

A Two Stage UV Based Photolytic/Photocatalytic Process For Water Treatment

Field of Invention

- 5 The invention relates to design of a light-emitting diode ultraviolet-based photolysis and photocatalysis reactor and process for water treatment.

Background

- 10 In the water industry, UV technology has been recognized as an environmentally friendly alternative method for many applications, such as disinfection and removal of some contaminants. However, there are also some technological limitations preventing UV from wider application. For example, certain species, like adenovirus, require a very high dosage of UV, which means that the energy required for treatment and therefore cost is increased.
- 15 Compared with traditional low pressure (LP) or medium pressure (MP) UV lamps, UV LED light sources have some advantages, including being mercury free, having a long life time, low heat production, good linearity of the light intensity with current, and suitability for operation in a pulsed regime at high frequencies. These properties will allow novel and flexible design of UV devices. Moreover, LEDs basically emit a single wavelength of light,
- 20 enabling the possibility for combinations of several light wavelengths in the same reactor, which is impossible for traditional LP or MP lamps. According to published research report and our own research, simultaneous irradiation with different UV wavelengths could have some synergistic effect (e.g. see Chevremont, A.C., *et al.*, *Science of the Total Environment*, 2012. 426: p. 304-310). However, the attempts to design a reactor matching simultaneous
- 25 irradiation have not been successful (Oguma, K., *et al.*, *Desalination*, 2013. 328: p. 24-30). Also, due to the limitations of traditional UV lamps, combining UV light with different wavelengths has not been tested yet. However, there are also some limitations for UV LED. Even though UVA LEDs can now work with high energy output and efficiency, UVC LED at present suffers from low energy efficiency, low power output and a relatively short lifetime.
- 30 Thus there remain a number of problems to solve.

- Heterogeneous photocatalysis is an attractive and environmental friendly solution for water and waste water treatment. But there are some technical limitations, such as post separation and loss of the catalytic capacity. A nanoparticle sized catalyst is believed to have higher
- 35 efficiency due to its high surface to volume ratio, but it is more difficult for post separation. Immobilization of the catalyst on support materials including glass, fiber, membrane and clay may solve the problem of catalyst post separation, but there is usually a performance drop

after immobilization due to limited illumination surface area and a reduction in the mass transfer process. Loss of light during the transmitting process and the wide band gap of TiO_2 together result in low utilization efficiency of light. The design of a photocatalytic reactor for various applications is an important topic for the water industry. A well designed reactor should have short light path, uniform light distribution and good hydraulic conditions. With LED production becoming more and more practical, a LED based photocatalytic reactor is desirable, but there remain problems in making such a system work well in practice.

Summary of Invention

This invention developed a two-stage UVA/UVC system with a synergistic effect when used in water treatment. In certain embodiments, an ultra-violet LED is used as the light source and a catalyst is immobilized to avoiding post separation. Stage 1 utilizes a high power output UVA, photolytic/photocatalytic process that can remove a part of the contaminants and serve as a pre-treatment step for stage 2. In stage 2, UVC or coupled UVA/UVC can further remove pollutants. The synergistic effect is found by the combination of these two stages. Each stage of this system can also function independently according to the purpose of application.

In a first aspect of the invention, there is provided a water purification and/or disinfection device, comprising:

- at least one treatment vessel;
- at least one UVA light source arranged to supply UVA light to an interior portion of the at least one treatment vessel; and
- at least one UVC light source arranged to supply UVC light to an interior portion of the at least one treatment vessel, wherein
- the at least one UVA light source and the at least one UVC light source are adapted such that a water for purification and/or disinfection is sequentially treated with a dose of UVA light followed by a dose of UVC light, optionally wherein the dose of UVC light may be accompanied by a further dose of UVA light.

In certain embodiments of the invention, the at least one treatment vessel may comprise at least one first treatment vessel and at least one second treatment vessel, where the at least one UVA light source is arranged to supply light to an interior portion of the at least one first treatment vessel and the at least one UVC light source is arranged to supply light to an interior portion of the at least one second treatment vessel. For example, the at least one first treatment vessel may be in fluid communication with the at least one second vessel,

such that a water for purification and/or disinfection is supplied in sequence to the first treatment vessel and then to the second treatment vessel.

In further embodiments of the invention:

- 5 (a) the interior portion of the at least one treatment vessel may comprise an outer section and an inner section separated by a filter, such that water must pass through the inner section to reach the outer section, or *vice versa*;
- (b) a photocatalyst may be supported on at least one surface of the interior portion of the at least one treatment vessel. In particular embodiments that may be
10 mentioned herein, the photocatalyst may comprise titanium dioxide doped with silver (e.g. the photocatalyst may comprise from 2 to 10 wt% silver relative to 100 wt% TiO₂);
- (c) the UVA light may be provided at a wavelength of from 330 to 380 nm (e.g. 365 nm) and/or the UVC light may be provided at a wavelength of from 230 to 280 nm (e.g. 265 nm);
- 15 (d) the at least one second treatment vessel (when present) may further comprise at least one UVA light source that is arranged to supply light to an interior portion of the at least one second treatment vessel;
- (e) the UVC light source may be a UVC LED (e.g. the at least one UVC LED may be adapted to be operated in a continuously lit mode and/or a periodically lit mode operating
20 on a microsecond-scale on/off pulse);
- (f) the dose of UVA light may be sub-lethal to a bacteria present in a water supplied to the device for purification and/or disinfection, optionally wherein the dose of UVA light in the first vessel may be sub-lethal to a bacteria present in a water supplied to the first vessel;
- 25 (g) the dose of UVC light may be lethal to a bacteria present in a water supplied to the device for purification and/or disinfection, optionally wherein the dose of UVC light in the second vessel may be lethal to a bacteria present in a water supplied to the first vessel;
- (h) the at least one treatment vessel may be a quartz vessel;
- (i) the at least one UVA light source may be at least one UVA LED;
- 30 (j) the at least one UVA light source UVA LED may be adapted to be operated in a continuously lit mode and/or a periodically lit mode operating on a microsecond-scale on/off pulse (e.g. the periodically lit mode involves a 100 ms cycle time, an example of a suitable 100 ms cycle time may include the UV light being on for 20 ms and off for 80 ms).
- 35 It will be appreciated that any technically feasible combination of the above embodiments is specifically contemplated in the current invention.

