since the end portions of the metal fibers that are abundant in the photocatalyst body 20 dance as free ends under ultrasonic vibration, the active oxygen species can be effectively shaken off from the photocatalyst body 20.

[0190]

1187 In addition, since the photocatalyst body 20 uses alumina fibers that can be well coated with titania as its carrier, the titania is relatively firmly bonded on the alumina surface and has high durability. Therefore, even in water under an ultrasonic environment, It can maintain practicality and endure long-term use.

1190 Especially when it is used in seawater where metals are likely to corrode, etc., this remarkably shows practicality.

[0191]

1195 In this way, due to the characteristics of the photocatalyst body 20 and the synergistic effect with ultrasonic waves, the active oxygen species generated on the surface of the photocatalyst body 20 are easily released in the water, so that the water contains a large amount of active oxygen species, and photocatalytic reaction water is generated.

[0192]

1202 Then, the water 31 continuously supplied from the water supply port 2 causes the photocatalytic reaction water inside the airtight container 6 to be squeezed out from the drain port 11 provided on the upper side of the airtight container 6. Therefore, the photocatalytic reaction water can be taken out from the airtight container 6 .

[0193]

1209 The reactive oxygen species contained in the photocatalytic reaction water produced in this way have very high reactivity and persistence, and their strong oxidative decomposition ability can quickly give life to microorganisms and parasites.

[0194]

1215 Example 2

[0195]

1219 Next, the case where the photocatalytic reaction water generator 1 described in Example 1 is used as a photocatalytic reaction water generator for sterilization will be described.

[0196]

1224 That is, as shown in FIG. 5, between the feed water pump 32 immersed in the water 31 in the water tank 33 and the photocatalytic reaction water generator 1, a sterilizer 23 equipped with a sterilization lamp 24 is provided so that the sterilization lamp The ultraviolet rays radiated from 24 can irradiate the water 31 circulating inside the sterilizer 23.

[0197]

1231 The germicidal lamp 24 provided in the sterilizer 23 can radiate ultraviolet rays having a wavelength of 245 to 265 nm, more preferably 256 nm, and impart damage due to mutational damage to the DNA of microorganisms in the water, thereby being able to sterilize the microorganisms.

[0198]

1237 In addition, the mirror surface and light-shielding piping provided on the wall surface of the photocatalytic reaction water generator 1 also have an effect of preventing light recovery.

1239 By preventing light recovery, damage to microorganisms caused by ultraviolet rays with a wavelength of 245 to 265 nm can be effectively given, thereby improving the sterilization effect.

[0199]

1244 In this photocatalytic reaction water generating device 1, active oxygen species and the like diffuse in the water. Therefore, microorganisms that are not sterilized in the sterilizer 23 and have damaged their cell membranes and reach the photocatalytic reaction water generating device 1 are active. Oxygen species further give it fatal damage and sterilize it.

[0200]

1251 In addition, the sterilizer 23 is arranged in the photocatalytic reaction water generator 1 through the connecting pipe 26, but it is not limited to this, and it can be arranged inside the photocatalytic reaction water generator 1 and arranged in the photocatalytic reaction water generator for sterilization. The light source used to excite the photocatalyst body 20 in the device 1 (for example, an ultraviolet lamp 9 that generates ultraviolet light with a wavelength of 350 to 370 nm) is provided with a germicidal lamp 24 that generates ultraviolet light with a wavelength of 245 to 265 nm, and the photocatalytic reaction water is generated. 1 and the sterilizer 23 are constituted as one body, and a light source that simultaneously emits light that can excite the photocatalyst body 20 and light that can be sterilized may be provided in the photocatalytic reaction water generator 1.

[0201]

1263 Example 3

[0202]

1267 Next, an example in which the photocatalytic reaction water generator 1 according to the present invention is used to sterilize microorganisms in practice is shown.

[0203]

1272 In this example, five types of tests with different configurations and operating times of the photocatalytic reaction water generator 1 were performed, and the respective results were examined.

1274 The contents of each test are as follows.

[0204]

1278 [Test 1] Verification of the sterilization and sterilization ability of photocatalytic reaction water (no oxygen supply and ultrasonic irradiation)

[0205]

1283 [Test 2] Verification of sterilization and sterilization effects when the wavelength of ultraviolet rays irradiated to the photocatalyst body 20 is changed (no oxygen supply and ultrasonic irradiation)

[0206]

1288 [Test 3] Verification of sterilization and bactericidal effects when combined with oxygen supply and ultrasonic irradiation

[0207]

1293 [Test 4] Verification of the duration of the sterilization ability of the photocatalytic reaction water

[0208]

1297 [Test 5] Verification of sterilization and sterilization effects when using a sterilizer together

[0209]

1301 The tests of the above tests 1 to 5 are described in detail below.

[0210]

1305 [Test 1] Verification of the sterilization and sterilization ability of photocatalytic reaction water

[0211]

1309 In the water tank 33 of the photocatalytic reaction water generator 1 constructed as shown in FIG. 1 (but without oxygen supply and ultrasonic irradiation), suspend Staphylococcus aureus (Staphylococcus aureus), Enterococcus faecalis (Enterococcus faecalis), and Bacillus cereus. (Bacillus cereus), Escherichia coli (E. coli), Klebsiella pneumoniae (pneumoniae) 5 kinds of live bacteria, the bacterial concentration is adjusted to about 106cfu/ml.

[0212]

1317 In the system constructed in this way, the underwater pump 32 and the black light 9 (EFD15BLB, manufactured by Toshiba Labtec Co., Ltd.) were energized and fed into the water while circulating the water for 3 hours to investigate the change over time in the number of viable cells.

1320 In addition, the water used in this test used 4L of distilled water for injection, and the photocatalytic reaction water generator, circuit, and water pump used facilities that were sterilized in advance and circulated and cleaned with distilled water.

1323 The temperature of the water in the experiment was unchanged, and the water was circulated at a stable temperature of 28° C.

1325 In Fig. 6, the morphology of 5 strains on agar medium is shown.

[0213]

1329 For the investigation of the number of viable cells, the samples collected over time were spread on the blood agar medium (Trypticase Soy Agar), and the growth was observed.

1331 In addition, in order to make it easier to see the gram-positive bacteria, a blood agar medium (Columbia Agar) mixed with CNA (Colistin-Nalidixic Acid: a drug that inhibits gram-negative bacilli) is used.

1333 The changes over time of the colonies formed on the blood agar medium in this way are shown in FIG. 7.

[0214]

1337 The results in Fig. 7 show that the photocatalytic reaction water has significant sterilization and antibacterial effects on all 5 types of bacteria suspended in the water.

1339 The number of bacteria that multiplied within 30 minutes after the introduction of bacteria decreased with

the passage of time thereafter.
1341 In particular, Enterococcus faecalis (Enterococcus faecalis) almost disappeared within 3 hours.

[0215]

1345 It was confirmed from the results of this test 1 that the photocatalytic reaction water generator 1 has sterilization and sterilization effects.
1347 However, it is considered that at this time, the active oxygen species caused by the photocatalyst only act on the surface of the photocatalyst body. By circulating the water in the water tank, it is possible to have frequent contact opportunities with the photocatalyst body, thereby exhibiting a sterilization effect.
1350 Therefore, it is judged that at this time, the photocatalytic reaction water produced in the photocatalytic reaction water generator 1 cannot be said to have sterilization and sterilization effects.

[0216]

1355 [Test 2] Verification of sterilization and sterilization effects when the wavelength of ultraviolet rays irradiated to the photocatalyst body 20 is changed

[0217]

1360 Next, in the same test system as the test 1, the case where the wavelength of the ultraviolet rays irradiated to the photocatalyst body 20 was changed was verified.

[0218]

1365 That is, the ultraviolet irradiation lamp 9 provided in the photocatalytic reaction water generator 1 used in Test 1 was replaced with a black light lamp that irradiated blue light that hardly irradiated the effective ultraviolet rays of the titanium dioxide fiber body, and the change in the number of bacteria was observed.
1368 The temperature does not change, and the water temperature circulates at a certain temperature of 28° C.

[0219]

1372 As a result, just after the start of the test, after a process of relatively slow increase in the number of bacteria, after 45 minutes, the total number of bacteria was greater than 108 cfu/ml and became unobservable.
1374 Generally, the growth rate of bacteria is doubled in 20 minutes.
1375 In the result of this test 2, the bacteriostatic effect could not be observed, and it could be confirmed that the photocatalyst body in the photocatalytic reaction water generator 1 could not observe the sterilization and sterilization effects.

[0220]

1381 Based on the results of the above experiments 1 and 2, it can be confirmed that the photocatalytic reaction water generator 1 exhibits the sterilization and sterilization effects caused by the photocatalytic reaction, rather than the sterilization and sterilization effects by the photocatalyst body.

[0221]

1387 However, it is considered that this reaction force is not sufficient for completely sterilizing the number of viable bacteria in the water, and some supplementary means is required.

[0222]

1392 [Test 3] Verification of sterilization and bactericidal effects when combined with oxygen supply and ultrasonic irradiation

[0223]

1397 Next, in the water tank 33 of the photocatalytic reaction water generator 1 for sterilization having the structure shown in FIG. 1, Staphylococcus aureus (Staphylococcus aureus), Enterococcus faecalis (Enterococcus faecalis), and Bacillus cereus (Bacillus cereus) are suspended in the water tank 33 of the photocatalytic reaction water generator 1 for sterilization. , Escherichia coli (E. coli), Pseudomonas aeruginosa (Pseudomonas aeruginosa) 5 kinds of live bacteria, the bacterial concentration is adjusted to about 106cfu/ml.

[0224]

1406 In the system constructed in this way, the underwater pump 32, the black light 9 (EFD15BLB, manufactured by Toshiba Labtec Co., Ltd.) and the ultrasonic oscillator 12 (vibrator for 2.4MHz atomization) are energized, and the oxygen supply unit 5 is fed at 250 ml/min. Pure oxygen was used to circulate water for 24 hours at the same time, and the change in the number of viable bacteria over time was investigated.

1410 In addition, this test 3 was performed with the same report as the test 1, and the change in the number of bacteria was gradually diluted by a spiral plate (Spiral Plate) to dilute the water in the water tank 33 collected at regular intervals, and the number of viable bacteria was measured.

1413 In addition, as in Test 1, the temperature was not changed, and the water temperature was cycled at a constant temperature of 28° C.

[0225]

1418 The results of this experiment 3 are shown in Table 1.

[0227]

1422 As can also be seen from Table 1, significant sterilization and sterilization effects on four types of bacteria suspended in water can be seen.

1424 In particular, Staphylococcus aureus (Staphylococcus aureus), a cause of nosocomial infections due to antibiotic resistance, and Bacillus cereus (Bacillus cereus), a cause of food poisoning, died about 1 hour after the start of the test. These bacteria show high effects.

1427 Moreover, although Bacillus cereus (Bacillus cereus) is a spore-like bacteria, it is generally difficult to kill it, but it is suggested that it also exhibits an effective bactericidal effect on spores.

[0228]

1432 At the same time, Escherichia coli (E. coli), which belongs to pathogenic E. coli O-157, etc., died quickly and could not start to proliferate again.

[0229]

1437 On the other hand, for Pseudomonas aeruginosa (Pseudomonas aeruginosa), although a temporary decrease in the bacterial count can be observed, a gradual increase in the bacterial count can be seen thereafter.

1439 In addition, for Gram-negative bacteria with a thick capsule cell membrane mixed into the test system, the number of bacteria tends to gradually increase.

[0230]

1444 In this way, through the synergistic effect of oxygen supply and ultrasonic vibration, it is actually proved that the photocatalytic reaction water has an effect on Staphylococcus aureus (Staphylococcus aureus), Enterococcus faecalis (Enterococcus faecalis), Bacillus cereus (Bacillus cereus), Escherichia coli (large intestine). Bacillus) confers a strong bactericidal ability, and also shows antibacterial power against Pseudomonas aeruginosa (Pseudomonas aeruginosa) and Gram-negative bacteria to inhibit the proliferation of their bacteria.

[0231]

1453 [Test 4] Verification of the duration of the sterilization ability of photocatalytic reaction water

[0232]

1457 Next, to verify the extent to which the sterilization effect of the photocatalytic reaction water continues, after the photocatalytic reaction water generator 1 has been operated for 1 hour, the photocatalytic reaction water generator 1 is stopped, and the bacterial cells are suspended in the water tank 33, and the history of the bacterial count is tracked. Time changes, there is a conjecture that promotes the continuation time of the line reaction.

[0233]

1465 In this experiment 4, as in experiment 3, the photocatalytic reaction water generator 1 was installed in the water tank 33 to prepare Staphylococcus aureus (Staphylococcus aureus), Enterococcus faecalis (Enterococcus faecalis), Escherichia coli (E. coli) , Pseudomonas aeruginosa (Pseudomonas aeruginosa) 4 kinds of bacteria, so that the concentration of viable bacteria is about 106cfu/ml.

1469 The results of this test 4 are shown in Table 2.

[0234]

1473 [Table 2]

[0236]

1477 As can also be seen from Table 2, the effect of the photocatalytic reaction water differs depending on the bacterial species, but it is suggested that it can continue for about 1 hour.

[0237]

1482 In this experiment, the time of bacterial circulation did not cause the photocatalytic reaction, but the sterilization effect caused by the photocatalytic reaction water generated by the operation of the photocatalytic reaction water generator 1 for 1 hour, which proved that the photocatalytic reaction water has The powerful bactericidal ability of the bactericide suggests that the action time can also continue for about 1 hour.

[0238]

1490 [Test 5] Verification of sterilization and sterilization effects when sterilizer 23 is used in combination

[0239]

1494 Next, in the photocatalytic reaction water generator 1 that performs oxygen supply and ultrasonic irradiation, the microbial behavior when irradiated with a black light lamp and ultraviolet rays is tested again.

[0240]

1499 The bacteria used in this experiment 5 were suspended in the water tank 33 Staphylococcus aureus (Staphylococcus aureus), Enterococcus faecalis (Enterococcus faecalis), Escherichia coli (Escherichia coli), Pseudomonas aeruginosa (Pseudomonas aeruginosa) Live bacteria of 4 kinds of bacteria.

1502 One hour after the start of the test, oxygen supply and ultrasonic irradiation were performed while operating the underwater pump 32.

1504 At this time, no photocatalytic reaction is caused, and the bacteria injected into the circuit recover from the damage caused by storage and become able to proliferate.

1506 Then, after 1 hour, the above state was maintained, the black light was turned on, and the photocatalytic reaction was excited on the photocatalyst 20, and the sterilization and sterilization reaction caused by the

photocatalytic reaction for 3 hours was observed.
1509 Then, 180 minutes after the start of the test, the germicidal lamp 24 of the sterilizer 23 was turned on again to confirm the additional effect.
1511 Table 3 shows the results of the investigation of the time-dependent changes in the number of viable cells of each bacteria in this test 5.

[0242]
1516 Here, the arrows in Table 3 indicate the operation of each machine.
1517 From the results shown in Table 3, the inhibition of the proliferation of each bacteria caused by oxygen administration and ultrasonic operation cannot be seen.
1519 By circulating at a water temperature of 28° C and an oxygen-rich condition, all the bacteria used in the test proliferate and activate.
1521 After the black light is irradiated, the proliferation cannot be inhibited immediately. Although its number temporarily increases, except for Pseudomonas aeruginosa, it is sterilized by cell damage caused by the oxidation caused by the active oxygen species contained in the photocatalyst water. And it is reproducible.
1524 Moreover, Pseudomonas aeruginosa can inhibit its proliferation even only by the photocatalytic reaction. After starting the combined use of the germicidal lamp, the number of bacteria decreases immediately, and it can be sterilized and sterilized.

[0243]
1530 That is, with regard to Pseudomonas aeruginosa with a low effect in Test 3, the combined use of a germicidal lamp has no antibacterial effect, but can eliminate bacteria and sterilize it. Moreover, bacteria other than the test bacteria such as gram-negative bacteria do not mix and proliferate, and there is no antibacterial effect. It becomes a place for the growth of new bacteria, and it is judged from this that there is a synergistic effect between the photocatalyst water and the germicidal lamp.

[0244]
1538 Example 4

[0245]
1542 Next, an example in which the photocatalytic reaction water generator according to the present invention is used as a photocatalytic reaction water generator for insect repellent will be described.
1544 The photocatalytic reaction water generator according to the present invention is a device that exhibits an excellent repellent ability against parasites parasitic in fish and the like.
1546 The following shows an example of the structure of the photocatalytic reaction water generator for repelling insects and the results of verification of the insect repellent effect caused by the same photocatalytic reaction water generator for repelling insects.

[0246]

1552 [Configuration example of photocatalytic reaction water generator for insect repellent]

[0247]

1556 Using FIGS. 8-14, the state of use is shown, and the photocatalytic reaction water generator for repelling insects and the method of repelling insects will be described.

[0248]

1561 Fig. 8 shows a state in which the water tank 133 is equipped with a photocatalytic reaction water generator 101 for repelling insects, and the seawater 142 in the water tank 133 is circulated in the photocatalytic reaction water generator 101 for repelling insects. The sea water 142 contains active oxygen species.

[0249]

1567 Here, a water supply pump 132 is provided at the tip of the water supply port 102. By operating the water supply pump 132, the oxygen-dissolved seawater can be supplied to the insect repellent photocatalytic reaction water generator 101 through the water supply pipe 103.

[0250]

1573 Then, in the seawater supplied to the photocatalytic reaction water generator 101 for repelling insects, the photocatalyst body 120 is excited by the ultraviolet rays irradiated from the ultraviolet lamp 109, and at the same time, ultrasonic waves are emitted from the ultrasonic vibrator 122. Therefore, the active oxygen species are emitted from the photocatalyst body. A large amount of 120 free, so that the active oxygen species can be effectively dissolved in seawater.

[0251]

1581 The seawater containing this large amount of active oxygen species is discharged from the drain port 111 through the drain pipe 110 and flows into the water tank 133 again.

[0252]

1586 Since the fish 145 is contained in the water tank 133 in advance, the water containing active oxygen discharged from the insect repellent photocatalytic reaction water generator 101 affects the microorganisms and parasites attached to the fish 145, thereby enabling the Parasites are repelled from fish 145.

1589 In addition, here, the concept of fish 145 includes not only adult fish, but also larvae and juvenile fish.

[0253]

1593 In addition, in FIG. 8, a photocatalytic reaction water generator 101 for repelling insects is arranged in one water tank 133, but as shown in FIG. 9, the number of fish 145 for comprehensive repelling insects, The amount of seawater contained in the water tank 133 and the desired active oxygen concentration in the seawater increase the number of photocatalytic reaction water generators 101 for repelling insects.

[0254]

1600 In addition, in FIG. 9, the insect repellent photocatalytic reaction water generator 101 is arranged in parallel in the water tank 133, but as shown in FIG. 10, the insect repelling device may be connected in series using a connecting pipe 126 or the like. Photocatalytic reaction water generator 101.

1603 At this time, the water discharged from the drain 111 through the two photocatalytic reaction water generators 101 for repelling insects contains a larger amount of active oxygen species than the water discharged from one photocatalytic reaction water generator 101 for repelling insects Therefore, when water containing high concentration of active oxygen is desired, it can be suitably used.

[0255]

1610 [Use state example 2 of the photocatalytic reaction water generator for repelling insects]

[0256]

1614 Next, while showing the state of use, the case where a sterilizer is provided in the photocatalytic reaction water generator for insect repelling using a photocatalytic reaction will be described.

[0257]

1619 That is, as shown in FIG. 11, between the water supply pump 132 immersed in the water 131 in the water tank 133 and the photocatalytic reaction water generator 101 for repelling insects, a sterilizer 123 equipped with a germicidal lamp 124 is provided. The ultraviolet rays radiated from the germicidal lamp 124 can irradiate the water 131 circulating inside the sterilizer 123.

[0258]

1626 The germicidal lamp 124 provided in the sterilizer 123 can radiate ultraviolet rays with a wavelength of 245 to 265 nm, more preferably 256 nm, and as described in the description of the photocatalytic reaction water generator for sterilization, can bring microorganisms in the water Damage caused by DNA mutation damage, thereby sterilizing microorganisms.

[0259]

1633 In addition, the pipes used for the sterilizer and for supplying the water that has passed through the sterilizer to the photocatalytic reaction water generator 101 for repelling insects are manufactured so as to block external visible light.

[0260]

1639 The mirror surface applied to the wall surface of the photocatalytic reaction water generator 101 for repelling insects also has an effect of preventing light recovery.

1641 By preventing light recovery, damage to microorganisms caused by ultraviolet rays with a wavelength of 245 to 265 nm can be effectively given, thereby improving the sterilization effect.

[0261]

1646 Then, the sterilized bacterial cells and the weakened microorganisms are supplied to the insect repellent photocatalytic reaction water generator 101, and by contact with the active oxygen species generated by the photocatalyst body, the bacterial cells are oxidized and decomposed or the weakened microorganisms are fatally damaged. , Which can reliably sterilize the microorganisms in the water.

[0262]

1653 The water 131 treated by the sterilizer 123 according to such a mechanism is supplied to the insect repellent photocatalytic reaction water generator 101 through the connecting pipe 126 connecting the sterilizer 123 and the insect repellent photocatalytic reaction water generator 101.

[0263]

1659 In this photocatalytic reaction water generator 101 for repelling insects, active oxygen species etc. diffuse in the water. Therefore, the sterilizer 123 for re-administration of active oxygen species is not sterilized and weakened and reaches the photocatalytic reaction water for repelling insects. The microorganisms of the device 101 are sterilized with fatal damage.

[0264]

1666 [Use state example 3 of the photocatalytic reaction water generator for insect repellent]

[0265]

1670 Next, FIG. 12 shows an example of removing parasites and microorganisms attached to the fish by contacting the water containing active oxygen species generated by the photocatalytic reaction water generating device 101 and the sterilizer 123 for repelling insects.

