Novel UV LED Advanced Oxidation System for Disinfection and Removal of Organic and Heavy Metal Contaminants in Water

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ABSTRACT

A novel technology is described, suitable for point of use (POU)/point of entry (POE) water purification systems, that uses a dual wavelength UV LED system to excite a fixed-substrate photocatalyst. This advanced oxidation process rapidly mineralizes organic and inorganic contaminants in water without the chemicals, consumables, toxic waste, pressure drop, or water wastage of traditional solutions. With a self-cleaning fixed photocatalytic substrate, uniform LED illumination, and extremely high surface area, the system is inherently compact, lightweight, scalable, and low-maintenance. The process combines photolysis, germicidal disinfection, photocatalysis, and photo-adsorption to effectively eliminate many contaminants in water without creating any waste stream. Reported tests confirm successful disinfection of Raoultella Terrigena bacteria and MS2 phage virus, removal of heavy metals including arsenic and lead, and the elimination of a wide range of organic chemicals from water, including phenol, MTBE, and PCE.

Key words: Photocatalysis; Advanced oxidation; LED; Titanium dioxide; Point of use; Photoreactor; Water purification.

INTRODUCTION

A number of technologies are available to remove known, regulated toxic contaminants in the production of municipal drinking water. However, US Environmental Protection Agency regulates fewer than 0.1% of the approximately 100,000 industrial chemicals in worldwide use (1), and the World Health Organization offers guidelines for a comparable fraction of organic chemicals (2). Unregulated organic contaminants found in US municipal drinking water sources include detergents, pharmaceuticals, herbicides, petrochemicals, and fire retardants (3). For example, within the past year pharmaceuticals have been reported in over twenty water supplies for major US cities (4).

While some of these contaminants may eventually be regulated, the evolution to regulation is a time-consuming process requiring development of monitoring and removal technologies and community implementation of these technologies. In addition, up to 5% of regularly tested municipal water samples may contain coliform bacteria and up to 10% of water samples may contain lead at concentrations exceeding the US EPA action level without raising alarm. As a result of these factors, drinking water will typically include contaminants for 20 years or more before the contaminants are regulated and their full health effects are known. Today, the available technologies are either impractical or ineffective for removing a broad range of contaminants from municipal or other water sources at point of entry/use:

- Filtration, including granular activated carbon, removes a moderately wide range of contaminants but requires monitoring and filter replacement to assure continuous performance, and saturated filter elements require regeneration or disposal.
- Reverse Osmosis typically wastes much more water than it purifies, and although it effectively removes inorganic minerals, it also removes those which are desirable for taste. It also fails to remove many soluble organic contaminants including some pharmaceuticals, petroleum byproducts, pesticides and herbicides.
- UV Germicidal Irradiation (UVGI) from lamps is an effective disinfectant, but monitoring, cleaning, and pre-filtration are required to assure germicidal performance.
- Advanced Oxidation Processes, including ozonation and UV-activated hydrogen peroxide, require production and storage of toxic chemicals and are therefore generally impractical in smaller-scale, point of entry/use applications.

Small-scale water purification applications require cost-effective, robust and non-selective processes and products for disinfection and removal of organic and heavy metal contaminants without added chemicals and/or frequent filter changes. **Table I** highlights the gaps in meeting this need with available technologies, and shows that the puralytic process herein reported can reduce chemical use, improve the reduction of organic contaminants, reduce maintenance, and extend the breadth of contaminants covered while achieving significant environmental benefits when compared to existing technologies.

Table I: Advantages/deficiencies of available technologies for point of use or other small-scale water purification applications.

Property / Technology	Germicidal Effectiveness	Organics Removed	Heavy Metals Removed	No Toxic Waste Stream	Water Conserved	Scalable to POU/POE	No Chemicals Added	Infrequent Service Req'd	Solar Power Practical
Chlorination	★★★★	★	-	★★★★	★★★★★	★	-	★	-
UV Germicidal	★★★★★	★	-	★★★★	★★★★★	★★★★★	★★★★★	★★★	-
Carbon Filtration	★★	★	★★	★	★★★★★	★★★★★	★★★★★	★★	-
Reverse Osmosis	★★	★★	★*	★	★	★★★★★	★★★★★	★★★	-
Ozonation	★★★★	★★★★	-	★★	★★★★★	★	-	★	-
UV/Peroxide	★★★★	★★★★	-	★★	★★★★★	★	-	★	-
Puralytic Process	★★★★	★★★★	★★★	★★★★	★★★★★	★★★★★	★★★★★	★★★★	★★★★★

PURALYTIC PROCESS PHOTOCHEMISTRY

The puralytic process reported herein involves four light-activated processes – photolysis, photoadsorption, germicidal irradiation, and photocatalytic oxidation. Each of these processes is wavelength and intensity dependent, and has relative advantages for specific contaminant removal, but all work synergistically in the puralytic process.