In a second aspect of the invention, there is provided a method for water purification and/or disinfection comprising the steps of:

- (a) supplying a water for purification and/or disinfection;
- (b) subjecting the water for purification and/or disinfection to a dose of UVA light
5 supplied by a UVA light source; and
- (c) subsequently subjecting the water for purification and/or disinfection to a dose of UVC light supplied by a UVC light source, optionally the UVC dose is accompanied by a further dose of UVA light supplied by the same or a different UVA light source.

- 10 In one embodiment of the invention, the method may be conducted in a batch fashion using a single treatment vessel or using a first treatment vessel where the water for purification is subjected to UVA light and a second treatment vessel where the water for purification is subjected to UVC light. In an alternative embodiment of the invention, the method may be conducted in a flow system having a first treatment vessel and a second treatment vessel,
15 where the water for purification is subjected to UVA light in the first vessel and the water for purification is subjected to UVC light in the second vessel.

In further embodiments of the invention:

- (a) the water for purification is subjected to filtration before being subjected to
20 UVA light;
- (b) when the method is conducted in a vessel, an inner surface of the vessel may support a photocatalyst (e.g. the photocatalyst may comprise titanium dioxide doped with silver, such as from 2 to 10 wt% silver relative to 100 wt% TiO₂);
- (c) the UVA light may be provided at a wavelength of from 330 to 380 nm (e.g.
25 365 nm) and/or the UVC light may be provided at a wavelength of from 230 to 280 nm (e.g. 265 nm);
- (d) the at least one second treatment vessel may further subject the water for purification to UVA light;
- (e) the dose of UVA light may be sub-lethal to a bacteria present in a water
30 supplied to the device for purification and/or disinfection, optionally wherein the dose of UVA light in the first vessel may be sub-lethal to a bacteria present in a water supplied to the first vessel;
- (f) the dose of UVC light may be lethal to a bacteria present in a water supplied to the device for purification and/or disinfection, optionally wherein the dose of UVC light in
35 the second vessel may be lethal to a bacteria present in a water supplied to the first vessel;

(g) the UVC light source may be a UVC LED (e.g. the at least one UVC LED may be adapted to be operated in a continuously lit mode and/or a periodically lit mode operating on a microsecond-scale on/off pulse);

(h) the at least one UVA light source may be at least one UVA LED;

5 (i) the at least one UVA light source (e.g. UVA LED) may be adapted to be operated in a continuously lit mode and/or a periodically lit mode operating on a microsecond-scale on/off pulse (e.g. the periodically lit mode may involve a 100 ms cycle time, an example of a suitable 100 ms cycle time may include the UV light being on for 20 ms and off for 80 ms).

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In certain embodiments of the invention, the method may be conducted using a device according to the first aspect of the invention and any suitable combination of embodiments thereof.

15 Drawings

Figure 1 depicts a schematic diagram of the overall system according to an embodiment of the invention.

Figure 2 depicts a cylindrical UV reactor according to an embodiment of the invention.

20 Figure 3(a) depicts a cross-section of a cylinder UV reactor and light path in the cylinder UV reactor according to an embodiment of the invention.

Figure 3(b) depicts a close-up of a portion of the cross-section depicted in Figure 3a.

Figure 4 depicts a cylinder hybrid UVA photocatalytic membrane reactor according to an embodiment of the invention.

25 Figure 5 depicts a cross-section of the cylinder hybrid UVA photocatalytic membrane reactor of Figure 4.

Figure 6 depicts a cross-section of a coupled UVA/UVC system used in stage 2 of the system according to an embodiment of the invention.

Figure 7 depicts a multi-unit system according to an embodiment of the invention.

30 Figure 8 depicts an embodiment of the invention.

Figure 9 depicts the disinfection performance of E.coli ATCC 15597 under batch conditions.

Figure 10 depicts the disinfection performance of E.coli ATCC 15597 under continuous flow conditions.

Figure 11 depicts the dark repair of E.coli ATCC 15597 after UVC or UVA+UVC radiation.

35 Figure 12 depicts the disinfection performance of a bench-scale flow through system under various flow rates.

Figure 13 is a schematic diagram of a flow through system prototype.

Figure 14 depicts the disinfection performance of UVA and UVC alone and sequential UVA+UVC processes in the system of Figure 13 under the following conditions: flow rate=170LPM; and *E.coli* 15597 initial concentration of around 10^5 CFU/mL.

Figure 15 depicts disinfection performance under a continuous flow system (M: UVC+membrane only; TM: UVC+TiO₂ immobilized ceramic membrane (2 layers of TiO₂ coating); TM2: UVC+TiO₂ immobilized on membrane (4 layers of TiO₂ coating); ATM: UVC + Ag doped TiO₂ immobilized on membrane).

Figure 16 is a schematic diagram of the experimental setup used in Example 1: 1.Current control panel, 2. UV265 LED, 3. Petri dish, 60mm in diameter, 4 Stir bar, 5. Magnetic stirrer.

Figure 17(a) and (b) are schematic diagrams views of a UVC unit used in the scale-up system of Example 3. Note: (1) The pipe diameters for both inlet and outlet are 5 cm; R1 is 10 cm; R2 is 2.5 cm; Column length is 60 cm; (2) The distance of inlet and outlet with column bottom are both 2 cm;(3) the black rod in the middle is a UVC lamp (300 Watt).