[0266]

1676 A water tank 133 contains 10 liters of sea water 142, and a photocatalytic reaction water generator 101 for repelling insects equipped with a sterilizer 123 is arranged on the upper part of the water tank 133.

[0267]

1681 The photocatalytic reaction water generator 101 for repelling insects was operated for 1 hour in advance, and the seawater temperature was adjusted to 28° C. and the dissolved oxygen concentration (DO) to 6.8 mg/L.

1684 The temperature of the seawater and the concentration of dissolved oxygen were kept constant thereafter, and the test was performed.

1686 The hydrogen peroxide concentration of the circulating photocatalytic reaction water is often below 3 ppm.

[0268]

1690 Then, as shown in Table 4, the test target fish was floated.

[0269]

1694 [Table 4]

[0271]

1698 As shown in Table 4, 4 red amberjacks and 4 tiger fish were contained in the water tank.

1699 In addition, the gill holes of these fish 145 were investigated in advance, and as a result, the average number of red yellowtails per fish was 20, and tiger porpoises were 30.

[0272]

1704 Then, the photocatalytic reaction water generating device 101 for repelling insects in the two water tanks was operated and circulated for 2 hours. Then, the two devices were stopped, two red yellowtail and two tiger fish were taken out, and the state of the fish 145 was observed.

1707 The remaining 2 red yellowtails and 2 tiger dolphins were returned to the sea cage, and after 20 hours, the heteroaxe status of fish 145 was confirmed.

1709 The results are shown in Table 5.

[0273]

1713 [table 5]

[0275]

1717 As shown in Table 5, the photocatalytic reaction water generator 101 for repelling insects was operated for 2 hours, and the number of heteroaxes attached to two red yellowtail and two tiger fish 145 was immediately after the end. The average number of red feet is 17 and the average number of tiger porpoises is 15. The number of parasitic heteroaxes has become about half, and the activity of parasitic heteroaxes has decreased.

[0276]

1724 After 20 hours of operation, the number of heteroaxes attached to the remaining 2 red amberjacks and 2 tiger puffer fish 45, the average number of red amberjacks was 0, and the average tiger porpoise was 2.5, which was significantly reduced.

[0277]

1730 From these results, it can be considered that the water containing active oxygen species generated by the photocatalytic reaction water generator 101 for repelling insects is not hydrogen peroxide water. Plays an extremely effective role in deworming different axe worms.

[0278]

1736 [Example 4 of the usage state of the photocatalytic reaction water generator for repellent]

[0279]

1740 Next, using FIG. 12, an example of removing parasites and microorganisms attached to the fish by contacting the water containing active oxygen species generated by the photocatalytic reaction water generating device 101 and the sterilizer 123 for repelling insects will be described.

[0280]

1746 30 liters of seawater 142 are accommodated in the water tank 133, and the photocatalytic reaction water generator 101 for insect repelling equipped with the sterilizer 123 is arrange|positioned in the upper part of this water tank 133.

[0281]

1752 Prepare two water tanks 133 equipped with such photocatalytic reaction water generators 101 for repelling insects, operate each photocatalytic reaction water generator 101 for repelling insects for 1 hour, and adjust the seawater temperature to 28° C and the dissolved oxygen concentration (DO) to 6.8mg/L.

1755 Keep the seawater temperature and the dissolved oxygen concentration constant and perform the test.

1756 In addition, as in Example 5, the hydrogen peroxide concentration of the recycled photocatalytic reaction water is usually 3 ppm or less.

[0282]

1761 Then, as shown in Table 6, the test target fish 145 was floated.

1762 In addition, here, of the two water tanks 133, one water tank 133 is referred to as water tank A, and the other water tank 133 is referred to as water tank B for description.

[0283]

1767 [Table 6]

[0285]

1771 As shown in Table 6, 6 red yellowtails and 1 tiger fish were accommodated in tank A, and 5 red yellowtails were accommodated in tank B.

1773 In addition, the gills of these fish 145 were investigated in advance, and as a result, the average number of heteroaxes per fish was 20 in both tanks.

[0286]

1778 Then, the photocatalytic reaction water generator 101 for repelling insects in the two water tanks was operated, and the test was started.

1780 Here, after the water tank A operates the insect repellent photocatalytic reaction water generator 101 for 4 hours, and the water tank B operates the insect repellent photocatalytic reaction water generator 101 for 6 hours, stop the device and confirm the difference of the fish 145 after 20 hours. Axe status.

1783 The results are shown in Table 7.

[0287]

1787 [Table 7]

[0289]

1791 As shown in Table 7, the photocatalytic reaction water generator 101 for repelling insects was operated for 4 hours, and the number of heteroaxes attached to the fish 145 in the water tank A after 20 hours was 3 on average.

[0290]

1797 In addition, the photocatalytic reaction water generator 101 for repelling insects was operated for 6 hours, and the number of heteroaxes adhering to the fish 145 in the water tank B after 20 hours had elapsed was one on average.

[0291]

1803 From these results, it is suggested that the water containing active oxygen species generated by the photocatalytic reaction water generator 101 for repelling insects exerts an extremely effective effect on the parasitic axe worms on the fish 145, and can repel the worms.

[0292]

1809 In addition, one aspect that should be noted in this result is that although it was a fish 145 that was weakened by the parasitism of the parasitic axe, one dead fish did not appear.

1811 It is thought that this suggests that although the water containing active oxygen species produced by the photocatalytic reaction water generator 101 for repelling insects has a strong insect repellent effect on Heterodactyls, it has a very stable effect on fish 145 and hardly brings any damage. Adverse effects.

[0293]

1817 Moreover, since the repellent effect of water containing active oxygen species on parasites is caused by active oxygen species, etc., there is no need to worry about parasites and microorganisms gaining tolerance and can be used for a long time.

[0294]

1823 In addition, even if water containing active oxygen species used in the elimination of parasites and microorganisms is discharged into nature, it rapidly changes into substances such as water and oxygen, so there is no need to worry about adverse effects on the environment.

[0295]

1829 At the same time, since the water containing active oxygen species attached to fish bodies, parasites, microorganisms, etc., rapidly changes into substances such as water and oxygen, there is no problem of chemicals remaining in the fish, and there is no need to worry about deteriorating consumers' impression.

[0296]

1835 In this way, the fish 145 can be treated by contacting the water containing the active oxygen species in the living water, but the same effect can be obtained even if the fish 145 is immersed in the water containing the active oxygen species stored in advance for a predetermined time.

[0297]

1841 In addition, in order to interfere with the attack of strong activated oxygen, slow-release calcium carbonate or burned new century uplift coral can also be injected into the circuit.

[0298]

1846 At the same time, sundries floating in the water and parasites such as heteroaxes that have fallen off from the fish are attached to the photocatalyst body 120. In order to prevent the reduction in the generation efficiency of active oxygen, it is also possible to transfer the photocatalyst from the water supply pump 132 to the insect repellent. A filter is provided in the flow path of the reaction water generator 101 for supplying water.

[0299]

1853 In this embodiment, the case where the fish 145 is a farmed fish is described, but it can of course also be applied when the fish 145 is an ornamental fish.

1855 In particular, when the photocatalytic reaction water generator 101 for repelling insects is applied to ornamental fish raised in general households, etc., in order to regularly supply water containing active oxygen species to the water tank 133, or to prevent the supply of excessive active oxygen species. Water can be equipped with a timer and limiter to suppress the energization of the ultraviolet lamp 109.

1859 With such a configuration, it is possible to always maintain good health of the ornamental fish.

[0300]

1863 Furthermore, when the energization to the ultraviolet lamp 109 is cut off, oxygen-enriched water is supplied from the drain 111 into the water tank 133, and therefore, a good living environment for the fish 145 can be maintained.

[0301]

1869 [Example 4 of the usage state of the photocatalytic reaction water generator for repelling insects]

[0302]

1873 As explained so far, the photocatalytic reaction water generator for repelling insects is arranged in a water tank or the like, thereby enabling parasitic parasites on fish contained in the water tank to be repelled. However, in the sixth embodiment, Shows an example in which the entire water tank is used as a photocatalytic reaction water generator for repelling insects.

[0303]

1880 That is, in the photocatalytic reaction water generating device 101 for repelling insects shown in FIG. 13, the bottom of the water tank 133 containing the parasitic fish 145 and sea water 142 is connected to an ultrasonic oscillator not shown. The ultrasonic vibrator 122, the underwater blade 151, and the oxygen supply unit 105.

[0304]

1886 In addition, a photocatalyst body 120 formed in a sheet shape is arranged on the water surface 155, and sunlight 153 emitted from the sun 154 is irradiated thereon to excite the photocatalyst body 120.

[0305]

1891 In addition, by making the carrier of the photocatalyst body 120 a raw material that floats in water, or attaching a float to the photocatalyst body, it can float on the water surface 155.

[0306]

1896 Then, by disposing the reflector 152 at a predetermined position of the water tank 133 in the sea water 142, the sunlight 153 can be guided to the sea water 142 and the sunlight can be irradiated from the inner surface of the photocatalyst body 120.

[0307]

1902 The reflector 152 is not particularly limited as long as it can guide light into the sea water 142 and irradiate it from the inner surface of the photocatalyst body 120. For example, it can be an optical fiber or a prism.

[0308]

1907 With this configuration, the photocatalytic reaction water generator 101 for repelling insects guides sunlight 153 with the reflector 152 and irradiates the inner surface of the photocatalyst body 120 with light, thereby exciting the photocatalyst body 120.

[0309]

1913 The excited photocatalyst body 120 generates active oxygen species that are diffused in the sea water 142 by the ultrasonic waves emitted from the ultrasonic vibrator 122 provided at the bottom of the water tank 133 and the underwater blade 151.

[0310]

1919 The diffused active oxygen species use seawater 142 as a medium, which can act on the parasites attached to the fish 145, showing an insect repellent effect.

[0311]

1924 However, it is considered that if the photocatalytic reaction water generator 101 for repelling insects is continuously used with such a configuration, organisms and dirt will adhere to the inner surface of the photocatalyst body 120 (the surface irradiated with light from the reflector 152).

1927 In particular, since seaweed spores and juvenile shellfish are floating in the seawater 142, if they grow on the photocatalyst body 120, the area where the photocatalyst body 120 can receive light is reduced and the production of active oxygen by the photocatalyst body 120 is prevented. Kind.

[0312]

1933 Therefore, the sheet-shaped photocatalyst body 120 shown in FIG. 13 is turned inside and out to immerse the surface where seaweed and shellfish do not adhere to water, so that active oxygen species can be efficiently generated.

[0313]

1939 In addition, the surface where the seaweed and shellfish are attached is exposed to the sun to dry, and the seaweed and shellfish die. The antifouling effect, which is one of the representative effects of the photocatalyst, causes these attachments to fall off.

[0314]

1945 In this way, by turning the inside and outside of the photocatalyst body 120 inside and outside the surface where the attached matter has fallen off, and being immersed in the sea water 142 again, the active oxygen species can be efficiently generated.

[0315]

1951 In addition, FIG. 14 shows an example in which this inverting operation is easier to perform.

[0316]

1955 The photocatalytic reaction water generator 101 for repelling insects shown in FIG. 14 and FIG. 13 are almost the same, but the structure of the photocatalyst body 120 is different.

[0317]

1960 That is, in the photocatalytic reaction water generator 101 for repelling insects shown in FIG. 14, two pillars 163, 163 erected on the bottom surface of the water tank 133 are erected with parallel rods 165 to form a supporting portion 166, and the supporting portion 166 Equipped with 2 feet.

1963 Then, a driving roller 161 is provided at one end of a parallel rod 165 that is arranged parallel to each other at a predetermined interval, and a driven roller 162 is provided at the other end, and an endless ring-shaped photocatalyst sheet-like body 167 is driven around. The roller 161 and the driven roller 162 allow the photocatalyst sheet 167 to rotate freely.

[0318]

1970 In addition, the parallel rod 165 is arranged on the water surface 155 of the sea water 142, so that approximately one-half of the photocatalyst sheet 167 is immersed in the sea water 142, and the remaining approximately one-half is exposed on the water surface 155.

[0319]

1976 Therefore, by operating the drive roller 161, the photocatalyst sheet 167 can rotate freely, so that the surface where the seaweed and shellfish adhere can be easily exposed on the water surface. In addition, on the water surface 155, the surface where the adherent has fallen off can be easily exposed. It is introduced under the water surface 155 so that it is immersed in sea water 142.

[0320]

1983 As a result, active oxygen species are efficiently generated from the photocatalyst sheet 167, and the parasites attached to the fish 154 can be repelled.

[0321]

1988 In addition, in FIGS. 13 and 14, the water tank 133 is used to constitute the insect repellent photocatalytic reaction water generator 101, but it is not limited to this. For example, instead of the water tank 133, a fishing net is stretched in seawater to form a net cage. It can deworm a large number of fishes while carrying out fish farming.

[0322]

1995 At this time, the fishing net of the formed net cage can also be provided with a photocatalyst function and become the photocatalyst body 120.

[0323]

2000 Especially in many cases, fish parasites are infected with other fish by the fishnet media of the cage. Therefore, the photocatalyst function of the fishnet is given to make it the photocatalyst body 120, and the parasite infection path can be easily cut off by irradiating light.

[0324]

2006 In addition, in FIGS. 13 and 14, the light radiated from the sun 154 is used as the light that excites the photocatalyst body 120 and the photocatalyst sheet 167, but as shown in the above embodiment, the photocatalyst body 120 and the photocatalyst are excited. Of course, the light source of the sheet-shaped body 167 may also be a light source capable of radiating at least ultraviolet rays including a wavelength of 350 to 370 nm, such as a black light lamp.

[0325]

2014 As described above, according to the photocatalytic reaction water generator according to the present invention, no additional chemicals or the like are used, and no load is imposed on the environment, and it can save electricity, be compact, and effectively repel parasites in fish.

[0326]

2020 Example 5

[0327]

2024 As shown in Example 3, the photocatalytic reaction water generator according to the present invention exhibits excellent sterilization and sterilization capabilities against microorganisms.

2026 Moreover, as shown in the photocatalytic reaction water generator for repelling insects in Example 4, it was confirmed that the effect of the photocatalytic reaction water is not only in the reaction part, but also in places where time and space are moved away. .

2029 The following shows an application example of a photocatalytic reaction water generator with such excellent antibacterial, sterilization, and insect repellent capabilities in daily necessities.

[0328]

2034 (i) Examples of use in circulating water sterilization devices

[0329]

2038 First, an example of processing microorganisms in circulating water in a bath that circulates warm water and an outdoor unit of cooling equipment is shown.

2040 By disposing the photocatalytic reaction water generator 1 in the circulating water treatment circuit, it is also possible to perform the sterilization of Legionella in water, which has become a problem in recent years.

[0330]

2045 That is, Legionella is a gram-negative bacillus that exists in water or humid soil and the optimal temperature is 15-43° C. It is attached to cooling equipment such as baths, air conditioners, freezers, and cold storage that circulate warm water. Protozoa (amoeba) cells that grow in water such as outdoor units proliferate in large numbers.

[0331]

2052 It is also known that Legionella proliferates in the cells of protozoa (amoeba) in large numbers, and direct inhalation of water vapor containing a large amount of bacteria released from the protozoa causes human infection.

2055 That is, as a countermeasure for the sterilization of Legionella, not only the sterilization of Legionella in the water itself, but also the destruction of the cell membrane of the protozoan, and the sterilization of the Legionella proliferated therein, methods to achieve both are important.

2058 The bactericidal power of Legionella in water alone is insufficient.

[0332]

2062 At this time, not only the usual sterilization is required, but also the protozoa parasites of the bacteria need to be repelled, which requires a more powerful oxidizing ability.

[0333]

2067 However, if the photocatalytic reaction water produced in the photocatalytic reaction water generator 1 shown in this embodiment is used, as shown in Example 4, parasites parasitic on fish can also be repelled, so It can get rid of protozoa that are weaker than parasites.

[0334]

2073 That is, the protozoa can be sterilized, and the Legionella that grows in the protozoa can be sterilized, and therefore, the infection caused by the Legionella can be prevented.

[0335]

2078 At this time, in order to maintain a wider sterilization effect and a strong sterilization power, it is recommended to use a germicidal lamp in combination.

[0336]

2083 (ii) Examples of treatment of ship's ballast water

[0337]

2087 Next, an example of processing harmful organic substances and microorganisms contained in ballast water that adjusts the center of gravity and buoyancy of a ship is shown.

2089 For example, by arranging the photocatalytic reaction water generating device according to the present invention in the ballast tank of a ship or at the discharge port of the ballast water, the ballast water can be safely and effectively treated without adding additional chemicals.

[0338]

2095 Ships are loaded with seawater in ballast tanks to adjust the center of gravity and buoyancy. In most cases, the water (ballast water) loaded in the ballast tanks is discharged on the ocean different from the loading location.

[0339]

2101 For example, for a large ship sailing overseas, when the load is small, ballast water is added to the ballast tank to increase the hull to ensure the stability of the hull, and when it arrives at a destination such as a foreign country to load the load, the ballast water is discharged to reduce the hull. , Adjust the weight of the hull.

[0340]

2107 However, there are many microorganisms and organic substances in seawater, which are discharged as ballast water at other distant places, so there is a concern that the ecosystem and environment of the drainage place will be damaged.

[0341]

2113 In particular, the marine organisms and the like transported in this way sometimes disrupt the food chain of the drainage site and proliferate abnormally, which is considered to cause great damage to the aquaculture industry.

[0342]

2119 Therefore, by arranging the photocatalytic reaction water generator 1 according to the present invention in the ballast tank of a ship, the ballast water can be circulated in the photocatalytic reaction water generator 1 to kill microorganisms contained in the ballast water. In addition, it can decompose harmful organic substances contained in ballast water.

[0343]

2126 Furthermore, when the ballast water is circulated in the photocatalytic reaction water generator 1 to become photocatalytic reaction water, it is possible to prevent shellfish, seaweeds, and the like from adhering in the ballast tank.

[0344]

2132 In addition, in this example, as the ballast water treatment means, the example is installed in the ship's ballast tanks and drains, but it is not particularly limited to this, and it can also be installed in the port where the ship is anchored, and recovered by pumps, etc. The ballast water is processed by the photocatalytic reaction water generator 1 and then discharged to the ocean.

[0345]

2139 In this way, the treatment of ballast water by the photocatalytic reaction water generator 1 can prevent the destruction of the ecosystem and the environmental pollution caused by harmful organic substances, and, compared with the treatment of ballast water by chemicals, etc., it is possible to suppress environmental problems. It affects, and can discharge the treated ballast water to the ocean.

[0346]

2146 (iii) Examples of cleaning dentures

[0347]

2150 Next, an example in which the denture 34 installed in the oral cavity is sterilized with photocatalytic reaction water will be described using FIG. 15.

2152 The photocatalytic reaction water generator 1 according to the present invention is arranged in a water tank 33 having a predetermined capacity, and the denture 34 is immersed in the water tank 33, and no additional chemicals or the like are added, so that an excellent cleaning effect, sterilization and sterilization effect can be obtained.

[0348]

2159 In other words, the denture 34 installed in the oral cavity is likely to settle with food residues, soot, and the like, and needs to be washed frequently.

2161 However, the settled dirt is not easy to fall off, and it takes a lot of effort to brush with a brush or the like for a long time.

[0349]

2166 In addition, since the denture 34 is installed in the oral cavity, detergents and bactericides that are harmful to the human body cannot be used, and a special commercially available bactericidal detergent is used for treatment, but it is not an effective means for removing the deposited dirt.

[0350]

2172 Therefore, for example, as shown in FIG. 15, the photocatalytic reaction water generator 1 according to the present invention and the denture cleaning device 35 are integrated, and they are immersed in the water 31 in the water tank 33 to generate the photocatalytic reaction water. By operating the device 1, the denture 34 can be washed effectively.

2176 In addition, in FIG. 15, as a means for increasing the concentration of dissolved oxygen in water, an oxygen generating agent 63 is immersed in water. The oxygen generating agent 63 contacts water to generate bubbles, and the oxygen contained in the bubbles dissolves into the water.

[0351]

2182 Then, the water tank 33 having a predetermined capacity is divided into two parts, the photocatalytic reaction water generator 1 according to the present invention is arranged in one part of the water tank, and the denture is immersed in the other part of the water tank 33 (washing tank)., No additional chemicals, etc. can be added, excellent cleaning effect, sterilization and sterilization effects can be obtained.

2

2189 There are underwater blades 61 between the two water tanks to enable the water to flow convectively, so that the photocatalytic reaction water can wash the denture 34 in the washing tank.

[0352]

2194 In particular, when the active oxygen-containing water rich in active oxygen species and hydrogen peroxide contacts the denture 34, the food residue and soot deposited on the denture 34 are strongly oxidized, and it becomes easy to remove the dirt from the denture 34.

[0353]

2200 Moreover, because the photocatalytic reaction water has a strong sterilization and sterilization effect, it can sterilize and sterilize the common bacteria in the oral cavity attached to the denture 34 and the bacteria and fungi that multiply in the food residue attached to the dentures. Denture 34 is hygienic.

[0354]

2206 In addition, since the water tank 33 is divided into two parts, the low-frequency ultrasonic vibrator 22 can be installed in the washing tank without damaging the photocatalyst body in the photocatalytic reaction tank, and the strong vibration force caused by the ultrasonic waves can be used to remove dirt. Floating can promote the oxidative decomposition reaction caused by active oxygen species.

[0355]

2213 The reactive oxygen species and hydrogen peroxide contained in the photocatalytic reaction water react with organic matter to quickly transform into harmless substances such as water (H2O) and oxygen (O2). Therefore, it does not have any adverse effects on the human body and can be assured. Install false teeth 34.