- **Photolysis.** Photolysis is the direct absorption by a contaminant molecule of photons with sufficient energy to directly dissociate chemical bonds. Shorter wavelengths are more energetic, and therefore more effective.

- **Photoadsorption.** While anatase TiO_2 is already an excellent medium for contaminant adsorption, under exposure to UV light it becomes a even more aggressive adsorber, and can also photoreduce and photodeposit certain contaminants. Compounds involving noble metals and non-noble heavy metals with favorable redox potentials have been shown to photodegrade (5) into molecular components, photoreduce into less toxic forms, and then photodeposit onto the catalyst. The surface area of the puralytic photocatalyst is sufficient to allow this to

occur for several years without system performance degradation.

- **Germicidal Irradiation.** Ultraviolet germicidal irradiation with mercury lamps is a well-established process for sterilizing pathogens. For germicidal applications, the 250-280 nm wavelength band is effective at disrupting the DNA of microorganisms. Monochromatic radiation within this band, such as the 254 nm radiation from a low-pressure mercury lamp, sterilizes microorganisms, but a band of wavelengths above 265 nm would be even more effective (6) and reduce dark repair of DNA (7). Higher-pressure mercury and xenon lamps produce broadband radiation – inefficient for disinfection or for activating a semiconductor photocatalyst. Moreover, UV lamp sources are fragile, and mercury lamps in particular are environmental hazards. More robust and efficient sources with optimized spectral output are preferred for germicidal systems.
- **Photocatalytic Oxidation.** Photocatalytic oxidation (PCO) by a photo-activated semiconductor photocatalyst has been actively studied (8-11) as an advanced oxidation process applicable to water purification. This process offers non-selective degradation of organic contaminants in water into simpler and less toxic compounds, and ultimately into inorganic ions, CO^2 and water. PCO involves the absorption of energetic photons by the semiconductor and the subsequent production of hydroxyl radicals at the semiconductor surface. Anatase TiO_2 is a particularly effective semiconductor photocatalyst in converting light into hydroxyl radicals – a more powerful oxidizing agent than ozone and twice as powerful as chlorine, with sufficient energy to completely mineralize organic contaminants. The critical reaction pathway is:

  $(TiO_2) + h\nu \rightarrow e^- + p^+$ [electron/hole production]

  $(H_2O \leftrightarrows H^+ + OH^-)_{ads} + p^+ \rightarrow H^+ + OH^\circ$ [hydroxyl radical production]

  Reactant + $OH^\circ \rightarrow$ Intermediates $\rightarrow CO_2 + H_2O$+ minerals

However, cost-effective production of sufficiently high photocatalyst surface area in contact with water, and delivery of enough energetic photons to the semiconductor to activate it, has proven difficult. Systems employing UV-activated TiO_2 slurries have been demonstrated to be effective in breaking down most organic contaminants (10-11), but require complicated, expensive systems for management of the slurry material. An order of magnitude increase in surface area and a significant improvement in mass transport is needed to enable smaller scale POU/POE PCO systems.

Optimized illumination sources are also needed for cost-effective water purification systems. At low UV intensities, below approximately 1 sun (about 2-3 mW/cm^2 below 400nm), production of hydroxyl radicals by UV-illuminated anatase TiO_2 photocatalyst is known to be linearly proportional to the UVA intensity, while the production of hydroxyl radicals has been reported (8-9) to increase sub-linearly at higher UVA intensities. Most research to date has been done with lamps illuminating a slurry. These lamps have typically been low pressure Hg lamps emitting at 254nm or Hg "black light" lamps emitting in the UVA band near 370 nm with limited optical flux and efficiency. An optimized, more photon efficient optical solution is needed for PCO systems.