Figure 18 depicts an antibacterial setup of a TiO₂ coated membrane: 1. Feed tank with bacteria needed; 2. Pump; 3. (TiO₂-modified) Membranes; 4. Reactor; 5. UV lamp; 6. Pump.

Description

In this invention, a two-stage process with special LED based photolytic/photocatalytic reactor is designed for water treatment. Some advantages of the system are listed below. It will be appreciated that one or more of the advantages listed below may apply to embodiments of the invention.

(1) Enhanced performance by combining stage 1 and stage 2 in this invention. This is due to a synergistic effect produced by this 2-stage process. In fact, the more resistant the bacteria are, the stronger the synergistic effect is.

(2) The LED based photolytic/photocatalytic reactor is highly compact, can distribute light uniformly and has short light path before reaching catalytic surface.

(3) Easy maintenance.

(4) TiO₂ is doped with silver which improves the separation of electron-hole pair and system performance. At stage 1, a high power UVA light is utilized for strong photolysis and photocatalysis.

(5) By using LED lamp and operating in periodic mode under high frequency, the system is able to increase photonic efficiency and reduce energy requirement significantly.

(6) According to the purpose of the particular application, each stage of this invention can function independently.

Figures 1 to 7 depict embodiments (or parts thereof) of the invention. While the device and method can potentially be conducted in a batch wise process using a single vessel where the sequencing of the exposure of UVA and UVC light is controlled to ensure that a first batch of material is pre-treated with a dose of UVA light, followed by a separate dose of UVC light (or a combined dose of UVC and UVA light), it will be appreciated that the device may be separated into modules, for example, as shown in Figure 1.

The example device 100 depicted in Figure 1 comprises: a power supply that may be an AC power supply 110 and a DC power converter 120; an auto-control unit 130, a Stage 1 vessel/unit 140 (described in more detail in Figures 2-5); a Stage 2 vessel/unit 150 (described in more detail in Figures 2, 3 and 6); an inlet 160; an outlet 170 and a pump 180. As can be seen in this schematic diagram, the device of the invention may be realised as a 2-stage system having separate vessels 140, 150 for the stages of treatment that are in fluid communication with one another. However, as noted above, the system may also be realised using a single vessel, or using separate vessels that are not in fluid communication with one another.

In the device depicted in Figure 1, the stage 1 vessel 140 serves as a pretreatment vessel for the stage 2 vessel 150. That is, vessel 140 is used to conduct the UVA treatment step, followed by a second step conducted using vessel 150, which uses UVC light (or a combination of UVA and UVC light). As shown, water from inlet 160 enters into pretreatment vessel 140 first and is pretreated with UVA before flowing to the treatment vessel 150 for treatment with UVC (or a combination of UVA and UVC light). The power supply system 110, 120 provides DC power for the LEDs that form part of the vessels 140, 150 (not shown). It will be appreciated that by adjusting the amperage, the output of the LEDs used in the system can be controlled. In the system depicted, this control may be provided by an auto-control system 130 that comprises a programmable logic controller or chip installed for periodic on/off operation of the LEDs on a millisecond scale. This arrangement may result in a reduction in power usage and thus make the system more economical to run, as well as extending the life of the LEDs used therein. It will be appreciated that the UVA and/or UVC light may be supplied by an alternative (non-LED) light source, such as a UV lamp in certain embodiments that may be mentioned herein.

Figures 2 and 3 provide a schematic depiction of a pretreatment 140 and/or a treatment 150 vessel according to embodiments of the invention. Figure 3 provides a schematic cross-section view through the housing 240 and vessel 200. For the purposes of illustration, the

vessel depicted in Figures 2 and 3 will be described in relation to a pretreatment vessel 140 (UVA LEDs), though the same description may also apply to a treatment vessel 150 (except that UVC LEDs are present, optionally in combination with UVA LEDs). The depicted vessel 200 comprises: a main body 210; an inlet 220; an outlet 230; one or more UVA LEDs (250) that are mounted on an inside surface of a housing 240. Again, it will be appreciated that the UVA and UVC light may be supplied by an alternative (non-LED) light source, such as a UV lamp in certain embodiments that may be mentioned herein.

While the housing 240 is shown as only covering a small portion of the main body 210, it will be appreciated that this covering may be varied depending on how many LEDs are required for the particular application. The inner surface of housing may be reflective to the UV light that is generated by the UVA and/or UVC LEDs that are used. This is to ensure that all of the UV light is directed into an inner portion of the vessel 200 that where the water to be (pre)treated is located in use. As the LEDs used in the current invention may produce heat, the housing may also comprise any suitable cooling system, such as a water cooling system.

The main body 210 may be made of any transparent material that is suitable, though in particular embodiments of the invention that may be mentioned herein the main body 210 may be made of transparent quartz. The inlet 220 and the outlet 230 may be made of any suitable tubing. While the main body 210 of the vessel 200 is shown to be cylindrical, it will be appreciated that any shape suitable may be used. In use, the water enters through the inlet 220 into an interior portion 280 of the vessel 200 and is then subjected to pretreatment with UVA before flowing to the outlet 230, whereupon it would enter a similar vessel 150 (Figure 1) configured to supply at least UVC light to purify and/or disinfect the water travelling therein. While the housing is shown as being cylindrical in shape, it also can be cuboid. This may be because for some high power output UVA LEDs may be limited in shape, thereby necessitating a differing shape for the housing. It will be appreciated that any suitable shape for the housing may be used, provided that it enables the UV light to penetrate into an inner portion of the vessel 200 to (pre)treat the water to be treated.