[0356]

2219 By using this denture washing system, the medical instrument 62 can also be washed.

[0357]

2223 (iv) Examples of use in the washing of tableware

[0358]

2227 Next, an example in which tableware is brought into contact with photocatalytic reaction water for sterilization and washing will be described.

2229 For example, the photocatalytic reaction water generator 1 according to the present invention is arranged between the water supply hoses of a dishwasher, and it is integrated with the dishwasher, and the photocatalytic reaction water generated by the photocatalytic reaction water generator 1 is sprayed on In this way, the tableware can be cleaned safely, effectively, and hygienically without adding a drug or the like separately.

[0359]

2237 That is, the tableware (plates, chopsticks, knives, and forks) used for meals have a lot of dirt on foods, especially oils derived from fish and meat, and proteins derived from cereals.

2239 Such dirt can easily become a place for microorganisms to multiply. In addition, when the tableware is used next time, it comes in contact with food, so it is not hygienic.

[0360]

2244 Therefore, dishwashing detergent and the like are used together with tap water to wash the dishes after meals, but dishwashing is also one of the heavy tasks in housework.

[0361]

2249 In addition, a dishwasher or the like that sprays tap water on the tableware to wash it can also be used. However, although oil stains can be effectively eluted with a tableware detergent or the like, the current situation is that protein stains are difficult to remove.

[0362]

2255 Therefore, by using the photocatalytic reaction water generated in the photocatalytic reaction water generator 1 of the present invention as the water sprayed from the dishwasher, it is needless to say that oil stains, even protein stains, etc., can be greatly enhanced by the photocatalytic reaction water. The oxidizing ability of oxidizing and eluting effectively, and it can sterilize the tableware into a hygienic state.

[0363]

2262 Moreover, even when eating fermented foods, such as natto and other fermented foods using spore-forming microorganisms, it can be fully removed from the verification result of the sterilization effect of the photocatalytic reaction water described above. bacteria.

[0364]

2268 In addition, in this example, as a means for bringing the photocatalytic reaction water into contact with the tableware, an example in which the photocatalytic reaction water is sprayed in a dishwasher is illustrated, but it is not particularly limited to this, and the photocatalytic reaction water may be stored in an appropriate amount of container. In the reaction water, tableware is immersed in the stored photocatalytic reaction water.

[0365]

2276 In this way, by washing the tableware with the photocatalytic reaction water, it is safe for the human body even when the photocatalytic reaction water is still attached to the tableware for use, and the tableware can be sufficiently brought into a hygienic state when the tableware is washed.

[0366]

2282 (v) Examples of use in food cleaning

[0367]

2286 Next, an example in which the photocatalytic reaction water is brought into contact with food and sterilized and cleaned will be described.

2288 For example, the photocatalytic reaction water generator 1 according to the present invention is installed in a food processing conditioning table, etc., and used for washing vegetables and fruits, so that safe and hygienic vegetables and fruits can be obtained without adding additional chemicals or the like. .

[0368]

2294 That is, since vegetables and fruits are mainly grown and harvested outdoors, dirt, microorganisms, insects, etc. may adhere.

2296 For example, vegetables with leaves such as cabbage are cultivated relatively low from the ground, so they tend to adhere to soil and the like. In addition, moths and butterflies lay eggs and attach and are also places where larvae proliferate.

[0369]

2302 Therefore, vegetables and fruits need to be washed before serving, but only washing with water lacks sterilization and washing ability, and it is hard to say that it is effective.

[0370]

2307 In addition, it is also possible to wash vegetables and fruits with food lotion, etc. However, there is a concern that the surfactant and other ingredients contained in the lotion will remain in the washed vegetables and fruits. As a consumer's feeling, I hope to avoid this The ingredients enter the mouth.

[0371]

2313 Therefore, the photocatalytic reaction water generator 1 according to the present invention is integrated with a conditioning table, etc., and the generated photocatalytic reaction water is used in the washing of vegetables and fruits, thereby effectively eluting attached dirt and Kill insects and microorganisms.

[0372]

2319 In addition, since vegetables and fruits are mostly sprayed with pesticides during cultivation, the photocatalytic reaction water is used to wash the vegetables and fruits, and the active oxygen species contained in the photocatalytic reaction water can decompose the attached pesticides, thereby reducing the damage to the human body. Adverse effects.

[0373]

2326 In addition, the so-called negative ions contained in a large amount of the photocatalytic reaction water can maintain the freshness of the appearance without wilting the leaves of vegetables and the like.

[0374]

2331 As a means of bringing the photocatalytic reaction water into contact with vegetables and fruits, it is possible to store the photocatalytic reaction water in an appropriate amount of the container and immerse it in the stored photocatalytic reaction water. In addition, it can also be applied in the form of mist or raindrops. With vegetables and fruits.

[0375]

2338 In this way, by washing the vegetables and fruits with the photocatalytic reaction water, it is possible to sterilize and clean the vegetables and fruits in a safe and hygienic manner without impairing the freshness of the vegetables and fruits.

[0376]

2344 (vi) Examples used in the cleaning of precision machines

[0377]

2348 Next, an example in which the photocatalytic reaction water generator 1 according to the present invention is used in the cleaning of precision equipment is shown.

2350 For example, the photocatalytic reaction water generator 1 of the present invention is arranged between the water supply hoses of a silicon wafer cleaning machine for semiconductor manufacturing, and the silicon wafer cleaning machine is integrated, and the light generated by the photocatalytic reaction water generator 1 The catalyzed reaction water contacts the silicon wafer, and the silicon wafer can be cleaned safely and effectively without adding additional chemicals or the like.

[0378]

2358 That is, in the manufacturing process of semiconductors used in electronic equipment, there are cases where fine dust is generated on the silicon wafer along with the removal of unnecessary parts.

2360 Since the dust is a cause of defective products in semiconductor manufacturing, organic compounds such as organic solvents or chelating agents are used for removal. However, the organic compounds used to remove the dust are also attached to the silicon wafer and need to be removed.

[0379]

2366 Hydrogen peroxide water is used for the removal of these organic compounds, but it is dangerous in the treatment, and it is necessary to dispose of the used hydrogen peroxide water.

[0380]

2371 Therefore, instead of hydrogen peroxide water, the photocatalytic reaction water produced by the photocatalytic reaction water generator according to the present invention can be used to remove the organic compounds adhering to the silicon wafer.

[0381]

2377 Moreover, compared with hydrogen peroxide water, even if the photocatalytic reaction water touches the human body, the effect is small, and the safety is high, so the operation is easy, and the work efficiency can be improved.

[0382]

2383 In addition, the active oxygen species contained in the photocatalytic reaction water have strong oxidizing power, but are extremely unstable and have a short reaction time. Therefore, even in continuous semiconductor manufacturing, it can be washed without hindering the manufacturing process in terms of time. net.

[0383]

2390 In addition, in this example, the cleaning target is a silicon wafer, but it is not limited to this, and it can be used for cleaning various precision equipment such as printed wiring boards and electronic components.

[0384]

2395 (vii) Examples of application in water storage tanks in toilets

[0385]

2399 Next, using FIG. 16, an example in which the photocatalytic reaction water generator 1 according to the present invention is integrally arranged in a water storage tank attached to a toilet, and the toilet is cleaned with the photocatalytic reaction water will be described.
2402 By washing the toilet in this way, it is possible to maintain the sanitation of the toilet without adding a medicine or the like.

[0386]

2407 That is, the toilet installed in the bathroom is used in a convenient place, so it is very easy to be contaminated.
2408 For example, if the feces are attached and solidified or the urine becomes petrified and settled, it is not easy to peel off only by scrubbing with a brush.

[0387]

2413 In addition, in a toilet of the type that is stored in a water tank in advance for flushing convenient dirt into the sewage pipe, the method of mixing a commercially available detergent such as a surfactant in the storage water prevents the dirt from adhering, and However, there is little effect on the dirt that has adhered.

[0388]

2419 Therefore, for example, the photocatalytic reaction water generator 1 according to the present invention is arranged as shown in FIG. 16 to form a toilet washing device 36, and the water 31 stored in the water storage tank 44 is circulated in the photocatalytic reaction water generator 1. By changing the storage water into photocatalytic reaction water, the dirt attached to the toilet can be oxidized and effectively fall off.
2423 In addition, in FIG. 16, the black light lamp 9 for irradiating ultraviolet rays on the photocatalyst body 20 contained in the photocatalytic reaction water generator 1 and the water 31 for supplying the water 31 in the water storage tank 44 from the water supply port 2 are omitted. The water supply pump 32 and the oxygen supply pipe 4 for mixing oxygen into the water 31.

[0389]

2430 Then, the photocatalytic reaction water stored in the water storage tank 44 passes through the operation handle 42 to release the water plug 45, and the photocatalytic reaction water flows from the communication pipe 43 into a toilet not shown.

[0390]

2436 In addition, since the photocatalytic reaction water has a strong sterilization effect as shown in Example 3, it can reliably sterilize the contaminated bacteria attached to the toilet and the periphery of the toilet and the fungi in the feces, and maintain the toilet. Of cleanliness.

[0391]

2442 In addition, the photocatalytic reaction water is used to flush the dirt in, and the sewage pipe through which the dirt flushed in from the toilet is also exposed to the photocatalytic reaction water, the dirt of the sewage pipe can also fall off, and therefore the sewage pipe can be prevented from being clogged.

[0392]

2448 At the same time, because the photocatalytic reaction water has an excellent deodorizing effect, it can deodorize the convenient odor filled in the toilet and the odor flowing back from the sewage pipe, so that the toilet can be used hygienically and comfortably environment of.

[0393]

2454 In this way, the photocatalytic reaction water flowing through the toilet together with the dirt will quickly become water and oxygen due to contact with the dirt and organic matter such as dirt, so there is no need to worry about adverse effects on the environment.

[0394]

2460 Since these effects are produced every time the dirt is flushed down in the toilet, the sanitation of the toilet can be always maintained, and the labor for cleaning the toilet can be greatly reduced.

[0395]

2465 (viii) Examples of use in washing machines

[0396]

2469 Next, an example in which clothes and cloths are brought into contact with photocatalytic reaction water for sterilization and washing will be described.

2471 For example, by disposing the photocatalytic reaction water generator 1 according to the present invention in a washing machine or the like, and using it for washing clothes and cloth, it can be brought into a sanitary state.

[0397]

2477 For example, clothing is mostly worn on the body for a long time, and it is mostly attached to sweat and oil secreted from the body.

[0398]

2482 Therefore, laundry must be washed after being worn, but washing with water alone lacks washing ability and is hardly effective.

[0399]

2487 In addition, it is possible to wash with a detergent or the like, but it is considered that components such as surfactants contained in the detergent remain in the clothes and become one of the causes of allergies.

[0400]

2492 Therefore, by using the photocatalytic reaction water generated in the photocatalytic reaction water generator 1 according to the present invention as the water supplied to the washing tub of the washing machine, the attached dirt can be effectively shed and the bacteria can be eliminated. Therefore, the clothes can be made hygienic. status.

[0401]

2499 In addition, wipes for wiping the table, wipes for cleaning, etc., because their role is to wipe off the dirt, it becomes a state where dirt is attached or microorganisms are easy to multiply. By washing with the washing machine according to the present invention, it is possible to maintain a hygienic state while preventing Dirt and microorganisms spread due to wiping.

[0402]

2506 The outer circumference of the washing tub is not usually seen, but because it does not come into contact with the laundry, dirt adheres to it, and it is also a place where bacteria can easily multiply.

2508 By installing this device in the washing machine, it is possible to prevent the growth of these dirt and bacteria on the periphery of the washing tub.

[0403]

2513 (ix) Examples of use in the cleaning of rice seeds

[0404]

2517 Next, an example in which the photocatalytic reaction water is brought into contact with rice seeds to be sterilized and cleaned is described.

2519 For example, by bringing the rice seed before sowing on the seedling bed into contact with the photocatalytic reaction water produced by the photocatalytic reaction water generator 1 according to the present invention, it is possible to prevent the growth of seedlings from being inhibited by bacteria, molds, and the like.

[0405]

2526 That is, when planting rice, it is necessary to cultivate seedlings for transplanting. Since the seeds germinate in the presence of water and air, microorganisms may multiply.

2528 Propagating microorganisms hinder the adaptive growth of seedlings and sometimes rot the seedlings.

[0406]

2532 Therefore, the rice seeds sown on the seedbed need to be sterilized, but the chemicals used in the sterilization flow out into the natural world, and there is a concern that it will have an adverse effect on the environment.

[0407]

2537 In addition, it is believed that the general bactericidal agents have more or less adverse effects on plant growth.

[0408]

2541 Therefore, the photocatalytic reaction water generated by the photocatalytic reaction water generator 1 according to the present invention is brought into contact with the rice seed to sterilize microorganisms and the like attached to the rice seed, and there is no need to worry about the adverse effect of the residual medicinal effect on the growth of the plant, and Can prevent adverse effects on the environment.

[0409]

2548 Moreover, since it is not necessary to add a chemical for the sterilization of rice seeds, it is possible to reduce the cost required for growing rice.

[0410]

2553 In this way, by bringing the photocatalytic reaction water generated by the photocatalytic reaction water generator 1 into contact with the washing object, it is safe for the human body and can be sterilized and washed while being in a hygienic state.

[0411]

2559 Industrial availability

[0412]

2563 In the photocatalytic reaction water generator described in claim 1, the photocatalyst body is irradiated with light from a light source to diffuse the generated active oxygen species in the water, thereby imparting the function of active oxygen species to the water, and using the water The oxidation reaction caused can carry out at least any one of microbial sterilization, parasite repellent, and protozoan repellent.

[0413]

2570 Specifically, by effectively dissociating active oxygen species with strong oxidizing ability, which have only appeared and acted on the surface of the photocatalyst body in the past, in the water, active oxygen species can be continuously and efficiently appearing, which is caused by the active oxygen species that rapidly migrate into the water. Strong oxidizing effect, even if the photocatalytic reaction water generator is miniaturized, it can generate a large amount of active oxygen species in the water, which can save electricity and be compact, and produce excellent sterilization, sterilization, cleaning, and flooding effects. The photocatalytic reaction of insect effect on water.

[0414]

2580 In addition, in the photocatalytic reaction water generator recited in claim 2, the photocatalyst body is arranged around the light source for exciting the photocatalytic reaction, and the light reflected from the light source can be effectively irradiated onto the photocatalyst body, so that the light reflected from the light source can be effectively irradiated on the photocatalyst body. Active oxygen species are fully generated in the water.

[0415]

2588 In addition, the photocatalytic reaction water generator recited in claim 3 includes a photocatalytic reaction tank, a feed pump that supplies water to the photocatalytic reaction tank, and a discharge circuit for discharging the photocatalytic reaction water from the photocatalytic reaction tank, and The photocatalytic reaction tank is equipped with a photocatalyst body for generating active oxygen in the water in the sealed container, a light source for radiating light for exciting the photocatalyst body, and a light source for irradiating the photocatalyst body in a closed container capable of storing water. The active oxygen species generated on the surface of the photocatalyst body is constituted by a diffusion means that diffuses the active oxygen species in the water, and the inner wall surface of the airtight container is made a mirror surface that reflects the above light. Thus, the photocatalytic reaction water can be continuously generated while reflecting the light. The light irradiated to the photocatalyst body and reaching the wall of the airtight container is irradiated on the photocatalyst body again, so that photocatalytic reaction water rich in active oxygen species can be generated.

[0416]

2603 In addition, in the photocatalytic reaction water generator described in claim 4, the light source for exciting the photocatalyst body uses sunlight and/or artificial light, and when the photocatalyst body is irradiated with sunlight, it can irradiate powerfully at low cost. In addition, when the photocatalyst body is irradiated with artificial light, ultraviolet rays of a predetermined wavelength can be selectively and effectively irradiated, and the photocatalyst body can be efficiently excited, thereby generating photocatalytic reaction water rich in active oxygen species.

[0417]

2612 In addition, in the photocatalytic reaction water generator recited in claim 5, when sunlight is used as a light source for exciting the photocatalyst body, the photocatalyst body can be directly irradiated in water using a reflector such as an optical fiber or a prism. The photocatalyst body is effectively irradiated with sunlight, so it is possible to efficiently generate photocatalytic reaction water rich in active oxygen species.

[0418]

2619 In addition, in the photocatalytic reaction water generator recited in claim 6, the ultraviolet irradiation lamp when using artificial light as a light source for exciting the photocatalyst body irradiates at least 350 to 370 nm wavelength ultraviolet rays, thereby enabling effective excitation The photocatalyst body can effectively generate photocatalytic reaction water rich in active oxygen species.

[0419]

2626 In addition, in the photocatalytic reaction water generating device recited in claim 7, the photocatalyst body is an organic or inorganic filter body, and the surface of the photocatalyst body is covered with a titanium dioxide thin film. Therefore, the surface area of the photocatalyst body can be enlarged, thereby being able to effectively Generate photocatalytic reaction water rich in active oxygen species.

[0420]

2633 In addition, in the photocatalytic reaction water generator recited in claim 8, the photocatalyst body is an aluminum-based metal filter body, and its surface is covered with a titanium dioxide thin film. Therefore, the photocatalyst body can be made flexible and capable of Gives good processability.

[0421]

2639 In addition, in the photocatalytic reaction water generator recited in claim 9, the photocatalyst body is a metal fibrous body with an aluminum oxide film formed on the surface in advance, and the surface is covered with a titanium dioxide film, so that the metal fibrous body is dense The titanium dioxide thin film can be formed so that active oxygen species can be efficiently generated and the durability of the photocatalyst body can be improved.

[0422]

2647 In addition, in the photocatalytic reaction water generator recited in claim 10, the aluminum oxide film of the metal fibrous body is heated to a temperature of half the melting point of the aluminum-based metal constituting the metal fibrous body at a rate of 5° C/min or less, and then It is formed by heating to the melting point of the aluminum-based metal, so that the aluminum oxide film can be densely formed on the metal fiber body, and the adhesion between the titanium dioxide film and the metal fiber body can be improved.

2653 That is, the durability of the photocatalyst body in water can be improved.

[0423]

2657 In addition, in the photocatalytic reaction water generator recited in claim 11, it is a glass fiber body, a ceramic fiber body, or a non-woven fabric, the surface of which is covered with a titanium dioxide film. Therefore, the surface area can be enlarged while being able to By manufacturing the photocatalyst body relatively inexpensively, the photocatalytic reaction water generator can be manufactured inexpensively.

[0424]

2664 In addition, in the photocatalytic reaction water generator described in claim 12, the titanium oxide constituting the titanium dioxide thin film includes an anatase type or rutile type crystal structure. When the titanium oxide includes an anatase type, the photocatalyst body can be carried out at a low temperature. It is possible to reduce the energy required for the firing, so that the photocatalytic reaction water generator can be manufactured inexpensively.

2669 In addition, when titanium oxide includes a rutile type, active oxygen species can be generated by irradiation with ultraviolet rays contained in sunlight, and active oxygen species can be generated even in the visible light range.

[0425]

2675 In addition, in the photocatalytic reaction water generating device recited in claim 13, the diffusion means for diffusing the active oxygen species in the water is an ultrasonic wave above 100 kHz caused by an ultrasonic vibrator and/or a water flow caused by a blade in the water, which moves the light The catalyst body and/or water can therefore rapidly release the active oxygen species generated on the surface of the photocatalyst body in the water.

[0426]

2683 In addition, in the photocatalytic reaction water generating device recited in claim 14, the water contacting the photocatalyst body is water whose oxygen concentration has been increased, so that a large amount of active oxygen species can be generated on the photocatalyst body, thereby being able to generate Photocatalytic reaction water rich in reactive oxygen species.

[0427]

2690 In addition, in the photocatalytic reaction water generator described in claim 15, the water whose oxygen concentration has been increased is produced by contacting at least any one of oxygen, air, and ozone with water. Therefore, the oxygen can be efficiently contained in the water. It can be dissolved in the ground and can produce a large amount of active oxygen species efficiently.

[0428]

2697 In the photocatalytic reaction water generator described in claim 16, the germicidal effect caused by the germicidal lamp irradiating ultraviolet rays with a wavelength of 254 to 265 nm occurs at the upstream or downstream or the same position of the germicidal effect caused by the photocatalytic reaction, thereby , It is possible to more effectively sterilize the microorganisms contained in the water contacting the photocatalyst body and the water generated in the photocatalytic reaction water generator.

DESCRIPTION CN201864596U

10 Floating body for water purification

[0001]

14 Technical field

[0002]

18 The utility model relates to a floating body for water purification. The floating body for water purification is used to be put into natural ponds, swamps, lakes, rivers or seas, or artificial swimming pools, reservoirs, channels, ditches, and fish tanks , Water tanks or fish ponds, etc. and float, degrade the organic matter in the water and effectively purify the water.

[0003]

25 Background technique

[0004]

29 When using a photocatalyst to purify water, oil, etc., a water purification material is used which is formed by supporting a photocatalyst on a porous material or other substrate.

[0005]

34 For example, Patent Document 1 proposes a technique of spreading a photocatalyst (water purification material) composed of a porous substrate with a photocatalyst on the surface of the water and making the photocatalyst (water purification material) float to use Light irradiation oxidizes and degrades organic matter to prevent the proliferation of harmful organisms.

[0006]

41 Patent Document 1: Japanese Patent Application Laid-Open No. 11-188269 (paragraph 0010, paragraph 0011, FIG. 1).

[0007]

46 Summary of the invention

[0008]

50 The more the photocatalyst is loaded, or the longer the period of directly receiving light such as ultraviolet light, the greater the oxidative degradation effect that can be expected in the water purification process using the photocatalyst as described above.

53 However, according to the photocatalyst disclosed in Patent Document 1, it is almost impossible to respond to visible light, and a long response time is also required, and the efficiency and economy are not good. Also, if water purification materials that are photocatalysts are spread on the water surface, it is very troublesome to recover these water purification materials. this is a problem.