The main body 210 (e.g. the quartz tube) may in certain embodiments have its inner surface 270 coated with a photocatalyst produced by the sol-gel process. In particular embodiments of the invention that may be mentioned herein, the catalyst may be TiO_2 doped with silver in the ratio of from 2 to 10%wt silver relative to 100 wt% TiO_2 to enhance the absorbance of UVA light and the separation of electron-hole pair in photocatalytic process. The modification of the photocatalyst (i.e. TiO_2 doped with silver) could further improve disinfection performance compared with pure TiO_2 . In addition, the Ag doping could also help to inhibit

biofilm formation on the inner surface 270 of the main body 210 of the vessel 200. Biofilm formation will negatively affect the transmission of UV light. In addition, the specific coating method mentioned herein (i.e. the sol-gel process) may also ensure that Ag would not leach into the water. This may be useful feature of the current invention because silver concentration in water is regulated. The control system for the one or more UVA/UVC LEDs is described above.

As illustrated in cartoon format in Figure 3, the UV LEDs 250 provide light to the interior portion 280 of the vessel 200, which light interacts with the water and with the photocatalyst on the inner surface of the main body 210 when present.

An alternative vessel that may be used in the current invention is depicted in Figures 4 and 5. This vessel may be of particular value where the water resource to be purified and/or disinfected may benefit from pre-filtration before (pre)treatment.

The depicted vessel 300 comprises: a main body 310; an inlet 320; an outlet 330; one or more UVA LEDs (not shown) that are mounted on an inside surface of a housing 340; and a membrane 315 (e.g. a ceramic membrane). As depicted, the membrane 315 is contained within the main body 310 of the vessel 300 and is in direct fluid communication with the inlet 320, such that water must enter into the interior portion of the membrane 325 and pass through the membrane into an interior portion 380 of the main body. The function of the membrane 315 is to remove certain particles and impurities within the water admitted to inlet 320. As such, the interior portion of the membrane 325 may be connected to a separate outlet where the remaining water (e.g. brine) containing the concentrated particles and other impurities that cannot pass through the membrane are removed from the device. It will be appreciated that it is the water contained in the interior portion 380 that is subjected to (pre)treatment with UV light generated from the LEDs.

When used herein "membrane" and "filter" may be used interchangeably. Particular membranes/filters that may be mentioned herein include ceramic filters/membranes. The filters/membranes may have a pore size of from 0.1 μm to 100 μm , such as from 0.5 μm to 50 μm , for example from 1 μm to 5 μm , such as 3 μm . Any suitable channel size may be used, for example from 1 mm to 10 mm, such as 5 mm.

As before, a photocatalyst can be deposited onto the inner surface 370 of the main body 310. In addition, a photocatalyst may also be deposited/immobilised on the outer surface 316 of the membrane 315 too in addition or in place of the photocatalyst on the inner surface 370 of

the main body 310. It will be appreciated that the use of a photocatalyst is not essential for the invention to work.

Figure 6 depicts a unit of the second vessel 150, which vessel is depicted as containing both UVA 250 and UVC 251 LEDs, but is otherwise identical to a first vessel 140 as depicted in Figures 2 and 3. As previously stated, the second stage vessel 150 only requires the presence of UVC LEDs, though some embodiments that may be mentioned herein may also contain UVA LEDs as depicted here. It will be appreciated that the embodiment depicted in Figure 6 enables the simultaneous irradiation of different UV wavelengths in the second vessel.

Figure 7 depicts a system 700 that contains multiple first vessels 740 (UVA LEDs only) and multiple second vessels 750 (UVC LEDs only or UVA and UVC LEDs). It will be appreciated that such a system may be useful to increase the total amount of water that can be treated, while limiting the footprint of the system, thereby saving space. Other aspects of this embodiment are similar to those described herein before.

Figure 8 shows a particular embodiment of the device 800 invention that may be of particular utility. This device is constructed using a first vessel 300 constructed in keeping with Figures 4 and 5 and a second vessel 200 that is constructed in keeping with Figures 2 and 3 (and/or 6). Inlet water 820 is directed into the first vessel 300 by way of membrane 315 (e.g. a cylindrical ceramic membrane) and the majority of the water is filtered and exits into inner portion 380 of the main body 310 of first vessel 310, whereupon it is exposed to UVA light generated by the UVA LEDs positioned in the housing 340. Catalyst is immobilized both on the surface of the membrane and the inner surface of the main body 310 and outer surface of the membrane 315/316. The unfiltered water, containing particles and unfilterable impurities exits the first vessel 300 through brine outlet 325. After pretreatment with UVA in the first vessel 300, the pretreated water is sent via outlet 330 (or inlet 220) to the second vessel 200, which is essentially as described herein before, with the application of UVC (or a combination of UVC and UVA) light supplied by one or more LEDs.

While not wishing to be bound by theory, it is expected that in some circumstances, the first stage of the system may benefit from the doping of transition metals (e.g. silver) in the photocatalyst, which may increase the utilization of UVA light and improve system performance by widening the absorbance of the catalyst and enhancing the separation of the electron-hole pair. UVA LED may also be operated under periodic operation for

enhanced photonic efficiency. In the second stage of the system, the pretreated water is treated with UVC or coupled UV with different wavelengths (UVC and UVA), which is shown herein to be very powerful in terms of bacteria inactivation. It will be appreciated that the UV LEDs used in this second stage reactor may also be operated in periodic mode.

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As noted herein, the UVA light that is first provided to a water supplied to the system may be provided at a dose that is sub-lethal to bacteria in the water. It will be appreciated that when used herein "sub-lethal" may refer to any dose of UVA in the first (or second) treatment step that is less than the dose of UVA needed to kill bacteria. In particular embodiments, this dose may be from 20% to 0.1% less than the dose required to kill bacteria, such as from 10% to 5% less. The exact dose may be readily determined by a person skilled in the art.

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When used herein, "lethal" refers to any dose that is sufficient to kill at least some of the bacteria in the water (e.g. the dose of UVC light provided in the second stage of the process as described herein is lethal to bacteria in the water). For example, the lethal dose of UVC in a single-step process (without a prior sub-lethal UVA dosing step) may cause a log removal of from 1 to 2 units of bacteria from the water, while the two-step process (with a prior sub-lethal UVA dosing step) may cause greater than a 2 log unit removal.