[0009]

60 The utility model is researched and developed to solve the above-mentioned problems.

61 Its purpose is to obtain a floating body for water purification, which is such that it can easily carry a large amount of photocatalyst on the substrate, and has a high-efficiency water purification effect for a long period of time., Can be easily recycled.

[0010]

67 In order to achieve the above-mentioned object, the present invention relates to a floating body for water purification. The floating body for water purification is formed by storing a water purification material in a water-permeable and light-permeable bag or container. The body can float on the water; the above-mentioned water purification material is formed by loading the visible light-responsive photocatalyst in the perlite or Shirasu Balloon of the inorganic hollow foamed porous body (balloon) Of water purification materials.

[0011]

75 In addition, here, the "state of floating on the surface of the water" includes the case where the entire floating body for water purification is floating slightly below the surface of the water.

[0012]

According to the present invention, because the matrix is an inorganic hollow foamed porous body that is formed by baking and foaming volcanic eruptions, that is, pearlite or pozzolan foamed porous body, the matrix is lightweight, high-strength, and has It is non-flammable and can be used stably for a long period of time, making it suitable for water purification applications.

[0013]

In addition, the perlite or pozzolan foam porous body has many independent bubbles and many continuous bubbles, which can be used to load a large number of photocatalysts. The productivity and economy are excellent. It also has many air layers, so it can be used for water purification. The floating body has been floating on the water surface for a long period of time and directly receives light, can continue the degradation effect for a long period of time, and can prevent the proliferation of harmful organisms.
In particular, because the substrate is loaded with a visible light-responsive photocatalyst, the water purification material not only responds to ultraviolet light, but also responds to visible light.
Therefore, the oxidative degradation power is stronger and the degradation effect is higher.

[0014]

Furthermore, since the bag or container containing the water purification material is water-permeable, the bag or the container does not prevent the water purification material from coming into contact with water.
Moreover, because the bag or the container is light-transmissive, it does not hinder the response effect of the photocatalyst.
In addition, since the water purification material is contained in a bag or container, it has the advantages of being easily taken in and easily recovered from the surface of the water.

[0015]

Description of the drawings

[0016]

Fig. 1 is a perspective view showing a floating body for water purification according to the first embodiment with a part cut away.

[0017]

2 is a cross-sectional view showing an example of use of the floating body for water purification according to the first embodiment.

[0018]

Fig. 3 is a perspective view showing a floating body for water purification according to a second embodiment with a part cut away.

[0019]

126 4 is a cross-sectional view showing a usage example of the floating body for water purification according to the second embodiment.

[0020]

131 -Symbol Description-

[0021]

135 1-Floating body for water purification; 3-water purification material; 5-bag; 7-container; W1-water surface.

[0022]

139 detailed description

[0023]

143 Hereinafter, embodiments of the present invention will be described with reference to the drawings.

[0024]

147 (First embodiment)

[0025]

151 Fig. 1 shows a floating body 1 for water purification according to the first embodiment of the present invention.

153 The floating body 1 for water purification is formed by storing a water purification material 3 in a bag 5.

154 As shown in Fig. 2, the floating body 1 for water purification is used in a state where the floating body 1 for water purification is placed in water W and floating on the water surface W1.

[0026]

159 The water purification material 3 is formed by supporting a visible light-responsive photocatalyst with a perlite or pozzolan foamed porous body, which is an inorganic hollow foamed porous body as a matrix.

[0027]

164 The inorganic hollow foamed porous body is formed by baking and foaming the volcanic effluent, and examples thereof include a pozzolan foamed porous body, pearlite, and the like.

166 In these inorganic hollow foamed porous bodies, a multi-layered shell and voids are formed due to many independent cells and many continuous cells. Therefore, the photocatalyst easily penetrates into the voids, and the inorganic hollow foamed porous body can be loaded A lot of photocatalyst.

169 In addition, when the inorganic hollow foamed porous body (water purification material 3) carrying the photocatalyst is suspended on the water surface W 1, although the water W penetrates into the voids, a lot of air is retained in the voids. The penetration rate of the water W is limited, the water purification material 3 is not easy to sink for a long time, the water purification material 3 can float on the water surface W 1 for a long period of time, and the effect of the photocatalyst can be continued for a long period of time.

[0028]

177 As long as the specific gravity of the inorganic hollow foamed porous body is less than the specific gravity of water W, the inorganic hollow foamed porous body can float on the water surface W 1, and a high-efficiency oxidative degradation effect can be obtained. However, if the photocatalyst loading and water absorption are also considered Preferably, the bulk specific gravity of the inorganic hollow foamed porous body is about 0.05 to 0.5.

[0029]

185 The particle size and specific surface area of the inorganic hollow foamed porous body are not specifically specified, and can be selected according to the purpose. For example, an inorganic hollow foamed porous body with an average particle size of 20 μm to 5000 μm is used, preferably an average particle size of 200 μm to 5000 μm inorganic hollow foamed porous body.

[0030]

192 The visible light responsive photocatalyst is used as the photocatalyst because the visible light responsive photocatalyst not only responds to ultraviolet rays, but also responds to visible light, and therefore has a strong oxidative degradation ability.

[0031]

198 The visible light-responsive photocatalyst may be a photocatalyst that has photocatalytic activity and/or hydrophilicity under visible light. Examples include: iron-titanium oxide composite series photocatalysts, tungsten compounds, oxygen or Titanium oxide or titanium dioxide with elements such as nitrogen.

201 In particular, the iron-titanium oxide composite series photocatalysts, such as the iron-titanium oxide composite series photocatalysts produced by compounding iron components to the titanium oxide series photocatalysts, not only emit strong degradability under visible light, but also in ultraviolet It also emits strong degradability under light, so the oxidative degradability is strong, and the cost is also low. Therefore, iron-titanium oxide composite series photocatalysts are preferred.

[0032]

209 One type of visible light-responsive photocatalyst can be used alone, or multiple photocatalysts can be used in combination.

211 In addition, a combination of a visible light-responsive photocatalyst and a photocatalyst other than the visible light-responsive photocatalyst can be used as necessary for the effect to be obtained.

[0033]

216 The bag 5 is formed using a material that is permeable to water and light.

217 Since the water purification material 3 is housed in the water-permeable bag 5, the water W, such as sewage, which is the object of purification, comes into contact with the water purification material 3, and light also passes through, so that the degradation reaction progresses reliably.

[0034]

223 For example, as the bag 5, a bag made of polyethylene, polypropylene, nylon, metal mesh, non-woven fabric, or the like can be cited.

225 Here, the mesh size of the bag 5 is appropriately designed so that the water purification material 3 will not be discharged.

227 For example, when the average particle size of the water purification material 3 is 200 μm, in order to set the mesh size to 100 μm to 149 μm, a bag with a mesh number of about 178 to 100 may be selected.

229 Similarly, for example, when the average particle size of the water purification material 3 is 0.9 mm, in order to set the mesh size to 300 μm to 599 μm, a bag with a mesh number of about 61 to 27 can be selected.

231 In addition, if a non-woven fabric is used, a non-woven fabric having a mass per unit area of about 20 g/m 2 to 200 g/m 2 is preferable.

[0035]

236 The floating body 1 for water purification constructed as described above can be put into water (sewage) W, and the water purification material 3 can be floated on the water surface W1, and the oxidative degradation of the photocatalyst can be induced by light irradiation to degrade organic matter. Treatment, thereby purifying the water (sewage) W.

240 In addition, by forming the floating body 1 for water purification, the water purification material 3 can be recovered more easily than when the water purification material 3 is dispersed on the water surface W1 of the water (sewage) W and floated.

243 The water W includes water in natural ponds, swamps, lakes, rivers or seas, or artificial swimming pools, reservoirs, channels, ditches, fish tanks, tanks or fish ponds, etc., and the sewage includes polluted water Of these waters, but not limited to this.

[0036]

249 In addition, the water purification material 3 used in the present invention is a material that can make the water purification material 3 singly spread on the water surface W1 of the water (sewage) W and float, using light irradiation The oxidative degradation of the photocatalyst is induced to degrade the organic matter, thereby purifying the water (sewage) W.

[0037]

256 Therefore, according to the present invention, because the matrix constituting the water purification material 3 is an inorganic hollow foamed porous body that is formed by baking and foaming volcanic effluent, that is, pearlite or pozzolan foamed porous body, the matrix is light. It has high volume, high strength and non-combustibility, and the substrate can be used stably for a long period of time, which is very suitable for water purification purposes.

[0038]

264 In addition, the perlite or pozzolan foam porous body has many independent bubbles and many continuous bubbles, which can be used to load a large number of photocatalysts. The productivity and economy are excellent. It also has many air layers, so it can be used for water purification. The floating body 1 floats on the water surface W1 for a long period of time and directly receives light, can continue the degradation effect for a long period of time, and can prevent the proliferation of harmful organisms.

269 In particular, because the substrate is loaded with a visible light-responsive photocatalyst, the water purification material 3 not only responds to ultraviolet light but also responds to visible light.

271 Therefore, the oxidative degradation power is stronger and the degradation effect is higher.

[0039]

275 Furthermore, since the bag 5 containing the water purification material 3 is water-permeable, the bag 5 does not prevent the water purification material 3 from contacting the water (sewage) W.

277 Moreover, since the bag 5 is light-transmissive, it does not hinder the response effect of the photocatalyst.

278 In addition, since the water purification material 3 is contained in the bag 5, it has an advantage that it can be easily taken in and can be easily recovered from the water surface W1.

[0040]

283 In order to confirm the above, the following experiment was carried out.

[0041]

287 -Experimental example-

[0042]

291 The pozzolan (Shirasu) was foamed in a baking furnace, and a matrix formed of a pozzolan foamed porous body with a volumetric specific gravity of 0.10 and an average particle size of 200 μm was obtained.

[0043]

296 The pozzolan foam porous body matrix is loaded with iron-titanium oxide composite series photocatalysts, and water purification material 3 is obtained.

[0044]

301 The water purification material 3 was housed in a polyethylene bag 5 having a mesh size of 100 μm and a mesh number of 178, which was water-permeable and light-permeable, to produce a water purification floating body 1.

[0045]

307 ＜Decolorization Test＞

[0046]

311 The floating body 1 for water purification was floated in a blue methylene blue aqueous solution that had been placed in a water tank, and it was placed outdoors in a good weather. After seven hours, the decolorization was observed with human eyes.

314 As a result, the aqueous solution was decolorized and became colorless, and the oxidative degradation effect of the photocatalyst was confirmed. In addition, the water purification material 3 can be easily recovered by simply taking out the water purification floating body 1 from the water tank.

[0047]

320 (Second embodiment)

[0048]

324 3 and 4 show the floating body 1 for water purification according to the second embodiment.

325 The floating body 1 for water purification is formed by storing a water purification material 3 in a box-shaped container 7 having a rectangular parallelepiped.

327 As shown in FIG. 4, the floating body 1 for water purification is used in a state where the floating body 1 for water purification is put in the water W and floating on the water surface W1.

[0049]

332 The entire container 7 is formed of a transparent resin material so as to be able to transmit light, and the bottom surface 9 submerged in water is formed of a mesh or non-woven fabric or the like so as to be able to transmit water.

[0050]

338 As a supplement, the entire container 7 may be water-permeable; a part of the container 7 may be transparent, and the other part may be opaque.

340 In addition to resin, the container 7 may be made of wood or metal.

[0051]

344 The water purification material 3 housed in the container 7 is the same as the water purification material 3 in the first embodiment.

[0052]

349 Therefore, as in the first embodiment, the floating body 1 for water purification according to the second embodiment can be put into water (sewage) W, and the water purification material 3 can be floated on the water surface W1 to utilize light The irradiation induces the oxidative degradation of the photocatalyst to degrade the organic matter and thereby purify the water (sewage) W. Therefore, the same actions and effects as those explained in the first embodiment can be obtained.

[0053]

357 -Industrial applicability-

[0054]

361 The utility model is useful as a floating body for water purification that floats on the water surface and degrades the organic matter in the water to effectively purify the water.

US006803023B1

(12) United States Patent
Ohmori et al.

(10) Patent No.: US 6,803,023 B1
(45) Date of Patent: Oct. 12, 2004

(54) COMPOSITE STRUCTURE FOR DEODORIZATION OR WASTEWATER TREATMENT

(75) Inventors: **Masahiro Ohmori**, Chiba (JP); **Akihiko Kotera**, Kawasaki (JP); **Hidenori Nakamura**, Chiba (JP); **Masayoshi Nobiki**, Chiba (JP)

(73) Assignee: **Showa Denko Kabushiki Kaisha**, Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 772 days.

(21) Appl. No.: **09/677,188**

(22) Filed: **Oct. 2, 2000**

Related U.S. Application Data

(60) Provisional application No. 60/162,231, filed on Oct. 29, 1999.

(30) **Foreign Application Priority Data**

Oct. 1, 1999 (JP) 11-282060

(51) **Int. Cl.**^{7} **B01D 50/00**; B01D 53/34

(52) **U.S. Cl.** **422/177**; 422/184.1

(58) **Field of Search** 422/177, 184.1; 252/186.2

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,541,096 A	*	7/1996	Nomura et al.	435/176
6,284,314 B1	*	9/2001	Kato et al.	427/245
6,342,128 B1	*	1/2002	Tabatabaie-Raissi et al.	204/157.15

FOREIGN PATENT DOCUMENTS

JP	07-148434	6/1995	B01J/35/02
JP	10-028875	2/1998	B01J/35/08
JP	10-219236	8/1998	C09K/3/32
JP	10-249210	9/1998	B01J/35/02
JP	11-188269	7/1999	B01J/35/02
WO	WO-92/08768	5/1992	C09K/3/32

* cited by examiner

Primary Examiner—M. Alexandra Elve

(74) *Attorney, Agent, or Firm*—Sughrue Mion, PLLC

(57) **ABSTRACT**

A composite structure having a photocatalytic function and can be used for deodorization and wastewater treatment, comprising a foamed or porous substrate having apparent specific gravity of 0.9 to 0.01 and finely divided titanium oxide particles having a photocatalytic function which are adhered onto the surface of the foamed or porous substrate. Gas such as air having offensive odor or wastewater is allowed to be in contact with the composite structure having a photocatalytic function, whereby smelly or harmful substances contained in the gas or wastewater are decomposed.

15 Claims, No Drawings

COMPOSITE STRUCTURE FOR DEODORIZATION OR WASTEWATER TREATMENT

CROSS-REFERENCE TO RELATED APPLICATION

This application is an application filed under 35 U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C.§119(e)(1) of the filing date of Provisional Application No. 60/162,231 filed Oct. 29, 1999, pursuant to 35 U.S.C. §111(b).

BACKGROUND OF THE INVENTION

(1) Field of the Invention

This invention relates to deodorization and/or wastewater treatment utilizing a photocatalytic reaction. More specifically it relates to a composite structure having a photocatalytic function, which is capable of decomposing smelly or harmful substances contained in air or other gas and/or wastewater effectively, and to the utilization thereof.

(2) Description of the Related Art

In recent years, researches and developments have been made actively for utilizing a photocatalytic function possessed by titanium oxide and other metal oxides. That is, these metal oxides such as titanium oxide and the like have excellent functions for preventing contamination by removing harmful substances, purifying the air by decomposing ammonia, a sulfur compound and the like contained in the air, sterilizing a kind of bacteria and so on. Therefore, applications of these metal oxides are expected in various fields.

Finely divided titanium oxide particles having a photocatalytic function (photocatalytic property), (hereinafter, photocatalytic titanium oxide particles are simply referred to as "titanium oxide" when appropriate), are used in a variety of forms such as bulk particles, sols, thin films and the like depending on purposes. However, in the field of deodorization and wastewater treatment, titanium oxide particles are usually used not alone, but used in combination with a substrate such as, for example, glass, ceramics or the like in such a form supported on the substrate in many cases. Many methods of supporting titanium oxide particles on a substrate have been proposed. In order to enhance adherence of titanium oxide particles to a substrate and to prevent detachment of titanium oxide particles from the substrate, the following methods are generally employed: (i) after a titanium oxide coating film being formed on a substrate, heat-treating the film to sinter on the substrate at high temperatures; (ii) impregnating a dispersion of titanium oxide particles into pores of a porous substrate; and (iii) forming a titanium oxide coating film on a substrate through a binder.

However, in the case of method (i) of heat-treating a titanium oxide coating film to sinter on a substrate at a high temperature, the titanium oxide particles grow largely to lower their specific surface area during heat treatment. Consequently, their photocatalytic function becomes decreased. In the case of method (ii) of impregnating a dispersion of titanium oxide particles into pores of a porous substrate, it is difficult to prevent sufficiently the detachment of the titanium oxide particles. The method (iii) of forming a titanium oxide coating film on a substrate through a binder is generally employed. However, this method is still unsatisfactory.

SUMMARY OF THE INVENTION

Considering the aforementioned background art, an object of the present invention is to provide a composite structure

for deodorization and/or wastewater treatment having finely divided titanium oxide particles having a photocatalytic function, supported on a substrate, which exhibits great photocatalytic activity, thereby having improved deodorization and/or wastewater-treatment properties, in general, the finely divided titanium oxide particles of which are hardly detached from the substrate to exhibit an enhanced photocatalytic property over a long period of time.

The present inventors made extensive researches into a composite structure having a photocatalytic function, which is capable of decomposing effectively smelly or harmful substances contained in the air or wastewater. As a result, it was found that the above-objects can be satisfied by a composite structure containing finely divided titanium oxide particles adhered to the surface of a foamed or porous substrate having small apparent specific gravity. The present invention has been completed on the basis of the above-finding.

Thus, in one aspect of the present invention, there is provided a composite structure, which has a photocatalytic function and can be used for deodorization and wastewater treatment, comprising a foamed or porous substrate having apparent specific gravity of 0.9 to 0.01 and finely divided titanium oxide particles which are adhered onto the surface of the foamed or porous substrate.

In another aspect of the present invention, there is provided a method for deodorizing air or other gas having offensive odor or treating wastewater, comprising the step of allowing air or other gas having offensive odor or wastewater to be in contact with a composite structure having a photocatalytic function, which comprises a foamed or porous substrate having apparent specific gravity of 0.9 to 0.01 and finely divided titanium oxide particles adhered onto the surface of the foamed or porous substrate, whereby smelly or harmful substances contained in the air or other gas or wastewater are decomposed.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The finely divided titanium oxide particles having a photocatalytic function used in the invention are not particularly limited. These particles can be commercially available titanium oxide powders. However, the finely divided titanium oxide particles are preferably in the form of a sol which can be obtained in the process of synthesizing a titanium oxide as described below.

It is known that titanium oxide has forms of anatase, rutile and brookite. A desirable titanium oxide is in a form of finely divided particles since the titanium oxide exhibiting a high photocatalytic property is desired. However, it is difficult to prepare titanium oxide particles having an average particle diameter of smaller than about 0.005 μm. Accordingly, the average particle diameter usually ranges from about 0.005 μm to 0.3 μm, and preferably from about 0.01 μm to about 0.1 μm. The specific surface area of the titanium oxide particles preferably at least about 20 m^2/g, and more preferably ranges from about 50 m^2/g to about 300 m^2/g.

Known processes for preparing finely divided titanium oxide particles include neutralizing/hydrolyzing titanyl sulfate or titanium tetrachloride, and hydrolyzing a titanium alkoxide compound.

Considering that a formed titanium oxide is highly active and its production cost is low, titanyl sulfate and titanium tetrachloride are desirably used as a raw material. A method of hydrolyzing a titanium alkoxlde compound is advantageous in that it can provide a very small sol of titanium oxide having excellent powder properties. However, this method has a very high production cost as compared with the method employing titanyl sulfate or titanium chloride as a raw material.

By drying the aqueous sol obtained by hydrolysis, there can be obtained fine titanium oxide powders. The powders are then dispersed again in water or a mixture of water and an organic solvent to obtain coating liquid for forming a thin film of titanium oxide particles. However, the coating liquid thus obtained is not preferable for the following reasons. The titanium oxide which is a hydrolyzed product aggregates easily because of its high surface activity which increases in inverse proportion to its particle size. Therefore, it is difficult to disperse in water again after drying. Further, the thin film obtained from the titanium oxide particles is deteriorated in transparency and a photocatalytic property, and weakly bonded to a substrate. Accordingly, the aqueous sol formed by hydrolysis is used as a coating liquid, preferably, after admixing a binder therewith, if desired, through steps of removing dissolved chlorine, and concentrating by dehydration or diluting with water. The aqueous sol may be used as a coating liquid, if desired, by incorporating an organic solvent therein, to make a dispersion of finely divided titanium oxide particles in a mixture of water and organic solvent.

A dispersing medium for use in preparing the above preferable titanium oxide sol is water or a mixture of water and a hydrophilic organic solvent. As examples of the hydrophilic organic solvent, there can be mentioned alcohols such as methanol, ethanol and ethylene glycol; ketones such as acetone; esters such as ethyl acetate; and cellosolves such as ethyl cellosolves.

A preferable titanium oxide sol is a water-dispersed titanium oxide sol disclosed in. Japanese Unexamined Patent Publication (Kokai) No. H11-43327. By using this sol, a titanium oxide thin film having excellent transparency and peel strength can be formed on a foamed or porous substrate.

When an aqueous titanium tetrachloride solution having a concentration of about 0.05 mol/l to about 10 mol/l while the aqueous solution is refluxed, a titanium oxide sol having a concentration of about 0.05 mol/l to about 10 mol/l is obtained. The as-obtained sol can be used, as it is, as a coating solution containing titanium oxide at a desired concentration. Alternatively, by adding water to the sol as obtained by hydrolysis or by concentrating the as-obtained sol, the concentration of titanium oxide in the sol can be varied within the above-mentioned preferred range.

If desired, a stabilizer for preventing aggregation can be added to the sol obtained by hydrolysis. The stabilizers include, for example, a variety of surfactants such as a commonly used non-ionic surfactants. The amount of the stabilizer used is generally in the range of about 0.1% to 1% by weight based on the aqueous sol.