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The invention has many possible industrial applications. Below are listed some possible embodiments of the invention showing these different applications.

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Thus, one application is a ballast water treatment system according to an embodiment of the invention. Ballast water plays a key role in the safe operation of ships, it also poses serious ecological, economic and health threats by bringing harmful invasive marine species into new environments due to the multitude of marine species carried in ships' ballast water, bio-film and sediment. Thus, ballast water should be treated before discharge and meet the regulations of the International Maritime Organization (IMO). For ballast water treatment, the main challenges are:

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- i) structural integrity of ships and the limited space in ships;
- ii) huge flow rate;
- iii) meet the safety requirement of ships for said treatment;
- iv) the great variability in shipping water holding time, flow rate and water quality.

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As discussed above, the current invention can be customized for ballast water treatment. The system's low footprint, integrated system and large capacity can meet the requirements (i) and (ii). The system of the current invention is flexible and has a stable performance

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under various conditions, so can meet the requirement (iv). The invention does not involve any addition of chemicals or generate any hazardous products, so it would not cause any additional safety issues and the invention can be fully automated and is easy to operate, so the crew can operate the system after simple training, thereby meeting requirement (iii).

5 Considering the huge flow of ballast water, the size of each unit and the number of units should be calculated according to the proposed treatment volume. This may be achieved by the use of multiple first (UVA) and second (UVC and optionally UVC) reactors, as shown in Figure 7.

10 A second application is as a drinking water unit for a community or a family. As the current system is flexible, it can be customized to provide drinking water treatment on a community scale or even for a house-based scale. In many places, the quality of tap water is not good enough or is not stable for drinking directly from the tap. Given this, a community or house based system is desirable in many areas of the world to improve water quality. The current
15 system is easy to assemble, operate and maintain, and there is no need for chemical additives, which make it especially suitable for this kind of application. The capacity of the system can be designed for a family or may make use of multiple units (or parallel units as described in Figure 7) for a community.

20 A third application is a system for providing safe drinking water in rural areas that have no access to tap water. There are many rural areas where clean tap water is inaccessible. In such areas, the water source could be a well, a reservoir or a river. Under such conditions, the quality of the source water can be unstable. In addition, the water body is even chemically contaminated by industry or agriculture activities. In such a case, filtration may
25 be a necessary pre-treatment, and so a unit as depicted in Figures 4 and 5 may be suitable for application in rural areas.

In this system, source water is filtered *via* a cross-flow filtration system under operation mode of inside-out. The filtered water then goes to the space between the out layer of
30 membrane and the inner surface of the quartz tube, which are both immobilized with catalyst. Photolytic and photocatalytic reactions will remove some contaminants under the UVA dosage. Then water goes to the stage-2 reactor for removal of microorganisms using UVC light.

35 A further application may be as a backup system for emergency situations. Under some emergency situations, like earthquakes or other natural or man-made disasters, providing safe drinking water is vital for public health. However, it may become impossible to obtain

sanitary water *via* normal treatment plants. It will be appreciated that the devices described herein can serve as a backup system for such situations. This is because the system can be started instantly and provides safe drinking water. More importantly, the system can be deployed as a highly integrated portable system that technicians can quickly assemble onsite according to demand. In addition, the invention does not require addition of any chemicals and is easy to transport as a whole device. Such a device is depicted in Figures 4 and 5.

This invention has several advantages that solve some technical problems noted hereinbefore:

1) Combining UVA and UVC with the two-stage process proposed in this invention. Pretreatment of UVA or UV induced photocatalysis followed by UVC irradiation are shown to provide a significant synergy effect even when the pretreatment itself barely has any removal performance (i.e the dose of UVA light is non-lethal to bacteria). For inactivation of bacteria in water, the removal performance via this two-stage system is better than the sum of the removal performance when each stage is used separately. Experiments using a batch reactor show that the more resistant to UVC the bacteria are, the stronger the synergistic effect (i.e. pretreatment with UVA followed by treatment with UVC). This synergy is clearly demonstrated in the results presented in Figures 9 and 10.

2) The photolytic or photocatalytic reactor can be enabled for simultaneous UVA/UVC irradiation simultaneously as shown in Figure 6. It is believed that the synergistic effect demonstrated in Figures 9 and 10 will also be observed in this reactor (pretreatment with UVA followed by treatment with UVC and UVA). That is, the coupled UVA/UVC is expected to show a higher inactivation performance compared with the total inactivation rate when UVA or UVC function individually or when combined simultaneously without a pretreatment step using UVA alone.

3) Reduced energy consumption may be achieved in this system by: i) applying a LED light source; ii) periodic operation mode; iii) less light loss during transition process by direct illumination on catalyst; and iv) increased utilization of light with long wavelength by metal doped catalyst.

4) Post separation of catalyst. By immobilization of the catalyst, there is no need to build a separation unit. This increases the efficiency of the system and makes it easier to operate.

5) Low footprint because of integrated system design. Firstly, LEDs are smaller in size than conventional UV lamps. Secondly, this invention can be used in a highly integrated flow system (e.g. Figure 7). For example, the commercial UV LED product, Shield 1000, from Puralytics claims a maximum treatment capacity of 4000 L/day with dimensions of 82×31×46 cm, which is 34.2 m³ treated water / m³ space. Using embodiments of this invention, it has

been possible to achieve 611.5 m³ treated water / m³ space under lab conditions. Thirdly, Figure 7 demonstrates one possible method of scaling up the current device without sacrificing foot print.

6) The device is highly flexible in terms of system treatment capacity by either adjusting the number of operating units, or the amperage of each treatment unit.

7) Better hydraulic conditions. Compared with traditional UV lamps which usually affect the hydraulic conditions of a flow reactor, this system can minimize the loss of water head during operation.

8) No addition of chemical and no hazardous by-products. This invention is environmentally friendly. It would not bring further contaminants to the environment. Also, it does not pose many safety issues to the operators.

9) When a photocatalytic membrane reactor (such as shown in Figure 4) is used, the first vessel may also function as a filtration—photocatalysis process. The benefit of this is to partially remove contaminants and stabilize the water quality prior to UV photolysis/photocatalysis. In addition, the porous structure of the membrane is ideal surface for photocatalytic reactions to take place.

10) Compared with UVC disinfection alone, our two-stage disinfection process significantly decreases the dark repair capability of microorganisms. This feature is may be very meaningful when our system is applied for ballast water treatment. Figure 11 provides supporting data showing that the two-stage device developed herein inhibits the dark repair capability of bacteria.

Examples

Methods

Bacteria cultivation

Escherichia coli (*E.coli*) strain 15597 used in this study was purchased from the American Type Culture Collection (ATCC). Overnight phase cultures were prepared by transferring one colony from a corresponding master plate to 30mL Tryptic Soy Broth (TSB, Sigma) and incubating overnight in a shaker at 37°C with a shaking speed of 135rpm. To prepare log phase *E. coli*, 30mL TSB solution was mixed with 1mL overnight phase and incubated in a shaker for 3.5 ~ 4 hours at 37°C with a shaking speed of 135rpm. After incubation, log phase solution was centrifuged at 3600 rpm for 10 min, the supernatant discarded and 30mL autoclaved DI water refilled (Purified by Milli-Q water purification system, Millipore Synergy 185, US). This washing procedure was repeated for 3 times, and a final 30mL suspension

was kept for further use. The resultant suspension concentration was approximately 10^9 CFU/mL. It was further diluted with sterile distilled water to yield a proper concentration before use. 15 mL *E.coli* suspension was dispensed into 60-mm diameter petri dish and exposed to UV radiation for certain time. All samples were magnetically stirred with a stir bar at a fixed speed. Then the samples were taken for enumeration or further experiments.

Example 1

The UVA LED system setup was described by Xiong *et al.*, (2013). Water Research, **47**(13): p. 4547-4555. Figure 16 provides a schematic drawing of the experimental setup: 1. Current control panel; 2. UV265 LED; 3. Petri dish; 60mm in diameter; 4 Stir bar; and 5. Magnetic stirrer.

In brief, high power UVA/LED lamps (3W, peak wavelength 365nm, SET, Inc, USA) were applied and connected together to serve as light source in this study. Eighteen UVA lamps were connected as three in series, six parallel groups and powered by a direct-current (DC) power supply (ISO-TECH, IPS-2303). The lamps were adhered with thermal grease to the lower surface of a hollowed aluminum cylinder (100 mm in diameter and 60 mm in height). Recycled cooling water at 25°C was pumped through the center of hollowed aluminum cylinder to protect the lamps from overheating. Light intensity was measured using ILT 1400 radiometer with a SED-033 probe (International light technologies, Inc, USA). In this research, the light intensity was fixed at 6 mW/cm². Changing of UVA dosage was achieved by varying radiation time. The UVA pre-radiation time was 20 min. UVC radiation time was 10 min.

UVC LED (TO39H) was purchased from TaoYuan Electron (HK) Limited Company. The typical power output of this LED is about 0.7 mW with a current of 20mA. The LED bulb itself already has heat-sink housing. The UVC radiation setup is shown in **Error! Reference source not found.**1. Only one single LED bulb was used. During experiment, the current was strictly controlled at 20 ± 0.1 mA. For all experiments in this study, the magnetic stirring speed was fixed at 300rpm. The distance between LED bulb and water surface was 7 mm. The position of radiation spot and petri dish was also fixed.

To minimize the impact of fast LED aging during experiment period, some measures were taken. At first, the LED bulb was burned for 60 hrs to avoid the sharp power output drop at initial period. Secondly, it was assumed that LED could maintain relatively stable state within

10 hrs so that the variation of power output would not be over 1%. All experiments were finished within 10 hrs.

The results of batch scale UVA-UVC experiment are provided in Fig.9. UVA did not contribute significant log removal, and UVC alone inactivated around 2 log *E. coli*, while UVA followed by UVC process inactivated around 3 log *E.coli*, which suggested a 1 log synergistic activation effect from the UVA-UVC process.

Example 2

Based on the results of batch study, a bench system was developed for further research. The skeleton diagram is provided in Figure 8. Stage 1 is the UVA reactor and Stage 2 is the UVC chamber. From the stand point of mounting the LEDs onto the inner wall, the cube reactor was built with a cooling system to keep the temperature of the UVA LED reactor under 25°C. The UVA transmittance of the quartz tube was >95% and the total volume of the quartz tube was 500mL. The total power output of the UVA LEDs is around 200 mW.

64 pieces of LED UVC were connected in series and each of them had a power output of 0.7 mW, thus, the total power output was around 45 mW. The UVC transmittance of the quartz tube was >85%. Around 5 cm of the quartz tube in length was radiated by UVC and the radiated volume was about 200 mL.

As shown in Figure 10, after the flow through system had been operated for both 15 and 20 min, UVA or UVC irradiation contributed less than 0.2 log or 0.9 log removal of *E.coli* separately. In contrast, the UVA-UVC process inactivated around 2 log *E. coli*, which indicated the synergistic disinfection performance of UVA-UVC was around 1 log.

As presented in Figure 12, at a flow rate of 0.11 LPM, without UVA pre-irradiation, UVC disinfection performance was lower than the disinfection performance of UVA-UVC. When various flow rates were applied to the flow through system, from 0.11 LPM, 0.16 LPM to 0.2 LPM, the UVC process presented at least 0.5 log less removal than the UVA-UVC process. Hence the UVA-UVC synergistic effect on disinfection performance was confirmed for the flow through system.