To enhance a film-forming property, a small amount, for example, about 10 ppm to about 10,000 ppm of a water-soluble polymer can be incorporated in the titanium oxide sol. The water-soluble polymers used include, for example, polyvinyl alcohol, methyl cellulose, ethyl cellulose, calboxycellulose and starch.

By the term "foamed or porous substrate" used herein, which is used for supporting finely divided titanium oxide particles on a composite structure of the invention, we mean a substrate having a multiplicity of pores communicating with the surface thereof. The substrate may have closed cells provided that it has open cells. There is no special limitation of shapes and materials of the foamed or porous substrate. However, substrates having a spherical shape or analogous shapes are preferably used in view of good handling property. The average particle diameter of the spherical substrate preferably in the range of about 1 mm to about 10 mm.

As specific examples of the foamed or porous substrates, there can be mentioned expanded obsidian, or foamed or porous perlite, a rounded product of small-gage wire, ceramic fiber or the like, and a foamed cement product. Among them, expanded obsidian and a foamed or porous perlite are preferred, because it can support a large amount of titanium oxide particles thereon and the supported titanium oxide particles are hardly detached therefrom. The expanded obsidian, and foamed or porous perlite are usually prepared by heat-treating pulverized obsidian or perlite at a temperature of about 500° C. to about 1,000° C.

The foamed or porous substrate has an apparent specific gravity ranging from about 0.9 to about 0.01, preferably from about 0.7 to about 0.01, and more preferably about 0.4 to about 0.01. A composite structure having a small apparent specific gravity can be obtained by using the foamed or porous substrate having such a small apparent specific gravity. When the composite structure having such a small apparent specific gravity is used for deodorization of a gas with offensive odor or treatment of wastewater, the composite structure can float or is fluidized in the air, or in and on wastewater. As a result, the contact of the composite structure with smelly gas or wastewater is greatly enhanced. Thus, a deodorization efficiency is increased. In the case of treating wastewater, the composite structure floats on the wastewater, therefore, UV irradiation efficiency is increased, and the effect of a wastewater treatment is improved. A foamed or porous substrate having a specific gravity exceeding about 0.9 cannot fully exhibit the aforementioned features as a material for deodorization and wastewater treatment. Also, a foamed or porous substrate having an apparent specific gravity of smaller than about 0.01 generally has a low strength and a poor shape-retention.

In the case of supporting finely divided titanium oxide particles on a foamed or porous substrate, to enhance the adhesion of the titanium oxide particles to the substrate, it is possible to sinter by heat treatment, to adhere with a binder, or to impregnate into pores of the substrate. Of these, in view of a photocatalytic property of the composite structure and operability for preparing the composite structure, adhering with a binder is the most effective and preferable.

As a binder, a phosphor-containing compound, a zirconium-compound and a silicon-containing compound are preferably used. These compounds may be used either alone or as a combination of at least two thereof.

As specific examples of the zirconium-containing compound, there can be mentioned water-soluble zirconium compounds such as zirconium oxychloride, zirconium hydroxychloride, zirconium nitrate, zirconium sulfate, zirconium acetate and zirconium ammonium carbonate; and organic solvent-soluble zirconium compounds such as zirconium propionate. Further, complexes of a zirconium compound having at least one of hydroxyl, carbonate and alkylcarboxyl groups and its polymer can also be used. The amount of the zirconium compound as a binder can be selected appropriately from the range of about 3 to about 200 parts by weight based on 100 parts by weight of the titanium oxide particles.

AS specific examples of the phosphor-containing compound, there can be mentioned orthophosphoric acid, pyrophosphoric acid, aluminum phosphate and polyphosphoric acid. The amount of the phosphor-containing compound as a binder can be selected appropriately from the range of about 1 to about 100 parts by weight based on 100 parts by weight of the titanium oxide particles.

As specific examples of the silicon-containing compound, there can be mentioned water glass; silicates such as calcium silicate, tetrachlorosilicate, tetrabromosillcate, tetraethylsilicate, tetramethylsilicate, tetra-n-propoxysilicate, tetrabuthoxysilicate, methyltrimethylsilicate, methyltriethylsilicate, methyltributoxysilicate, ethyltrimethylsilicate, ethyltriethylsilicate, phenyltrimethylsilicate, phenyltriethylsilicate, dimethyldimethylsilicate, dimethyldiethylsilicate, phenylmethyldimethylsilicate and phenylmethyldiethylsilicate; these hydrolysates; and their dehydrates. The amount of the silicon-containing compound as a binder can be selected appropriately from the range of about 10 to about 100 parts by weight based on 100 parts by weight of the titanium oxide particles.

For the formation of a film by coating an aqueous sol of finely divided titanium oxide particles or a coating liquid comprising the finely divided titanium oxide particles and a binder on a foamed or porous substrate, the following methods are employed: impregnating the substrate with the sol or coating liquid; spraying the sol or coating liquid on the substrate; coating the substrate with the sol or coating liquid by a brushing and other coating methods. Among them, a method of impregnating the substrate with the titanium oxide-containing sol or coating liquid is preferable. The amount of the sol or coating liquid applied on the substrate is in the range of about 0.01 mm to about 0.2 mm expressed in terms of a thickness of the liquid coating film.

A target thin coating film can be obtained by drying to remove a solvent after coating, and can be used, as it is, for a catalyst. However, heat treatment is generally carried out to enhance the adhesion of the titanium oxide particles to the substrate. The heat-treating temperature ranges commonly from about 20° C. to about 200° C. preferably from about 20° C. to about 150° C. The heat-treating time is in the range of about 5 minutes to about 30 minutes.

If the foamed or porous substrate is made of a heat-resistant material such as metal or ceramic material, a thin coating film after being formed can be sintered. Thereby, the thin coating film becomes adhered to the substrate more strongly, and increases its hardness still more. A preferable sintering temperature is about 200° C. or higher. However, sintering under severe conditions must be avoided because sintering sometimes causes growth of particles during heat treatment in the course of sintering. Thus, the specific surface area of the titanium oxide particles may be decreased, and the photocatalytic property is possibly deteriorated. Generally, the highest sintering temperature may be decided depending on the heat resistance of the foamed or porous substrate. Usually the sintering temperature is determined commonly up to about 800° C. Sintering may be performed in any atmosphere, of course, in the air. The sintering time is not particularly limited, but usually ranges from about 1 minute to about 60 minutes. The thickness of the thin film obtained by sintering ranges from about 0.02 μm to about 1.0 μm when the amount of the sol or coating liquid is as mentioned above.

A composite structure of the invention can be utilized for deodorizing air or other gas with offensive odor and/or treating wastewater, i.e., for decomposing smelly or harmful substances contained in the gas or the wastewater.

In the case when using the composite structure as a deodorant, deodorization for indoor space can be attained by placing the composite structure in a netted bag or the like, and then by irradiating the composite structure with UV rays of black light. A deodorizing effect will be increased by stirring the air in the indoor space with a fan or the like. Further, the highest deodorizing effect will be obtained by using a deodorizing apparatus designed so as to whirl up the composite structure irradiated with UV rays, because frequency of bringing the composite structure into contact with smelly components is increased.

In the case when using the composite structure to decompose harmful substances contained in wastewater, the composite structure may be allowed to float on a flow of wastewater containing harmful substances. If desired, adequate artificial light source such as a UV lamp or the like can be provided in place of or in addition to the sunlight. In order to prevent sink of the composite structure into wastewater, the composite structure can be placed on a netted receiver pan. Otherwise, the composite structure contained in a netted bag can be provided in a wastewater treatment machine so as to bring the composite structure into contact with a flow of wastewater.

The present invention will now be specifically described by way of the following working examples, which should not be construed as limiting the scope of the invention. In the working examples % represents percent by weight unless otherwise specified.

Preparation of Titanium Oxide Sol

A reaction vessel equipped with a reflux condenser was charged with 954 ml of distilled water, followed by heating up to 95° C. Then, 46 ml of an aqueous solution of titanium tetrachloride (Ti content: 16.3%, specific gravity: 1.59, purity: 99.9%) was dropwise added into the reaction vessel at a rate of about 5 ml/min, while keeping the stirring rate of the reaction mixture in the vessel at about 200 rpm. At this time, care was taken so that the temperature of the reaction liquid would not fall. Consequently, the concentration of titanium tetrachloride in the reaction liquid was 0.25 mol/l (which corresponds to 2% in terms of the weight of titanium oxide particles).

In the reaction vessel, the reaction liquid started to become turbid immediately after the beginning of dropwise addition. However, the reaction liquid was kept at the temperature as it was. After the dropwise addition was completed, the temperature was raised up to about a boiling point (104° C.) by heating. The reaction liquid was held for 60 minutes in this state to terminate the hydrolysis reaction completely. After cooling, residual chlorine produced by the reaction was removed by electrodialysis to indicate pH=1.9 (chloride ion content: 600 ppm). Thereafter, as an auxiliary for film-forming, 0.1%, based on the weight of the produced titanium oxide, of polyvinyl alcohol which is a water-soluble polymer was added to prepare a titanium oxide sol (TiO_2 content: about 0.25 mol/1). This sol was stable, and sedimentation of the produced titanium oxide particles was not observed even after the lapse of more than 30 days.

A part of the thus-prepared sol was filtered and then dried at 60° C. in a vacuum oven to prepare a titanium oxide powder. Quantitative analysis of the titanium oxide powder by the X-ray diffraction method revealed that the ratio of (a peak intensity of brookite-type 121 face) to (a peak. intensity where the three types of crystals are superimposed) was 0.38; and the ratio of (a main peak intensity of rutile-type) to (a peak intensity where the three types of crystals are superimposed) was 0.05. These ratios tell that the produced titanium oxide was crystalline and contained about 70.0% of brookite type, about 1.2% of rutile type and about 28.8% of anatase type. When the titanium oxide particles were observed by a transmission-type electron microscope, the average particle diameter of primary particles was 0.015 μm. The BET measurement showed that the specific surface area of the particles was 100 m^2/g.

Preparation of Coating Liquid B

To the foregoing titanium oxide sol, 5% (in terms of the weight of SiO_2), based on the weight of the titanium oxide content, of tetramethyl-orthosilicate [$Si(OCH_3)_4$] was added as a binder to prepare a titanium oxide coating liquid B.

Preparation of Coating Liquid A

A titanium oxide sol was prepared in the same manner as for the preparation of the coating liquid B, except that conditions of condensation and electrodialysis were changed to obtain an aqueous titanium oxide sol of pH 5.5 containing 11% of titanium oxide particles. To 36.6 g of this aqueous titanium oxide sol, an aqueous solution containing 2.2 g of zirconium hydroxychloride (20% in terms of ZrO_2 weight) and 11.4 g of pure water were added to prepare a coating liquid A.

EXAMPLE 1

Into 100 ml of coating liquid A, 100 g of "Fuyolite #2" (expanded obsidian supplied by Fuyo Perlite Co.: apparent specific gravity: 0.10–0.16 g/cm^3, average particle diameter: 1.2–2.5 mm) as a substrate for supporting a titanium oxide thereon was placed. After being stirred well, the mixture was allowed to stand for 1 hour so as to have a full affinity for the substrate. Then, the substrate was taken out by filtration, then dried and heated at 150° C. for 1 hour. Thus, titanium oxide particles contained in the coating liquid A was supported on the substrate to prepare a composite structure. The amount of the titanium oxide supported was about 2% based on the weight of substrate weight.

The photocatalytic property (deodorizing property) of the composite structure having supported thereon the titanium oxide particles, thus obtained, was evaluated by the following way. At first, 100 g of the composite structure was put into 100 ml of pure water to be thereby washed with water for removing dust and unreacted residue. About 0.19 of the composite structure was spread uniformly in a cylindrical perforated cell having an area of 8.5 cm^2 to set the same in the central portion inside a chamber of 1.3 liter in volume made of Pyrex glass provided with a fan. Then, 500 ppm of acetaldehyde that is a smelly constituent was injected into the chamber. Thereafter, while whirling the inner air at an air flow rate of 0.1 l/min., the cell was irradiated with UV rays by a UV lamp (light intensity at 365 nm: 0.4 mW/cm). The deodorizing property was investigated by decomposition percentage calculated from the residual amount of acetaldehyde after 60 minute UV irradiation. The results are shown in Table 1.

Then, the wastewater treatment property of the composite structure was evaluated. Measurement was carried out by the following method. Water dyed with an organic colorant (red) was taken as wastewater. 100 ml of this wastewater was poured into a wide-mouthed bottle. Then, 1 g of the composite structure was incorporated into the wastewater. Thereafter, the wastewater was irradiated with UW rays lamp by a UV lamp (light., intensity at liquid level: 0.2 mW/cm^2 at 365 nm) located above the bottle. Color change (fading degree) of the wastewater was observed by the naked eyes and evaluated according to the following three ratings 1, 2 and 3.

Rating 1: fading was observed, i.e., wastewater was almost changed into crystal-clear water.

Rating 2: fading was observed admitted to some extent, but remaining color was observed.

Rating 3: fading was not admitted.

The results are shown in Table 1.

EXAMPLE 2

The same procedure as that of Example 1 was repeated except that the substrate was replaced by "Fuyolite #.1" (expanded obsidian supplied by Fuyo Perlite Co.: apparent specific gravity: 0.18–0.26 g/cm^3, average particle diameter: 0.6–1.2 mm) with all other conditions remaining the same to obtain a composite structure. The deodorizing property and the wastewater treatment property were evaluated by the same way as described in Example 1. The results are shown in Table 1.

EXAMPLE 3

The same procedure as that of Example 1 was repeated except that coating liquid B was used in place of coating liquid A with all other conditions remaining the same to prepare a composite structure. The deodorizing property and the wastewater treatment property were evaluated in the same manner as described in Example 1. The results were shown in Table 1.

COMPARATIVE EXAMPLE 1

The same procedure as that of Example 1 was repeated except that volcanic glass (apparent specific gravity: about 2.4) was used as a substrate instead of expanded obsidian used in Example 1 with all other conditions remaining the same to prepare a composite structure having supported thereon a titanium oxide. The deodorizing property and the wastewater treatment property of the composite structure were evaluated in the same manner as described in Example 1. The results are shown in Table 1.

TABLE 1

Examples/ Comparative Example	Coating liquid	Deodorizing performance (Decomposition %)	Wastewater treatment capacity (Rating)
Example 1	A	50	1
Example 2	A	60	1
Example 3	B	40	1
Com. Ex. 1	A	20	2

The composite structure of the invention comprises a foamed or porous substrate with a small specific gravity having supported thereon finely divided titanium oxide particles. Accordingly, when it is used for deodorization, it can float or is fluidized in the air or water to enhance the contact of the composite structure with gas having offensive odor. Therefore, a deodorizing property can be improved. Also, when it is used for wastewater treatment, the composite structure floats on the surface of the wastewater. Consequently, irradiating efficiency of UV rays is enhanced, leading to improvement of a wastewater treatment property. As such, a great photocatalytic activity can be exhibited. Further, generally, titanium oxide particles are hardly detached from the substrate. Accordingly, photocatalytic function can continue for a longed period of time.

What is claimed is:

1. A composite structure having a photocatalytic function which can be used for deodorization and wastewater treatment, comprising a foamed or porous substrate having apparent specific gravity of 0.9 to 0.01 and finely divided titanium oxide particles having an average particle diameter of 0.005 μm to 0.3 μm which are adhered onto the surface of the foamed or porous substrate.

2. The composite structure according to claim 1, wherein said composite structure is capable of floating on water.

3. The composite structure according to claim 1, wherein the finely divided titanium oxide particles are adhered to the substrate through a binder.

4. The composite structure according to claim 3, wherein the binder is at least one compound selected from the group consisting of phosphor-containing compounds, zirconium-containing compounds and silicon-ontaining compounds.

5. The composite structure according to claim 1, wherein the substrate is made of at least one material selected from the group consisting of expanded obsidian, and foamed or porous perlite.

6. A method for deodorizing gas having offensive odor or treating wastewater, comprising the step of allowing gas having offensive odor or wastewater to be in contact with a composite structure having a photocatalytic function, which comprises a foamed or porous substrate having apparent specific gravity of 0.9 to 0.01 and finely divided titanium oxide particles having an average particle diameter of 0.005 μm to 0.3 μm which are adhered onto the surface of the foamed or porous substrate, whereby smelly or harmful substances contained in the gas or wastewater are decomposed.

7. The method for deodorizing air having offensive odor or treating wastewater according to claim 6, wherein the air having offensive odor or wastewater is allowed to be in contact with the composite structure having a photocatalytic function, which floats on water.

8. The method for deodorizing air having offensive odor or treating wastewater according to claim 6, wherein the finely divided titanium oxide particles are adhered to the substrate through a binder.

9. The method for deodorizing air having offensive odor or treating wastewater according to claim 8, wherein the binder is at least one compound selected from the group consisting of phosphor-containing compounds, zirconium-containing compounds and silicon-containing compounds.

10. The method for deodorizing air having offensive odor or treating wastewater according to claim 6, wherein the substrate is made of at least one material selected from the group consisting of expanded obsidian, foamed or porous perlite, a rounded product of wire, ceramic fiber, and a foamed cement product.

11. The composite structure according to claim 3, wherein the binder is a water-soluble zirconium compound.

12. The composite structure according to claim 11, wherein the water-soluble zirconium compound is selected from the group consisting of zirconium nitrate, zirconium sulfate, zirconium acetate, zirconium ammonium carbonate, zirconium propionate, complexes of a zirconium compound having at least one of hydroxyl, carbonate and alkylcarboxyl groups, and polymers thereof.

13. The composite structure according to claim 3, wherein the binder is a silicate.

14. The composite structure according to claim 1, wherein the foamed or porous substrate has an apparent specific gravity of 0.7 to 0.01.

15. The composite structure according to claim 1, wherein the foamed or porous substrate has an apparent specific gravity of 0.4 to 0.01.

* * * * *

US 20130118995A1

(19) **United States**

(12) **Patent Application Publication**

Hawkins, II et al.

(10) **Pub. No.: US 2013/0118995 A1**

(43) **Pub. Date: May 16, 2013**

(54) **SOLAR-ACTIVATED PHOTOCHEMICAL PURIFICATION OF FLUIDS**

(75) Inventors: **R. Thomas Hawkins, II**, Aloha, OR (US); **Mark D. Owen**, Beaverton, OR (US)

(73) Assignee: **UVCleaning Systems, Inc.**, Beaverton, OR (US)

(21) Appl. No.: **13/811,615**

(22) PCT Filed: **Jul. 22, 2011**

(86) PCT No.: **PCT/US11/45089**

§ 371 (c)(1), (2), (4) Date: **Jan. 22, 2013**

Related U.S. Application Data

(60) Provisional application No. 61/367,305, filed on Jul. 23, 2010.

Publication Classification

(51) **Int. Cl.**
B01J 35/00 (2006.01)

(52) **U.S. Cl.**
CPC ***B01J 35/004*** (2013.01)
USPC **210/748.14**; 210/251; 422/186; 422/119

(57) **ABSTRACT**

Disclosed herein are embodiments of a solar-activated photochemical fluid treatment system, some of which comprise a fluid vessel, a porous enclosure positioned inside of the fluid vessel, a porous enclosure positioned inside of the fluid vessel, a fiber substrate contained within the enclosure, and a semiconductor photocatalyst coupled to the fiber substrate. The fluid vessel can be configured to contain a fluid in contact with the photocatalyst such that the fluid treatment system, responsive to solar radiation applied to the photocatalyst and to the fluid in the vessel, induces photochemical modification of contaminants and living organisms in the fluid. Related methods are also disclosed.