Example 3

To further study the disinfection performance of the proposed system in large scale, a prototype was built to achieve a treatment flow rate up to 170 LPM. The diagram of the prototype flow-through system is shown in Figure 13. Water from feed tank 1310 was pumped into the UVA 1340 and UVC 1350 reactors in sequence. The UVA chamber 1340 was a 50cm×20cm chamber with a quartz window facing the UVA unit. The UVA transmittance of the quartz window was >85%. The UVA LED unit (TAOYUAN ELECTRON (HK) LIMITED) was assembled with 100 UVA LEDs. With a distance of 5 cm from the UVA LEDs, its light intensity was about 14.60mW/cm². Traditional low pressure UVC was used here to develop the UVC unit.

Tap water was used to prepare feed water and Na₂S₂O₃ was overdosed to quench residual chlorine before the microorganisms were dosed. In the experiment, LP UVC was warmed up for a few minutes and then the feed water was pumped through the system. 50ml samples were taken at each sampling point and timing for enumeration.

E.coli 15597 was dosed into the dosing tank and tested. The synergistic effect was successfully found in the sequential UVA+UVC radiation process as shown in Figure 14. UVA alone still did not give any disinfection performance, and compared with UVC only radiation, a 50% enhancement in log removal was found in the sequential UVA+UVC process at 30 s and 45 s operation time. The results of this prototype testing proved that the proposed two-stage process can be scaled up and retain the significant synergistic disinfection performance shown on the bench scale.

Example 4

After batch UV experiment, 5mL UVC or UVA+UVC irradiated samples were pipetted into a small bottle wrapped with aluminum foil to avoid light exposure for dark repair study. Samples were taken at a 2 h interval for enumeration.

Figure 11 presents the comparative study of dark repair capabilities for *E.coli* after UVC disinfection with or without UVA pre-radiation. It was found that dark repair capacities after sequential UVC+UVA radiation were significantly inhibited compared with that after UVC radiation alone. The dark repair after sequential UVA+UVC process dropped from 19.5% (UVC radiation alone) to 7.6% after 4 hrs in dark.

Example 5

To demonstrate the photolytic/photocatalytic process can improve the disinfection performance, a flow through system was developed with UVC coupled with TiO₂ coated ceramic membrane as shown in Figure 18. Two peristaltic pumps (Cole-parmer) were fixed and adjust the flowrate in the antibacterial testing lines to pump in feed water and out the tested bacteria sample. Ceramic membranes were used in out-side-in mode. Mercury LP UV lamp (Sankyodenki, 7.5 W) served as UVC light source.

- 10 The ceramic membranes are SiC in chemical composition, with a nominal pore size of 3 μm , a channel size of 5 mm and a dimension of 2.5 cm $\times$ 30 cm, contributed by Liqtech international. To coat the membrane with TiO₂, the procedure was provided as below. 100ml of absolute ethyl (EtOH, Sigma-Aldrich) alcohol, 15 ml titanium (IV) isopropoxide (TTIP, Sigma-Aldrich, 97%) and 0.25 ml 65% HNO₃ were mixed and magnetically stirred for 15 min.
- 15 Another solution containing 1ml deionized water (DW), 0.6 g polyethylene glycol (PEG 6000), 0.3 ml 65% HNO₃ and 30 ml EtOH was added into previous solution drop wise under stirring. The mixture was further stirred for 1 h to achieve a homogeneous solution and then 10 ml acetylacetone (Sigma-Aldrich) and 5 ml DW were mixed and added into the prepared solution. For preparation of metal/TiO₂, proper amount of AgNO₃ or Pd(acac)₂ (>97%, Sigma-
- 20 Aldrich) was dissolved in DW or acetone and added into the solution. The prepared solution was stable for at least 48 hours. Membranes were dip coated. All membranes were pre-cleaned ultrasonically in DW for 15 min, submerged in 10% HNO₃ for 2 h and dried at 100 °C for 1 h. Cleaned membranes were submerged into prepared solution for 30s and pulled out at a speed of 2 mm/s. Then the membranes were dried at 80 °C for 1h and then heated at
- 25 500 °C for 2.5 h with a heating rate of 2 °C/min. To obtain multi layers coating, these processes were repeated.

- The log phase *E.coli* was used to test the performance of the system's disinfection performance. The disinfection experiments over the different coated membranes were
- 30 performed with flow rate of 0.5 L/min, UVC intensity of 0.68 mW/cm². The average retention time was 3 min. By combination of UVC irradiation, the log removal of the membrane reached about 2 (Figure 15). The log removal of the TiO₂ coated membrane reached about 2.5 with UVC irradiation, higher than the membrane without coating. As for the silver/TiO₂ coated membrane, the log removal was about 4. The above data demonstrate more *E. coli*
 - 35 can be killed photocatalytically by the help of coating of TiO₂ and Ag-TiO₂ film. It is clear that the modification of catalyst (Ag doping into TiO₂) significantly improved the disinfection performance compared with pure TiO₂. Ag doped TiO₂ could bring up to 1.7 Log removal (up

to 85%) enhancement of disinfection performance. In addition, the Ag doping could also help to inhibit biofilms formation on the inner wall of quartz reactor. Biofilm formation will negatively affect transmit of UV light.