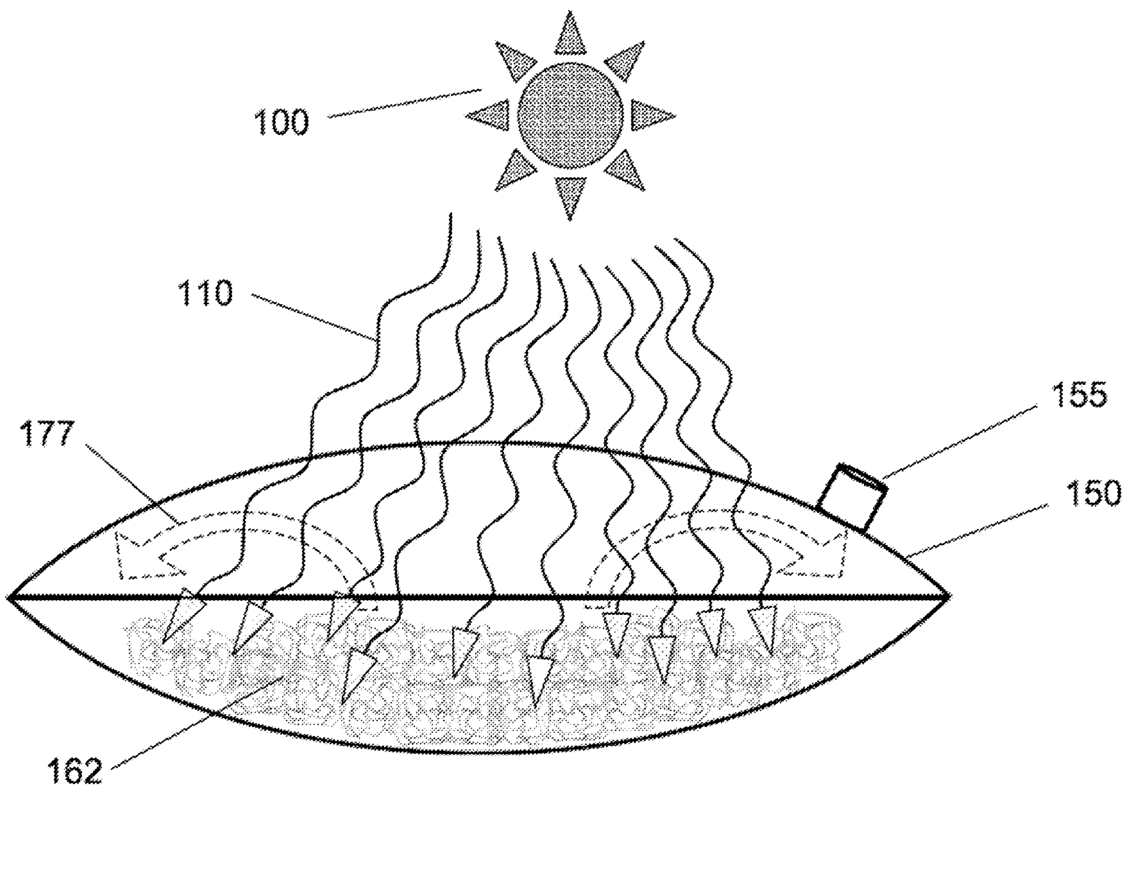
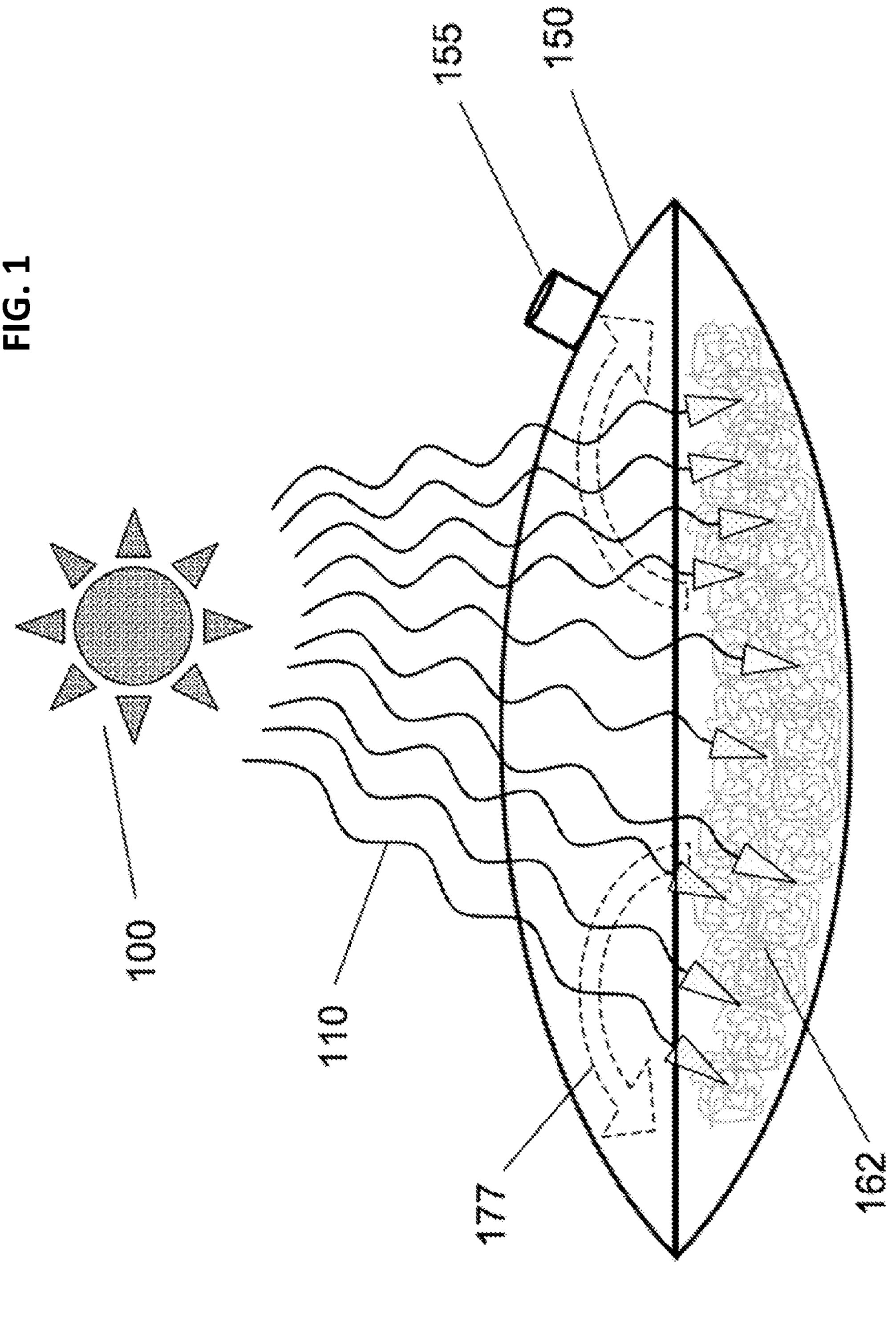


FIG. 1



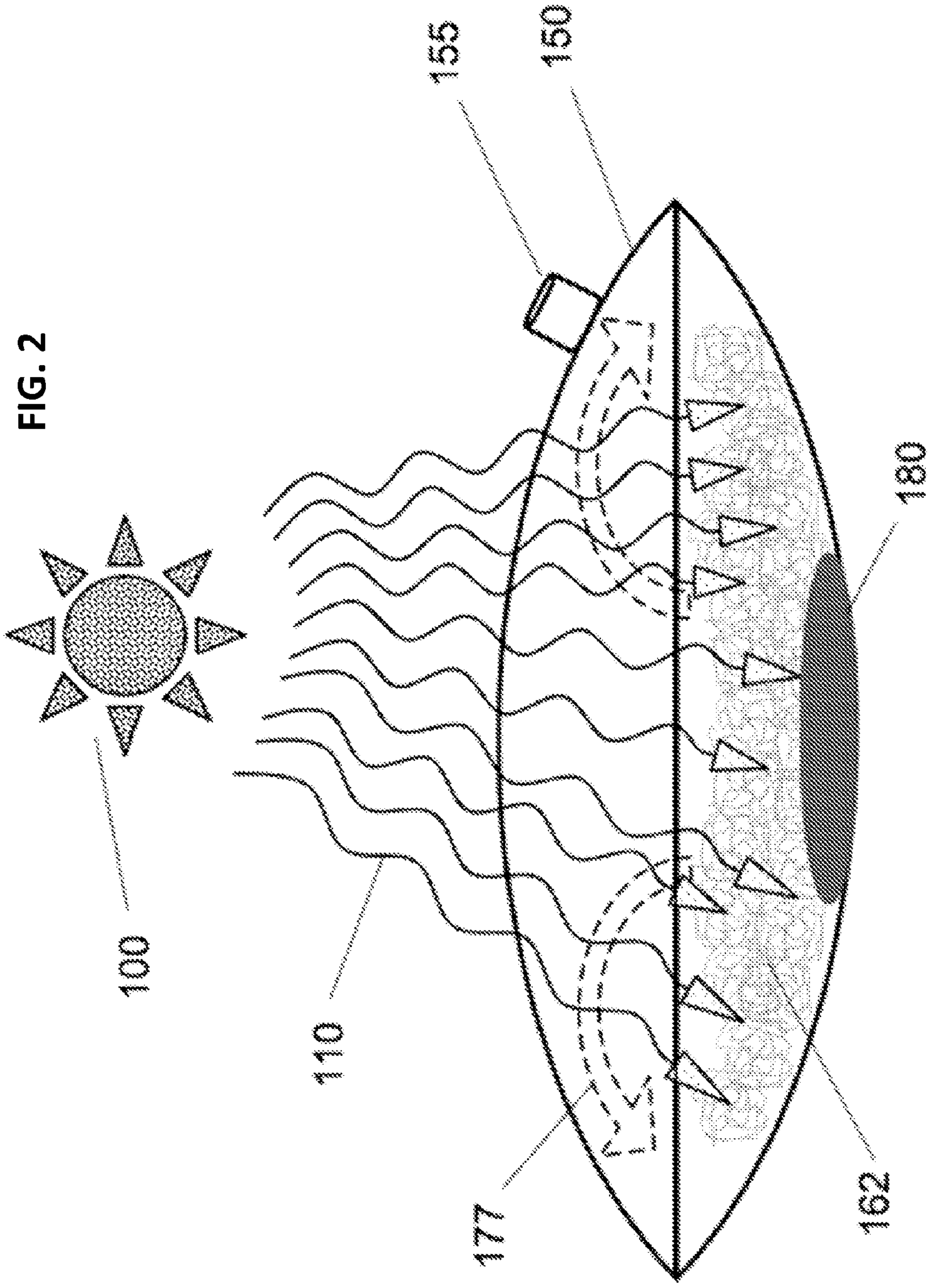


FIG. 2

FIG. 3

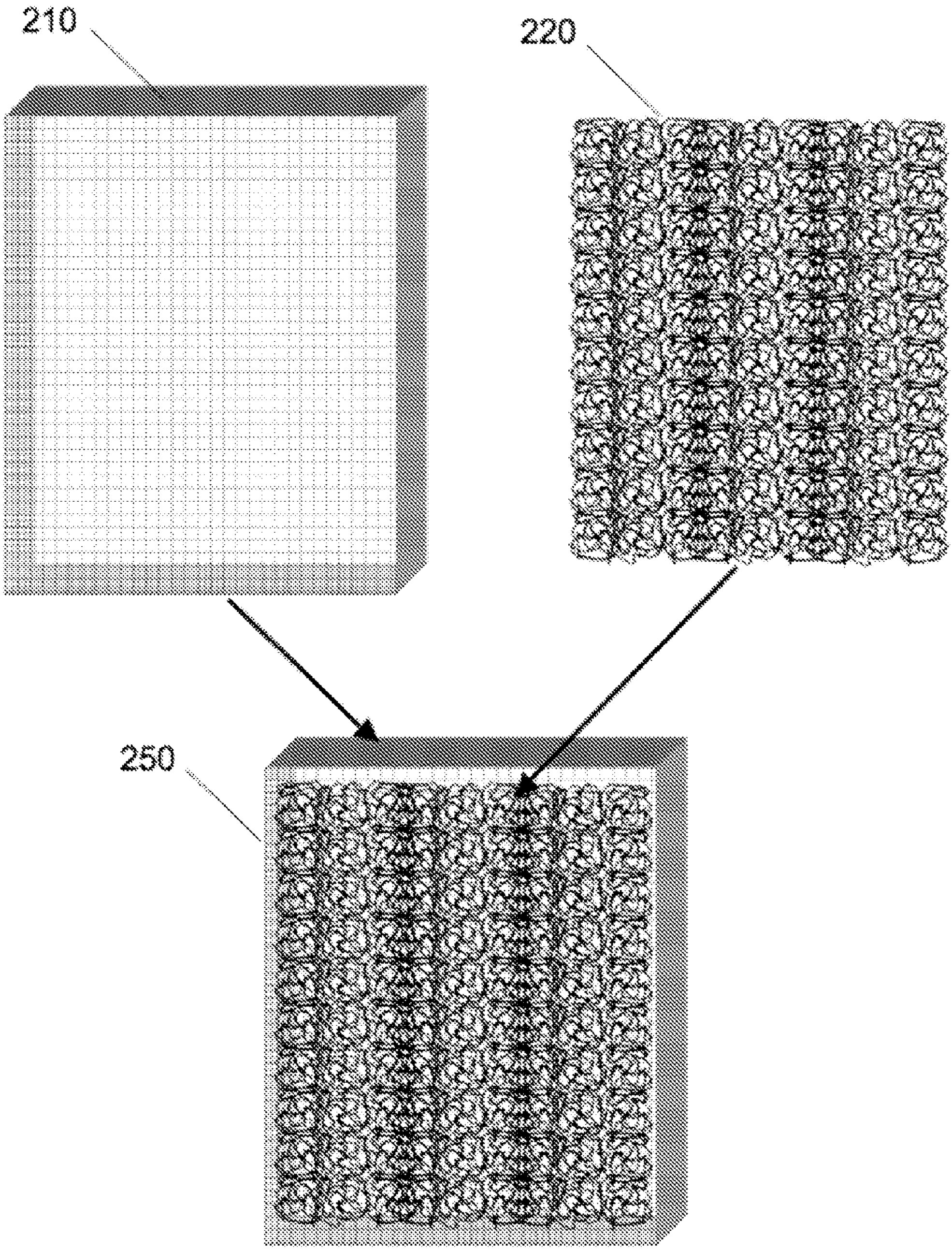


FIG. 4

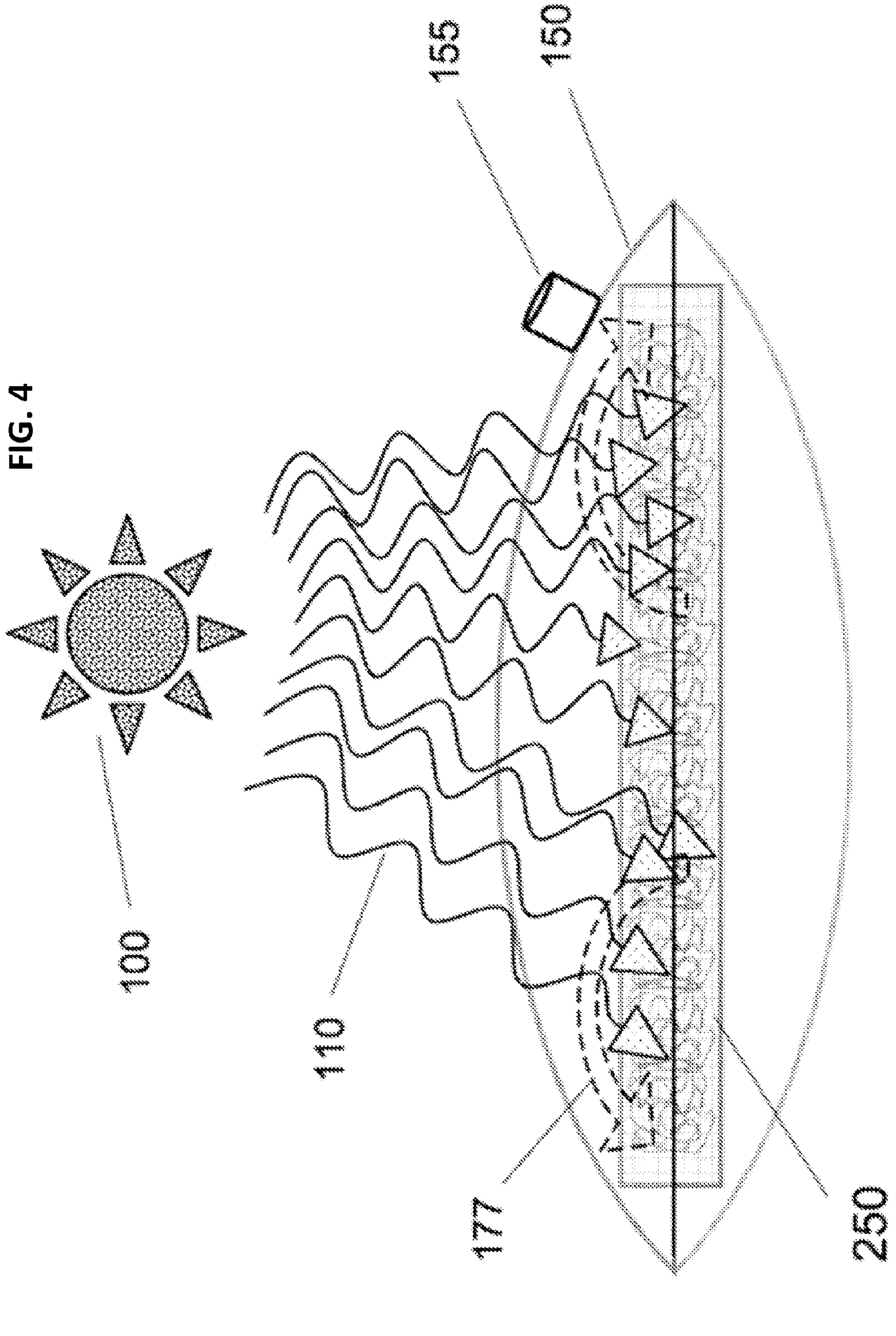


FIG. 5

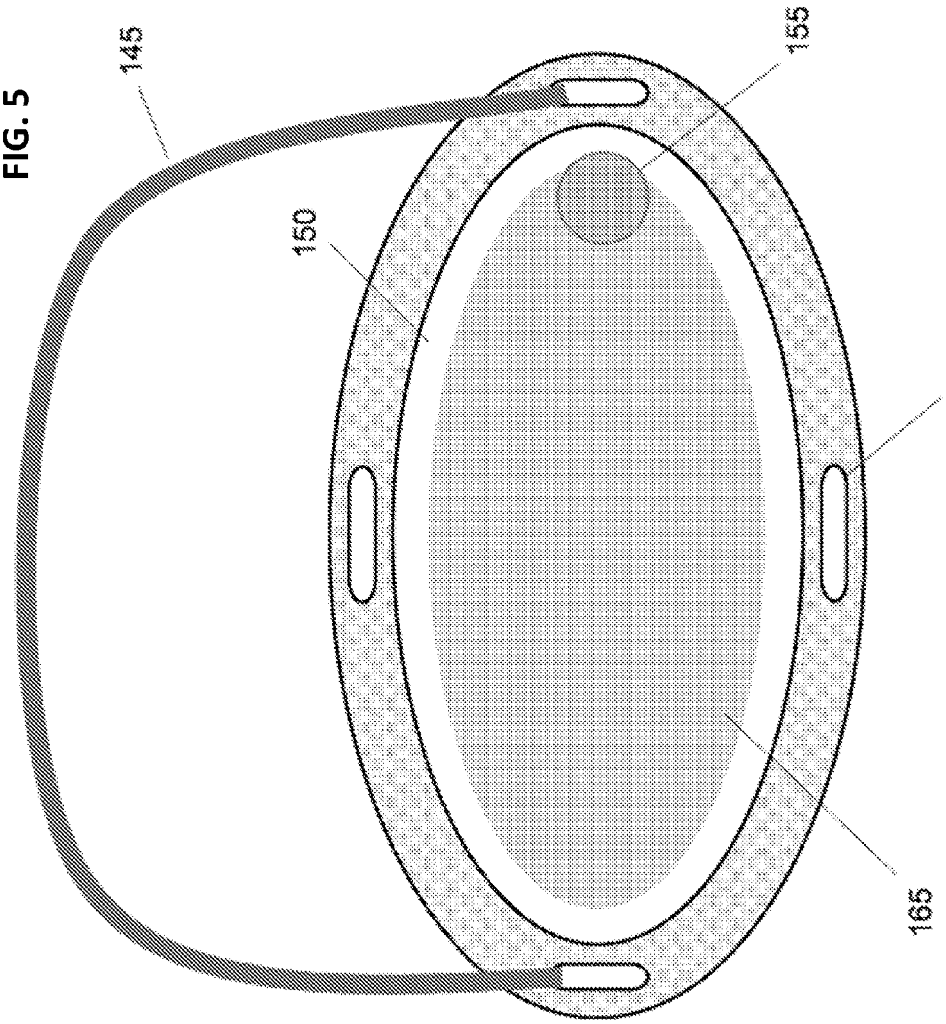
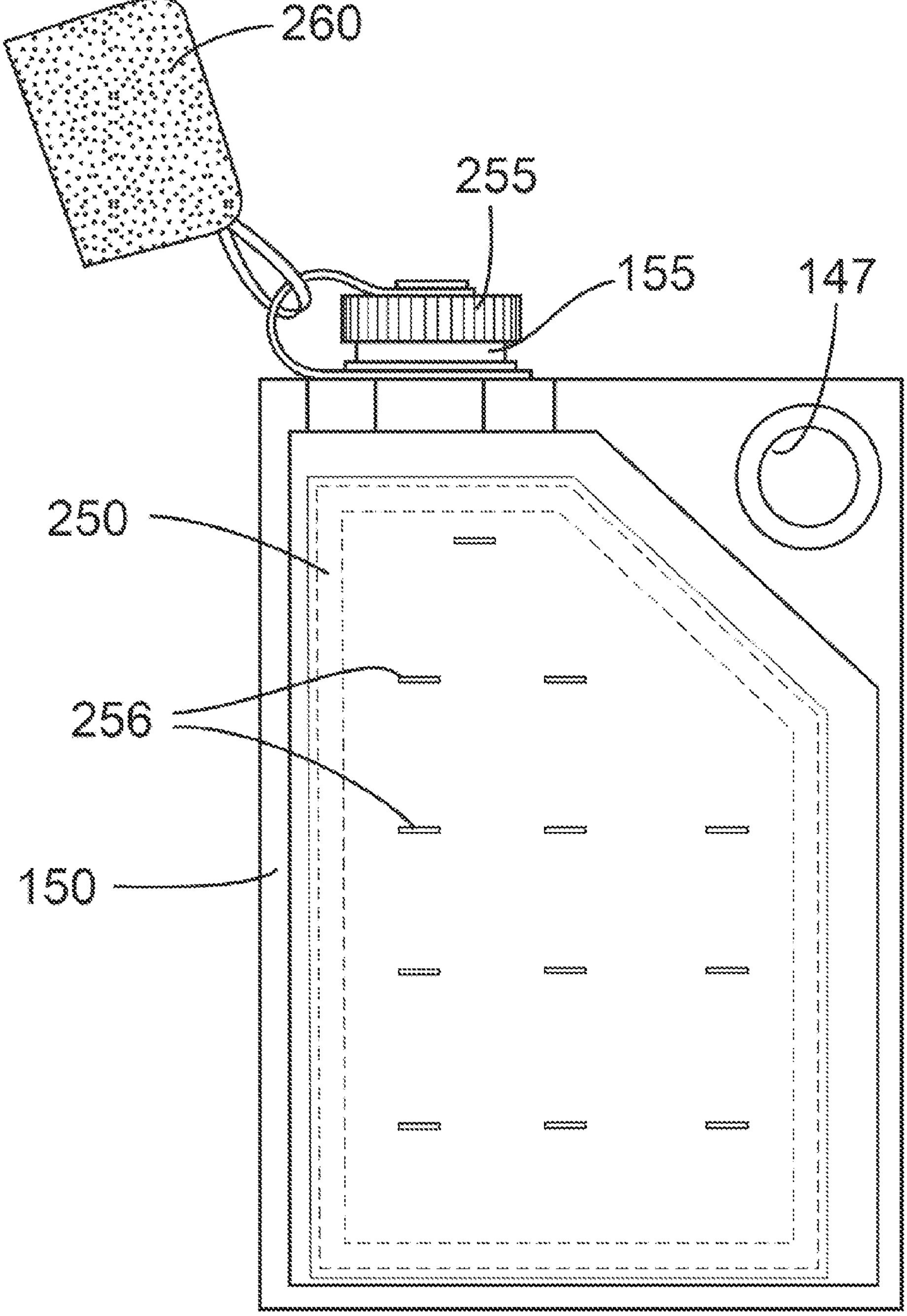


FIG. 6



SOLAR-ACTIVATED PHOTOCHEMICAL PURIFICATION OF FLUIDS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to and the benefit of U.S. Provisional Patent Application No. 61/367,305, filed on Jul. 23, 2010, which is herein incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] This disclosure relates to the purification of a fluid, such as water, and more particularly to the removal, reduction and/or detoxification of contaminants in the fluid, such as organic chemicals, inorganic chemicals, heavy metals, microorganisms and others through sunlight-activated photochemical means.