Claims

1. A water purification and/or disinfection device, comprising:
 - at least one treatment vessel;
 - at least one UVA light source arranged to supply UVA light to an interior portion of the at least one treatment vessel; and
 - at least one UVC light source arranged to supply UVC light to an interior portion of the at least one treatment vessel, wherein
 - the at least one UVA light source and the at least one UVC light source are adapted such that a water for purification and/or disinfection is sequentially treated with a dose of UVA light followed by a dose of UVC light, optionally wherein the dose of UVC light may be accompanied by a further dose of UVA light.
2. The device of Claim 1, wherein the at least one treatment vessel comprises at least one first treatment vessel and at least one second treatment vessel, where the at least one UVA light source is arranged to supply light to an interior portion of the at least one first treatment vessel and the at least one UVC light source is arranged to supply light to an interior portion of the at least one second treatment vessel.
3. The device of Claim 2, wherein the at least one first treatment vessel is in fluid communication with the at least one second vessel, such that a water for purification and/or disinfection is supplied in sequence to the first treatment vessel and then to the second treatment vessel.
4. The device of any one of the preceding claims, wherein the interior portion of the at least one treatment vessel comprises an outer section and an inner section separated by a filter, such that water must pass through the inner section to reach the outer section, or *vice versa*.
5. The device of Claim 4, wherein the filter is a ceramic filter.
6. The device of any one of the preceding claims, wherein a photocatalyst is supported on at least one surface of the interior portion of the at least one treatment vessel.
7. The device of Claim 6, wherein the photocatalyst comprises titanium dioxide doped with silver.

8. The device of Claim 7, wherein the photocatalyst comprises from 2 to 10 wt% silver relative to 100 wt% TiO₂.
9. The device of any one of the preceding claims, wherein the UVA light is provided at a wavelength of from 330 to 380 nm (e.g. 365 nm) and/or the UVC light is provided at a wavelength of from 230 to 280 nm (e.g. 265 nm).
10. The device of any one Claims 2 to 9, wherein the at least one second treatment vessel further comprises at least one UVA light source that is arranged to supply light to an interior portion of the at least one second treatment vessel.
11. The device of any one of the preceding claims, wherein the UVA light source is a UVA LED and/or the UVC light source is a UVC LED.
12. The device of any one of the preceding claims, wherein the dose of UVA light is sub-lethal to a bacteria present in a water supplied to the device for purification and/or disinfection, optionally wherein the dose of UVA light in the first vessel is sub-lethal to a bacteria present in a water supplied to the first vessel.
13. The device of any one of the preceding claims, wherein the dose of UVC light is lethal to a bacteria present in a water supplied to the device for purification and/or disinfection, optionally wherein the dose of UVC light in the second vessel is lethal to a bacteria present in a water supplied to the first vessel.
14. The device of any one of the preceding claims, wherein the at least one treatment vessel is a quartz vessel.
15. The device of any one of the preceding claims, wherein the at least one UVA light source is adapted to be operated in a continuously lit mode and/or a periodically lit mode operating on a microsecond-scale on/off pulse.
16. The device of Claim 15, wherein the periodically lit mode involves a 100 ms cycle time, optionally wherein the 100 ms cycle time involves 20 ms on and 80 ms off.
17. The device of any one of Claims 10 to 16, wherein the at least one UVC light source is adapted to be operated in a continuously lit mode and/or a periodically lit mode operating on a microsecond-scale on/off pulse.

18. A method for water purification and/or disinfection comprising the steps of:
- (a) supplying a water for purification and/or disinfection;
 - (b) subjecting the water for purification and/or disinfection to a dose of UVA light supplied by a UVA light source; and
 - (c) subsequently subjecting the water for purification and/or disinfection to a dose of UVC light supplied by a UVC light source, optionally the UVC dose is accompanied by a further dose of UVA light supplied by the same or a different UVA light source.
19. The method of Claim 18, wherein the method is conducted in a batch fashion using a single treatment vessel or using a first treatment vessel where the water for purification is subjected to UVA light and a second treatment vessel where the water for purification is subjected to UVC light.
20. The method of Claim 18, wherein the method is conducted in a flow system having a first treatment vessel and a second treatment vessel, where the water for purification is subjected to UVA light in the first vessel and the water for purification is subjected to UVC light in the second vessel.
21. The method of any one of Claims 18 to 20, wherein the water for purification is subjected to filtration before being subjected to UVA light.
22. The method of any one of Claims 19 to 21, wherein an inner surface of the vessel supports a photocatalyst.
23. The method of Claim 22, wherein the photocatalyst comprises titanium dioxide doped with silver.
24. The method of Claim 23, wherein the photocatalyst comprises from 2 to 10 wt% silver relative to 100 wt% TiO_2 .
25. The method of any one of Claims 18 to 24, wherein the UVA light is provided at a wavelength of from 330 to 380 nm (e.g. 365 nm) and/or the UVC light is provided at a wavelength of from 230 to 280 nm (e.g. 265 nm).

26. The method of any one of Claims 19 to 25, wherein the at least one second treatment vessel further subjects the water for purification to UVA light.
27. The method of any one of Claims 18 to 26, wherein the dose of UVA light is sub-lethal to a bacteria present in a water supplied to the device for purification and/or disinfection, optionally wherein the dose of UVA light in the first vessel is sub-lethal to a bacteria present in a water supplied to the first vessel.
28. The method of any one of Claims 18 to 27, wherein the dose of UVC light is lethal to a bacteria present in a water supplied to the device for purification and/or disinfection, optionally wherein the dose of UVC light in the second vessel is lethal to a bacteria present in a water supplied to the first vessel.
29. The method of any one of Claims 18 to 28, wherein the method is conducted using a device according to any one of Claims 1 to 17.
30. The method of any one of Claims 18 to 29, wherein the UVA light source is a UVA LED and/or the UVC light source is a UVC LED.
31. The method of any one of Claims 18 to 30, wherein the at least one UVA light source is adapted to be operated in a continuously lit mode and/or a periodically lit mode operating on a microsecond-scale on/off pulse.
32. The method of Claim 31, wherein the periodically lit mode involves a 100 ms cycle time, optionally wherein the 100 ms cycle time involves 20 ms on and 80 ms off.
33. The method of any one of Claims 30 to 32, wherein the at least one UVC light source is adapted to be operated in a continuously lit mode and/or a periodically lit mode operating on a microsecond-scale on/off pulse.