SUMMARY

[0003] In this disclosure, it is to be understood that the terms "a", "an" and "at least one" encompass one or more of the specified elements. That is, if two of a particular element are present, one of these elements is also present and thus "an" element is present. The phrase "and/or" means "and", "or" and both "and" and "or". Further, the term "coupled" generally means electrically, electromagnetically, and/or physically (e.g., mechanically or chemically) coupled or linked and does not exclude the presence of intermediate elements between the coupled or associated items absent specific contrary language. Unless specifically stated otherwise, processes and methods described herein can be performed in any order and in any combination, including with other processes and/or method acts not specifically described. The exemplary embodiments disclosed herein are only preferred examples of the invention and should not be taken as limiting the scope of the invention.

[0004] Photochemical processes comprise a range of light-activated chemical reactions that have broad application in purification of fluids. A variety of these photochemical processes can be activated by sunlight. Light-activated photocatalytic oxidation is an advanced oxidation process that involves the creation of nonselective, strongly oxidizing hydroxyl radicals at the fluid-photocatalyst interface that mineralize (i.e., convert to carbon dioxide, water, and inert byproducts) a wide range of organic compounds in water or in the presence of water. The photocatalytic process also produces reduction sites that participate in reduction of inorganic ions as well as photoadsorption of toxic heavy metals. Still further, the photocatalytic process also produces "super oxygen" ions and other species that contribute to further fluid purification reactions. Semiconductor chalcogenides (particularly oxides and sulfides) namely TiO_2, ZnO, WO_3, CeO_2, ZrO_2, SnO_2, CdS, and ZnS, have been evaluated for photocatalytic effectiveness, with anatase titania (TiO_2) generally delivering the best photocatalytic performance with maximum quantum yields. Titania is known to have strong sorption affinities for heavy metals, including toxic metals such as lead, arsenic and mercury. Photoadsorption is one example of a photo-enhanced sorption process that can efficiently remove heavy metals dissolved in a fluid to stable sorption sites on the surface of a photoactivated semiconductor material. As yet another example of a photochemical process, illumination of a fluid such as water or air with light, especially with ultraviolet (UV) light, can directly induce breaking of chemical bonds through photolysis within some first organic compounds in the fluid, forming new compounds and thereby reducing the concentration of said first organic compounds. As still another example, illumination of a fluid such as water or air with light, especially UV light, of sufficient intensity can be used to disinfect the fluid photochemically by directly killing or sterilizing microorganisms therein. As yet another example, illumination of a fluid such as water or air with light of sufficient intensity can disinfect the fluid indirectly by photothermally heating the fluid and thereby killing microorganisms therein. A plurality of photochemical processes, such as selected from the group comprising photocatalytic oxidation, photocatalytic reduction, photolysis, photodisinfection, photoadsorption and photothermal disinfection, as well as other photo-activated processes, acting synergistically, can be used in the optimization of photochemical treatment systems.

[0005] One aspect of embodiments of the present disclosure is the enabling of multiple photochemical processes in a solar-activated photochemical fluid treatment system. A further aspect of selected embodiments of the present disclosure is optimizing the performance of each photochemical process enabled in a photochemical fluid treatment system to maximize synergies among the processes. A still further aspect of selected embodiments of the present disclosure is the improvement of mass transport of contaminants in the fluid to the surface of a photocatalyst within the fluid through the enhancement of convective flow of the fluid within the treatment system. A still further aspect of selected embodiments of the present disclosure is the use of a photocatalyst coated onto or otherwise adhered to a stationary substrate within a fluid treatment vessel to effect photochemical processes for purifying fluid within the vessel. A still further aspect of selected embodiments of the present disclosure is the use of an internal mechanism within the fluid vessel to retain the photocatalyst and thereby keep it within the vessel during filling, emptying and other operations.

[0006] Photochemical processes at photocatalyst surfaces involve the illumination of the semiconductor photocatalyst with photon energies at or above the band gap energy of the semiconductor in order to create the electron-hole pairs that effect photochemical reactions at or near the semiconductor surface. Solar radiation incident on the Earth's surface comprise a broad spectrum of wavelengths, including ultraviolet (UV), visible and infrared (IR) wavelengths. A number of semiconductor photocatalyst materials, including titania (TiO_2) in its anatase structure, have band gap energies that correspond to wavelengths of light present in this solar radiation incident on the Earth's surface, and photocatalytic processes at photocatalyst surfaces can therefore be activated by this solar radiation. Solar radiation in various wavelength bands can also contribute to the activation of other photochemical processes, including but not limited to direct photodisinfection of microorganisms in the fluid and indirect disinfection through photothermal heating of the fluid.

[0007] Photochemical purification processes, including photolysis, photodisinfection, photoadsorption and photocatalysis, can require delivery of light and contaminants to reaction sites. Mass transport limits can result in practical limits on both illumination flux and photochemical reaction rates. Therefore, an exemplary approach that optimizes photochemical removal of contaminants from a fluid can involve maximizing the mass transport of contaminant species to adsorption sites on the photocatalyst material in such a photochemical system. Maximizing available photocatalyst surface area can also be desirable for an improved photochemical fluid decontamination system. In addition, flow of the fluid adjacent to a photocatalyst surface can also be desirable to improve mass transport of contaminants from the fluid to the surface. Inducing and maximizing turbulence in fluid flow near the photocatalyst surface can be a desirable aspect of a method involving a photochemical fluid decontamination system.

[0008] Suspensions of photocatalyst nanoparticles in a fluid can provide a high photocatalyst/fluid contact surface area. Nanoparticle suspensions can have, for example, surface area densities up to approximately 50 square meters per liter of treated fluid. However, suspended particles can be effectively stationary relative to the fluid, limiting fluid flow near the semiconductor-fluid interface and thereby limiting mass transport of contaminants to the surface. Additionally, a nanoparticle slurry system can require that the nanoparticles be introduced into the fluid prior to processing and then removed from the fluid after processing. A exemplary treatment system in accordance with an aspect of this disclosure improves on these nanoparticle slurry limitations by, for example: (1) permitting or inducing microscopic turbulence in flow over a photocatalyst bonded to a stationary substrate within the fluid treatment vessel, and (2) retaining the catalyst on its stationary substrate within the fluid vessel during use without requiring active management of the photocatalyst to preserve its effectiveness.

[0009] A need therefore exists for a solar-activated photochemical fluid treatment system that provides improved photochemical process rates and efficiencies and desirably without requiring active systems for photocatalyst management.

[0010] Some aspects of the present disclosure relate to an apparatus and method for fluid treatment that employs one or more photochemical mechanisms to provide efficient removal of multiple contaminants from the fluid. Exemplary embodiments can incorporate at least one treatment vessel containing a photocatalyst on a fixed porous substrate within the vessel. Such embodiments can have a fluid inlet to the treatment vessel and a fluid outlet from the treatment vessel. The inlet and the outlet can be the same opening. The inlet and/or outlet can incorporate closure mechanisms, such as valves or covers, to secure the contents of the treatment vessel during storage, transport and operation. Furthermore, the inlet and/or outlet can incorporate filtration mechanisms, such as particulate filters, in the fluid flow path.

[0011] Exemplary embodiments desirably treat fluid within the vessel by irradiating the fluid and photocatalyst with solar radiation. The vessel can comprise an at least partially sunlight transmissive portion, such as a clear plastic portion or window, to transmit solar radiation into the vessel and to the photocatalyst.

[0012] Exemplary embodiments can treat the fluid in a flowing state, wherein fluid flows from the inlet to the outlet during the treatment process, or in a stationary (batch) state, wherein the fluid is retained within the treatment vessel during the treatment process. In a stationary fluid treatment process, the fluid inlet and fluid outlet can comprise a single port for fluid flow both into the vessel prior to treatment and out of the vessel after treatment.

[0013] Exemplary embodiments disclosed can be efficient. Exemplary embodiments can enable a plurality of photochemical processes to act synergistically in a single apparatus. One or more of the following features can be included in exemplary embodiments: features that improve mass transport of contaminants to photocatalyst surfaces within the treatment vessel such as through the use of a randomly oriented, narrow fiber photocatalyst substrate, with resulting increase in photochemical process rates; features that enhance convective flow of the fluid within the treatment vessel by directly heating at least one portion of the treated fluid by absorbed solar radiation or by indirectly heating at least one portion of the treated fluid by directly heating at least one surface of the treatment vessel adjacent the treated fluid by absorbed solar radiation; and features that enhance the optimization of the amount and distribution of photocatalyst within the photochemical fluid treatment vessel to maximize process rates.

[0014] In some embodiments, photocatalyst can be placed in one or more containers, such as one or more bags (that can be small or large and that can operate in the same manner as tea bags), which can comprise buoyant material or can be supported by buoyant material, such that the container can float within a fluid to be treated so as to position the photocatalyst near a sunlight source, and near to the top of the chimney of thermal convection.

[0015] The foregoing and other features of the invention will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. **1** is a side elevational view of an embodiment in accordance with the present disclosure.

[0017] FIG. **2** is a side elevational view of another embodiment of in accordance with the present disclosure.

[0018] FIG. **3** is a view of an enclosure containing fibrous material that can be included within a fluid vessel in an embodiment in accordance with the present disclosure.

[0019] FIG. **4** is a side elevational view of an embodiment in accordance with the present disclosure with FIG. **3** enclosure included therein.

[0020] FIG. **5** is a perspective view of an embodiment in accordance with the present disclosure comprising handles, handle openings, and/or handle straps.

[0021] FIG. **6** is a view of an embodiment in accordance with the present disclosure.

DETAILED DESCRIPTION

[0022] In accordance with desirable embodiments, one or more photocatalysts can be affixed to or coupled to, such as bonded to, a fibrous substrate in a solar-activated photochemical reactor apparatus and method for the disinfection and purification of a fluid, such as water or air, for use in commercial and industrial applications. Applications include, but are not limited to, point-of-use markets, for cleanup of contaminated process outflow such as waste water and exhaust gases, and environmental remediation. Of course these are just examples and one skilled in the art will recognize a wide range of additional applications of the present disclosure, including, but not limited to, producing drinking water or process water and removing biological oxygen demand and total organic carbon from waste water and greywater. Transportable embodiments are also useful for remote applications such as purification of water in the developing world, for crisis response, or for hiking, boating, or as an emergency back-up purification system.

[0023] An effective and efficient solar-activated photochemical system for fluid disinfection and purification with photocatalytic functionality can utilize the delivery of sufficient solar illumination intensity to a photocatalyst to activate its photochemical performance, and the incorporation of sufficient photocatalyst to effectively absorb that light. Furthermore, the illuminated photocatalyst can be dispersed or distributed within at least a portion of the fluid being treated in order to purify and disinfect substantially all, or all, the fluid effectively. Still furthermore, contaminants in the fluid can be substantially, if not entirely, purified and disinfected at the surface of the photocatalyst, so that it can be desirable that the surface area of the photocatalyst is relatively large. It can also desirable that contaminants be delivered to that surface through mass transfer induced by fluid flow over the photocatalyst surface. It can be still further desirable that this mass transfer is further enhanced by inducing turbulent fluid flow over the photocatalyst surface. Additionally, the photochemical processes involved can be accelerated by temperature increase, so it can be further desirable to heat the fluid during the process if the resulting warmed fluid (if not thereafter cooled) is acceptable for its final use.

[0024] In some exemplary embodiments for disinfecting and purifying a fluid, the fluid to be treated can be presented to, or exposed to, an inert, semi-rigid, fibrous material that is at least partially transmissive to light, such as sunlight (i.e., the fibrous material allows at least a portion of sunlight incident upon it to pass into and/or through the fibrous material), and through which fluid can flow, and onto which one or more high-surface-area photocatalysts can be permanently bonded. The terms "sunlight", "solar light", "solar radiation", "solar illumination" and the like are used interchangeable herein. The terms "transmissive to sunlight", "sunlight transmissive", and the like can be defined with respect to specific sunlight wavelengths, such as a spectrum of UV sunlight that is between 350 nm and 400 nm. A fibrous material is defined to be partially transmissive to sunlight if at least 30% of the sunlight in the 350 nm to 400 nm spectral range incident on the fibrous material penetrates to a depth of 1 cm into the fibrous material. The light transmissivity is affected not only by the material forming the fibers, but also by the packing density thereof. A material is defined to be light transmissive (e.g., a material for an overall bag or enclosure, or individual fibers of a firbrous material) if at least 30% of the sunlight in the 350 nm to 400 nm incident on the material passes through the material. In this disclosure, the term substantially transmissive to sunlight means greater than 70% transmissive of sunlight in the 365 nm to 390 nm range and greater than 80% transmissive of sunlight in the 400 nm to 1000 nm range.

[0025] Embodiments of the photocatalyst material described in the present disclosure and the exemplary apparatuses and methods for its use in photochemical disinfection and purification of fluids can be further characterized by high mass transfer efficiency resulting from fluid flow through the photocatalyst material with low pressure drop in a flow-through configuration. Embodiments of means for effecting fluid flow through an inert, semi-rigid, fibrous material onto which one or more high-surface-area photocatalysts are permanently bonded, and further for effecting fluid flow through this material, can be characterized by the use of selective absorption of solar radiation within the fluid, or otherwise within or exterior to the fluid treatment vessel, to enable and/or to enhance convective flow of the fluid within the fluid treatment vessel, especially for batch treatment processes.

[0026] Some desirable embodiments can comprise a photocatalyst bonded to a narrow, at least partially sunlight transmissive fiber substrate material to provide improved photocatalytic performance. The substrate material can be, for example, quartz, glass or another ceramic, or it can be a polymer or other plastic that can be readily formed into fiber. The photocatalyst can be selected, for example, from the semiconductor chalcogenides including TiO_2. Some embodiments employ titania (titanium dioxide, TiO_2) nanoparticle material for the photocatalyst coating because of its established effectiveness in photocatalytic degradation of organic materials, and quartz fiber for the substrate because titania bonds particularly well to quartz. Some embodiments further employ a specific surface area density of >500 m^2 per gram of photocatalyst.

[0027] One exemplary embodiment comprises a coating of TiO_2 on a loosely woven silica fiber substrate, prepared so that a majority (more than 50%) of the TiO_2 is in its anatase form and so that the specific surface area of the coating is approximately 1000 times the surface area of the fiber substrate, and the coating thickness is less than one micron. Quartzel® is a commercially-available example of such a substrate with TiO_2 adhered thereto and is available from Saint-Gobain.

[0028] The fiber substrate can be prepared as a mass of fibers with random fiber orientation and spacing. The mass distribution of the photocatalyst can therefore be determined by the thickness of the photocatalyst coating, the diameter of the fibers comprising the substrate, and the density of the fiber mass. For example, with a 9 μm fiber diameter and a 0.5 μm coating thickness, and with approximately 100 m of this coated fiber per mL of volume, the specific photocatalyst area density can be greater than 2000 m^2/L. The fiber mass in this example comprises approximately 1% of the volume it occupies, so that the fiber mass presents low impedance to fluid flow and therefore a low fluid pressure drop in flow across the fiber mass. The fiber-to-fiber spacing in this example varies from zero to more than 1 mm, with average spacing of approximately 0.5 mm, presenting a wide range of effective pore sizes and diverging pathways to fluid flowing through the fiber mass.

[0029] In an application where a fluid flows through a treatment vessel containing such a fiber substrate coated with photocatalytic material, this tortuosity of flow paths can result in microturbulence that disrupts the flow as well as the boundary layer at the photocatalyst surface, and can thereby improve mass transport of contaminants in the fluid to the reactive photocatalyst surface. Macroscopic screens, woven meshes and reticulated or foam structures can be less desirable because, in many cases, they cannot achieve the tortuosity and porosity of this fibrous embodiment.

[0030] Moreover, a substrate fiber mass can be readily compressed, so that tortuosity and microturbulence within the fiber mass can be increased by compressing an appropriate quantity of the photocatalyst fiber material into a fluid containment vessel. Through this process, the mean fiber spacing and the resulting porosity of the fiber mass can be adjusted to optimize the flow of fluid across photocatalyst surfaces within the fluid.

[0031] Furthermore, in one example, the fibrous material can comprise or consist of a quartz or other fiber substrate that is highly transmissive to sunlight over a wide range of wavelengths useful for creating electron-hole pairs in multiple photocatalyst systems. This transmissivity provides pathways through the substrate for sunlight to penetrate to the photocatalyst coating even in the presence of strong optical absorption by contaminants in the fluid being treated.

[0032] In some embodiments, photocatalyst coated onto a fibrous substrate can be captured and contained in a porous bag or enclosure that permits fluid flow through the enclosure and allows sunlight to pass through the enclosure to activate the photocatalyst. One exemplary enclosure material is an open mesh made of a heat-sealable polymer or other plastic material. The term "porous" means that the enclosure can comprise sufficiently small pores or openings to mechanically contain the fiber substrate while having sufficiently large enough pores to allow the fluid to flow into and through the enclosure, and permit transmission of UV light to and through the photocatalyst coated fibers therein. The photocatalyst/fiber material can be inserted through a suitable opening into a partially formed enclosure of such mesh and then the opening can be sealed to capture the photocatalyst/fiber within the enclosure formed. Alternatively, the mesh material can be placed on either side of a photocatalyst/fiber mass and the mesh material on the opposing sides can then be heat sealed, welded or otherwise bonded around the perimeter of the photocatalyst/fiber mass.

[0033] In some embodiments, this seal of the enclosure material around the photocatalyst/fiber mass can overlap the edges of the mass, capturing the mass so that it cannot mechanically collapse to fill less than a desired portion of the enclosure and thereby have reduced photochemical interactions with fluid passing through the mass. Furthermore the enclosure material and construction methodology can be selected to create a photocatalyst/fiber filled bag that is flexible and that can therefore be easily rolled or folded to fit into a pre-formed solar fluid treatment vessel having an opening smaller than the size of the unfurled enclosure.

[0034] Still furthermore, the enclosure material and construction methodology can be selected to create a photocatalyst/fiber filled bag that has an overall density near or below the density of the fluid being treated, so that the photocatalyst/fiber containment enclosure tends to float in, or rise toward the top of, the treatment vessel, increasing and/or maximizing the amount of UV solar radiation entering the enclosure to activate the photocatalyst inside. The enclosure material can comprise buoyant material, such as floats, such that the photocatalyst can float and/or can be positioned in fluid being treated near the upper surface of such fluid. In some embodiments, the enclosure can remain near the center of the fluid vessel due to the geometry of the vessel and the enclosure. Alternatively, the treatment vessel can comprise one or more supports that position the enclosure therein at a desired location within the treatment vessel. As yet another alternative, the enclosure can be coupled to or affixed to the treatment vessel to hold it at a desired location therein.

[0035] In some embodiments, food coloring or other dye can be added to the fluid being treated within the fluid treatment vessel to provide a visual indication of progress and/or completion of a purification process within the vessel. For example, the dye can gradually lighten or fade away as the purification process progresses. In some embodiments, the dye can comprise Brilliant Blue FCF dye, which comprises an organic chemical. The fading of the dye from blue to clear can serve as an indicator of the treatment of other organic elements within the fluid, as well as an indicator of overall treatment of the all contaminants in the fluid. In some embodiments, the die can bleach from blue to clear in about 2-4 hours when the treatment vessel is exposed to full sunlight. The bleaching time can vary based on the strength of the incident sunlight and other variables.

[0036] The treatment time of the fluid can vary based on many variables, such as total volume of fluid, fluid to photocatalyst ratio, strength of incident sunlight, ambient temperature, positioning/orientation of the treatment vessel, amount/density of contaminants in the fluid, etc. In general, no minimum amount of incident sunlight is required to complete the treatment processes, but the processes can be completed faster with more or stronger sunlight.

[0037] In some embodiments, the treatment vessel can be formed from or comprise rigid or flexible sunlight transmissive materials, or combinations of such materials, including quartz, glass, ceramic and/or a wide range of polymers such as nylon, polyurethane, polyethylene, polyester or blends or laminates involving these compounds or other polymer materials. In one embodiment, the treatment vessel can comprise a laminate comprising a layer of biaxially oriented nylon, such as 25 μm thick, and a layer of polyethylene, such as 165 μm thick. At least one surface of the treatment vessel can be exposed to sunlight, such as the top surface of the treatment vessel, through which solar radiation can be admitted to the photocatalyst within. The sunlight transmissive materials can comprise a window or other sunlight transmissive portion of a flexible bag or other vessel. This at least one surface or portion thereof can be at least partially transmissive to solar UV light and desirably remains at least partially transmissive after extended outdoor use and exposure to sunlight. Other surfaces of the vessel can be at least partially sunlight transmissive as well, and/or they can comprise materials that absorb sunlight and thereby directly heat the fluid within the vessel, and/or they can be coated with, on or near optically absorbent materials that absorb sunlight and indirectly heat the vessel and the fluid within it.

[0038] In some embodiments, the treatment vessel can be a fluid treatment device large enough to contain more fluid than is needed for immediate use. Such a large treatment vessel can incorporate channels to route fluid through an extended path with an influent port at one end and an effluent port at the other end of this flow path. Influent contaminated fluid can traverse this extended path, and thereby receive extended solar-activated photochemical treatment, before being withdrawn through the effluent port for use. Furthermore, the treatment vessel can be tilted in such a manner that fluid flow through the vessel can be compelled and/or assisted by gravity. Still further, fluid flow can be regulated by a valve or other mechanism at any point in the extended flow path, such as at or near the treatment vessel's effluent port, to permit extraction of treated fluid on demand.

[0039] In some embodiments, a solar fluid treatment vessel can be placed on or above another device, such as a photovoltaic array or a solar fluid heater, that can use the ultraviolet, visible and/or infrared solar radiation not absorbed by the photocatalyst within the fluid treatment vessel.

[0040] In some embodiments, the photocatalyst coating on a fiber substrate, such as quartz, glass or polymer fiber, can be enhanced by electroless or otherwise plating of a metal onto the photocatalyst in order to improve the performance of the photocatalyst in disinfection, to increase the range of light absorption, to improve the catalytic activity of the catalyst, and/or to enhance other photochemical fluid treatment processes. Exemplary photocatalysts can comprise metal chalcogenide semiconductors, including metal oxides such as titania, which exhibit good adhesion to quartz and ceramics. Electroless plating of metals onto such semiconductor coatings after the semiconductor is bonded or coupled to the fiber substrate can avoid compromising the strength of the semiconductor-fiber bond while allowing accurate control of the amount of metal added. Other methods of applying particles into the catalyst nanoparticle matrix can also be compatible with this invention, as would be apparent to those skilled in the art.

[0041] Referring now to an exemplary embodiment, FIG. **1** is a side elevational view of one form of a solar-activated photochemical treatment system schematic in accordance with the present disclosure. Electromagnetic radiation **110** from the sun **100** illuminates at least a portion of the fluid and the photocatalyst on a fiber substrate **162** within fluid treatment vessel **150**. The substrate **162** can be stationary. At least a portion of this solar radiation is absorbed by at least a portion of the photocatalyst and/or directly by the contaminants in the fluid, inducing photochemical reactions that beneficially remove or otherwise detoxify contaminants present in the fluid. The semiconductor photocatalyst strongly absorbs a portion of solar radiation with wavelengths shorter than the band gap wavelength. Absorbed solar energy heats the photocatalyst, the vessel and the fluid, and nonuniformities in this heating process result in convective currents **177** within the fluid. These convective currents serve to move the fluid through the stationary substrate **162** and thereby to improve transport of contaminants in the fluid to the activated surface of the photocatalyst on the stationary substrate. The fluid treatment vessel can be fabricated from or comprise one or more flexible or rigid materials such as polymers or other plastics with at least one portion of the vessel being substantially, or at least partially, transmissive to the portion of the solar spectrum that activates the photocatalyst. At least one inlet/outlet port **155** on the fluid treatment vessel provides or comprises means for introducing fluid into the vessel for treatment and/or for removing fluid from the vessel following treatment. The at least one inlet/outlet port can incorporate or have attached at least one particle filter to remove particles from an influent fluid stream into the treatment vessel and or to remove particles from an effluent stream from the treatment vessel. More than one inlet/outlet port can be incorporated into the vessel in order to provide for flow into at least one port and out of at least one additional port so that fluid can be treated during flow through the vessel. Alternatively, a single port or opening can be used as both the inlet port and the outlet port.

[0042] Referring now to a second exemplary embodiment, FIG. **2** is a side elevational view of a solar-activated photochemical treatment system schematic in accordance with the present disclosure. Electromagnetic radiation **110** from the sun **100** illuminates at least a portion of the fluid and the photocatalyst on a substrate **162** within the fluid treatment vessel **150**. Again, the substrate **162** can be stationary. At least a portion of this solar radiation is absorbed by at least a portion of the photocatalyst and/or directly by the contaminants in the fluid, inducing photochemical reactions that beneficially remove or otherwise detoxify contaminants present in the fluid. The photocatalyst strongly absorbs a portion of solar radiation with wavelengths shorter than the band gap wavelength. Another portion of this solar radiation, including that portion that has wavelengths longer than the band gap wavelength of the photocatalyst, passes through and/or around the photocatalyst and is absorbed by an optically absorbent material **180** within, on or exterior to the vessel. This absorbed solar energy heats the optically absorbent material, and this heated material in turn heats at least a portion of the fluid within the vessel, increasing convective current flows **177** within the fluid. These convective currents serve to move the fluid through the stationary substrate **162** and thereby to improve transport of contaminants in the fluid to the activated surface of the photocatalyst on the stationary substrate. Improved transport of contaminants to the activated photocatalytic surface can increase the rate of photochemical reactions that remove or otherwise detoxify these contaminants.

[0043] Referring now to a third exemplary embodiment, FIG. **3** illustrates schematically an enclosure, housing, or photocatalyst module, **250** comprising a mass of photocatalyst **220** (e.g., a fibrous substrate such as described above with photocatalyst carried thereon) captured within housing **210**. The photocatalyst housing can be made of a material that is porous to the fluid being treated so that the fluid can readily pass through the housing during normal operation. In addition, the housing can be constructed so that sunlight can readily pass through the housing and into the photocatalyst. The module can have an overall density less than that of the fluid, in which case the photocatalyst module can float near the top of the fluid in the vessel. Materials well suited for construction of this exemplary housing can include woven or otherwise formed plastic fabric, webbing, mesh or other material that can be readily formed into suitable shapes and joined together or sealed (while still allowing contact by the photocatalyst with the fluid to be treated) to capture the photocatalyst material within the housing. Sealing the housing to capture the photocatalyst material can be accomplished by a number of means, including ultrasonic welding and heat sealing. Another mechanism for capturing the photocatalyst material within the housing involves capturing the edges of the photocatalyst material so that the shape of the photocatalyst material is preserved by the structure of the housing and does not clump into only one portion of the housing during flow of fluid into or through the housing. One approach for capturing the photocatalyst is to seal at least a portion of the housing material through edges of the photocatalyst and/or substrate material. In some embodiments, the housing material can be flexible, so that the housing containing the photocatalyst can be rolled or otherwise formed for insertion into a fluid treatment vessel, or distorted by handling or filling of the fluid vessel, without damage to the housing or photocatalyst. Still further, the housing material can be of or comprise a substantially elastic material, so that it returns substantially to its original form when stresses causing distortions of the housing are removed. One of ordinary skill in the art will recognize that a broad range of materials and sealing technologies can be utilized for fabricating this housing.

[0044] Referring now to yet another exemplary embodiment, FIG. **4** is a side elevational view of a solar-activated photochemical treatment system schematic in accordance with the present disclosure. Electromagnetic radiation **110** from the sun **100** illuminates at least a portion of the fluid and the photocatalyst on a stationary fiber substrate inside containment housing **250** within fluid treatment vessel **150**. At least a portion of this solar radiation is absorbed by at least a portion of the photocatalyst and/or directly by the contaminants in the fluid, inducing photochemical reactions that beneficially remove or otherwise detoxify contaminants present in the fluid. The semiconductor photocatalyst strongly absorbs a portion of solar radiation with wavelengths shorter than the band gap wavelength. Absorbed solar energy heats the photocatalyst, the vessel and the fluid, and nonuniformities in this heating process result in convective currents **177** within the fluid. These convective currents serve to move the fluid through the photocatalyst on its substrate, which can be stationary, within an internal housing **250** and thereby to improve transport of contaminants in the fluid to the activated surface of the photocatalyst on the substrate. The fluid treatment vessel can be fabricated from or comprise one or more flexible or rigid materials such as polymers or other plastics, with at least one portion of the vessel substantially transmissive to the portion of the solar spectrum that activates the photocatalyst. The housing **250** can comprise a buoyant material such that housing **250** can float within treatment vessel **150** and/or rise toward the top of the fluid.

[0045] Referring now to yet another exemplary embodiment, FIG. **5** is a top view of a solar activated photochemical treatment system schematic in accordance with the present disclosure. Photocatalyst on a stationary fiber substrate **165** is contained within fluid treatment vessel **150**. At least one inlet/outlet port **155** in the fluid vessel provides means for introducing fluid into the vessel for treatment and/or for removing fluid from the vessel following treatment. At least one handle **147**, for example comprising a handle opening through a side seam of the treatment vessel **147** that can be reinforced, such as be a grommet ring (not shown), and/or strap **145** can be incorporated into or attached onto the fluid treatment vessel **150**, such as for convenience in handling and/or to facilitate advantageous placement and/or orientation of the fluid treatment vessel for solar illumination.

[0046] In some embodiments, the fluid treatment system can be configured for ease of transportation. In some of these embodiments, the treatment system can be configured in the form of a backpack. In other embodiments, the treatment system can be configured in the form of a suitcase or briefcase, having a handle for carrying it in one hand. In some embodiments, the treatment system can comprise a grommet ring or similar holder adapted to attach the treatment system to another object, such as a backpack or tree. In some embodiments, the treatment system can comprise an at least partially sunlight transmissive upper surface and can comprise a dark or reflective lower surface. In some embodiments, both the top and bottom major surfaces of the treatment system can be at least partially sunlight transmissive.

[0047] FIG. **6** shows another exemplary embodiment of a fluid treatment system. In this embodiment, the fluid vessel **150** comprises a generally rectangular, non-porous polymeric bag and the photocatalyst enclosure **250** comprises a porous mesh material that is positioned loosely within the bag **150**. The bag **150** can comprise flexible nylon and/or polyethylene, for example. A clear laminate comprising 100ga biaxially oriented nylon and 6.5 mil polyethylene is one desirable exemplary material. The bag **150** can be formed by folding a sheet of the polymeric material in half and bonding the edges together, or by bonding or heat sealing two layers of the polymeric material together around the perimeter. The bag **150** can comprise opposed first and second major surfaces. At least a portion of the first major surface can be at least partially sunlight transmissive, such that when the first major surface is exposed to sunlight, at least a portion of the sunlight is admitted into the bag and to the photocatalyst. More desirably, the first major surface is substantially sunlight transmissive, or at least the portion of the first major surface covering the fluid to be treated is substantially sunlight transmissive. The second major surface of the bag **150** can also be at least partially sunlight transmissive, such that sunlight can enter the bag **150** from both sides. The first major surface can be an upper surface if the bag **150** is laid flat and facing upwardly and the second major surface can be a lower surface placed on the ground or other support. In other embodiments, the second major surface can be at least partially opaque, reflective, and/or can comprise a dark colored portion. A reflective portion of the lower surface can reflect light passing through the bag **150** and/or through the enclosure **250**, such that a portion the reflected light can pass through the enclosure again and enhance the photochemical processes. A dark portion on the second major surface of the bag **150**, such as in the form of writing or a logo for example, can absorb solar radiation and generate heat to create convective currents in the fluid within the bag **150**, which can enhance the fluid treatment processes.

[0048] Sunlight transmissive portions of the bag **150** can allow at least some of the incident sunlight in the spectrum between 350 nm and 390 nm to be transmitted into or out of the bag, such as at least 75% of incident sunlight in this spectrum. In some examples, more than 90% of the incident sunlight in the 350 nm to 390 nm spectrum can be transmitted through sunlight transmissive portions of the bag **150**. The bag **150** can comprise an opening or port **155**, which can function as an inlet and an outlet for fluid, and a closure **255** for sealing the opening **155**. The opening **155** can have a diameter of about 42 mm. In addition, a filter **260** can be included, such as attached to the closure **255** by a lanyard (as shown in FIG. **6**), for positioning over the opening **155** for use in filtering the fluid entering or exiting the bag **150**. The filter **260** can be tethered to the closure **255** or another portion of the bag **150**, and the filter can be removable from and reinsertable into the opening **155**.

[0049] The bag **150** can further comprise a handle **147**, such as a grommet ring or other holding device, for attaching the bag to another object. For example, the handle **147** can be used to hold the bag with a hand, to attach the bag to a backpack during transportation, and/or to hang the bag from a tree branch to expose the bag to sunlight. The handle **147** can occupy one corner of the bag **150**, such that the internal cavity within the bag forms a five-sided polygon, or a rectangular shape with one corner truncated, as shown in FIG. **6**. Accordingly, the enclosure **250** can have the same general shape, but slightly smaller, to fit within the bag **150**. The enclosure **250** can comprise a mesh fabric, such as comprised of flexible polypropylene, with the fiber substrate and photocatalyst contained therein. The mesh fabric can be folded over the substrate and heat sealed and/or sewn around the edges to enclose the substrate. Spaced apart staples or other fasteners (one being numbered **256** in FIG. **6**) passing through the substrate and walls of the enclosure **250** can also be used to hold the substrate within the enclosure. In some embodiments, the enclosure **250** can have an average thickness of less than 2 cm, such as about 1 cm. When the bag **150** is filled with fluid, the thickness of the bag can expand to several inches, such as between 2 and 3 inches, or about 2.5 inches. Like a tea bag, the enclosure **150** can be free to move and/or float within the fluid within the bag **150**. However, the tight-fitting geometry of the enclosure **250** within the cavity of the bag **150** (the enclosure can have about the same length-width dimensions as the bag cavity) can keep the enclosure **250**

positioned at about the middle of the thickness of the bag when it is filled with fluid. In other words, when the bag **150** is filled with fluid and laid flat, the top surface of the enclosure **250** can be spaced from the upper major surface of the bag and the bottom surface of the enclosure can be spaced from the lower major surface of the bag, except that portions of the enclosure around the perimeter of the enclosure can remain in contact with the bag (see FIG. **4**). Alternatively, the enclosure can be buoyant, with an overall density less than water so that it floats in the bag. As another alternative, the enclosure can be of an overall density such that it is near the density of the fluid. As a further alternative, spacers can hold the enclosure at a desired position within the bag from the major surfaces (e.g., equal distance away) or closer to a surface such as the first or upper surface. The enclosure can also be coupled to the outer bag, although in a desirable example it is loosely positioned therein. During manufacture, the enclosure can be made and rolled up or folded so as to be insertable through the opening **255** to complete the assembly of the treatment system.

[0050] In use, water or other fluid to be treated can be admitted to the bag **150** through the opening **155** and the filter **260** and into contact with the enclosure **250** and photocatalyst within the bag. The opening **155** can then be sealed with the closure **255** and the bag can be exposed to sunlight, such as by laying it out on its bottom major surface or by hanging it by the handle **147**. The sunlight can pass through the bag **150** and the fluid and can interact with the photocatalyst and the fluid to treat the fluid gradually over a treatment period. Convective currents caused by uneven heating patterns in the fluid can cause the fluid to move through the enclosure, like a tea bag in a cup of hot water, where it interacts with the photocatalyst. After the treatment period, the treated fluid can be dispensed through the opening **155** and be used.

[0051] In testing, 3 liters of water in the bag can be treated in 1 to 2 hours in full midday sunlight at about 80° F., and in 2 to 4 hours on a cloudy day at about 65° F.

[0052] In view of the many possible embodiments to which the principles of the disclosed invention may be applied, it should be recognized that the illustrated embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention. Rather, the scope of the invention is defined by the following claims. We therefore claim as our invention all that comes within the scope of these claims.

1. A solar-activated photochemical fluid treatment system comprising:

a fluid vessel having at least one opening and comprising an at least partially sunlight transmissive portion;

at least one enclosure positioned inside of the fluid vessel, the enclosure comprising material that allows fluid and sunlight to pass into the enclosure;

an at least partially sunlight-transmissive fiber substrate contained within the at least one enclosure; and

a semiconductor photocatalyst coupled to the fiber substrate;

wherein the fluid vessel is configured to contain a fluid such that, responsive to solar radiation passing through the at least partially sunlight transmissive portion of the fluid vessel and into the at least one enclosure and to the semiconductor photocatalyst, photochemical modification of contaminants and living organisms in the fluid occurs.

2. The system of claim **1**, wherein the at least one enclosure comprises a porous bag that contains the fiber substrate and the photocatalyst and allows the fluid and solar radiation to pass into the porous bag.

3. (canceled)

4. (canceled)

5. (canceled)

6. (canceled)

7. (canceled)

8. (canceled)

9. (canceled)

10. (canceled)

11. (canceled)

12. (canceled)

13. (canceled)

14. (canceled)

15. The system of claim **1**, wherein the at least one enclosure is not attached to the fluid vessel and can move within the fluid relative to the fluid vessel.

16. The system of claim **1**, wherein the at least one enclosure has an overall density of less than or equal to a density of the fluid, such that the at least one enclosure floats or rises toward the top of the fluid in the fluid vessel.

17. The system of claim **1**, wherein the at least one enclosure comprises a buoyant material such that the at least one enclosure floats or rises toward the top of the fluid in the fluid vessel.

18. The system of claim **1**, wherein the at least one enclosure is foldable or rollable such that is insertable through the at least one opening in the fluid vessel and unfurlable within the fluid vessel.

19. The system of claim **1**, wherein the at least one enclosure comprises a polymeric mesh.

20. The system of claim **1**, wherein the mesh is comprised of a material that is at least partially sunlight transmissive.

21. The system of claim **1**, wherein the fluid vessel comprises a flexible polymeric material.

22. The system of claim **1**, further comprising at least one filter positionable in the at least one opening for filtering the fluid to prevent at least some particulate or other contaminants from entering or exiting the fluid vessel.

23. The system of claim **1**, wherein the fluid in the fluid vessel comprises a dye that is an indicator of the purification of the fluid.

24. The system of claim **1**, wherein the fluid vessel comprises at least one handle or strap for supporting the vessel during operation or transportation.

25. The system of claim **1**, wherein the combined volume of the photocatalyst and the fiber substrate is less than 5% of the volume of the fluid within the fluid vessel.

26. The system of claim **1**, wherein the specific surface area of the photocatalyst within at least one portion of the fluid is greater than 100 square meters per liter of the fluid.

27. The system of claim **1**, further comprising a solar radiation absorber positioned external to the enclosure, the solar radiation absorber being operable to convert absorbed solar radiation into heat and to thereby heat a portion of the fluid adjacent to the solar radiation absorber and thereby drive convective circulation of the fluid within the fluid vessel.

28. (canceled)

29. A solar-activated photochemical fluid treatment system comprising:

a fluid vessel;

an at least partially sunlight-transmissive fiber substrate contained within the fluid vessel;

a semiconductor photocatalyst coupled to the fiber substrate; and

means for driving convective circulation of the fluid within the fluid vessel;

wherein the fluid vessel is configured to contain a fluid in contact with the semiconductor photocatalyst such that the fluid treatment system, responsive to solar radiation applied to the semiconductor photocatalyst, is configured to induce photochemical modification of contaminants in the fluid.

30. (canceled)

31. The system of claim **29**, wherein the means for driving convective circulation of the fluid within the fluid vessel comprises optically absorbent material attached to the exterior of the fluid vessel.

32. A method for purifying a fluid by introducing the fluid into a photochemical treatment system, the method comprising:

providing at least one non-porous fluid vessel with at least one porous enclosure position within the at least one vessel;

providing a semiconductor photocatalyst coupled to an at least partially sunlight-transmissive fiber substrate that is confined within the at least one enclosure;

introducing a fluid into the at least one fluid vessel such that the introduced fluid is in contact with at least a portion of the semiconductor photocatalyst; and

admitting solar radiation into the at least one fluid vessel to illuminate at least a portion of the fluid and at least a portion of the photocatalyst within the at least one enclosure to induce photochemical modification of contaminants in the fluid.

33. The method of claim **32**, further comprising modifying the photocatalyst after it is coupled to the fiber substrate.

34. The method of claim **32**, wherein a metal is deposited onto the photocatalyst by an electroless process after it is coupled to the fiber substrate.

35. An enclosure apparatus for positioning inside of a fluid containing vessel that has an at least partially sunlight transmissive portion and for use in solar-activated photochemical treatment of fluid to be treated when the enclosure apparatus and fluid to be treated is placed inside of the vessel, the enclosure apparatus comprising:

an enclosure housing comprising a material that allows fluid and sunlight to pass into the enclosure;

an at least partially sunlight transmissive fiber substrate contained within the enclosure housing;

a semiconductor photocatalyst coupled to the fiber substrate;

wherein positioning of the enclosure module inside the fluid vessel with fluid to be treated, responsive to solar radiation passing through the at least partially sunlight transmissive portion of the fluid vessel and to the semiconductor photocatalyst in the enclosure housing, results in photochemical modification of contaminants and living organisms in the fluid occurs.

36. The enclosure apparatus of claim **35** which has an overall density of less than or equal to a density of the fluid to be treated, such that the enclosure apparatus can float or rise toward the top of the fluid in the fluid to be treated in the vessel.

37. The enclosure apparatus of claim **35** which has an overall density of less than or equal to a density of the fluid to be treated, such that the enclosure apparatus can float or rise toward the top of the fluid in the fluid to be treated in the vessel.

38. The enclosure apparatus of claim **35** which is foldable or rollable.

39. The enclosure apparatus of claim **35** wherein the enclosure housing comprises a polymeric mesh.

40. The enclosure apparatus of claim **39** wherein the mesh is at least partially sunlight transmissive.

* * * * *