In the puralytic process, the PCO process parameters are optimized to meet the requirements discussed above:

- The UVA intensity is as large as possible without exceeding the range of linear proportionality between intensity and hydroxyl radical production.
- The source photon energies are just above the semiconductor band gap to be efficiently absorbed by the semiconductor. UVA photons with wavelengths in the 360-390 nm range are preferred for production of hydroxyl radicals by anatase TiO_2 (band-gap near 388 nm) – photons with longer wavelengths are not strongly absorbed and those with shorter wavelengths waste their excess energy in heating the semiconductor.
- The photocatalyst is applied to a transparent substrate increasing both surface area and mass transport compared to slurry systems.
- UV LEDs are used for illumination to avoid the issues associated with lamp technologies.

PHOTO-REACTOR TECHNOLOGY

Reported herein is a patent pending advanced oxidation process technology and photoreactor with improved photocatalytic oxidation performance, improved germicidal performance, and identification of synergies resulting from combining optimized UVA and UVC wavelengths for water purification. This technology processes water in a single pass, flow-through system, without the bypass water flow and resulting water waste stream required for membrane filter systems. This technology also does not require addition of chemicals, nor does it require activated carbon filters needing frequent replacement.

This reactor technology was developed based on a novel, extremely-high-surface-area anatase TiO2 semiconductor photocatalyst on glass wool. The specific surface area of this new photocatalyst is more than ten times that of the typical Degussa P25 slurries used and reported in prior photocatalytic research studies. Because this photocatalyst is stationary on the glass wool substrate within the reactor, turbulence in water flow through the wool promotes significant mass transfer improvement compared with a slurry reactor without a significant pressure loss through the reactor. Moreover, the production rate of hydroxyl radicals with this technology is up to ~20 times greater than has been reported for slurry reactors. Thus, this novel

photocatalyst provides for photodegradation rate improvements through improved mass transfer and higher

rates of hydroxyl radical production than have been possible with photocatalyst slurries.

Another advantage of this high photocatalyst surface area is the improved photoadsorption and photodeposition of heavy metals from contaminated water onto the photocatalyst without a corresponding reduction in PCO activity. This novel photoreactor and technology have been shown to effectively photo-reduce and photo-adsorb heavy metals, particularly lead, arsenic, selenium, uranium, and mercury.

Tests to determine saturation levels for these metals (marked by reduction of photocatalytic activity) are ongoing, but are predicted to be in excess of several years at municipal water contamination levels.

To activate the photocatalyst, an LED source with optimized wavelengths and intensities was developed to efficiently produce hydroxyl radicals on the semiconductor surface. This allows treating water at flow rates over 1 liter per minute, efficiently removing >99% of most organic materials and heavy metals while also achieving full disinfection. A photograph of the photocatalyst in water inside an LED-illuminated reactor is shown in **Figure 1** below.

Figure 1: Interior of photo-reactor showing UV LED illuminated photocatalyst immersed in water.

TEST METHOD

A dual wavelength photoreactor was constructed with variable contaminant concentrations, flow rates, photocatalyst density, and illumination intensity. A diagram of the system is shown in **Figure 2** below.

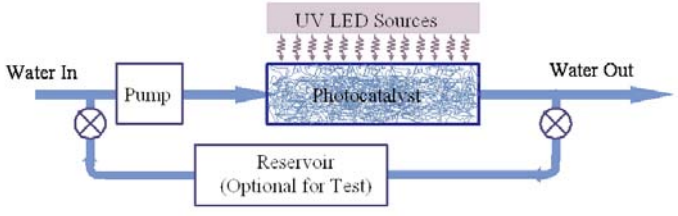

Figure 2: Schematic of test set-up for evaluating Puralytics reactor and process.

Water with controlled contaminant levels was introduced into the reactor via a peristaltic pump, and samples from the resulting output stream were tested at different points in time. Organic contaminants were tested by gas chromatography/mass spectrometry at an external water testing facility, or by use of a Total Organic Carbon meter. Pathogens were tested in an EPA Biosafety Level 2 Laboratory using both Type 1 and Type 2 water. Heavy metals were measured using cyclic voltammetry or tested by an external laboratory. Control tests were done with illumination off, with individual wavelengths acting alone, and with all illumination sources on. A reservoir was included in the test reactor system to allow recirculation as a diagnostic tool.

RESULTS

Four different photo-activated processes were identified in the test results that contribute to the overall results – photoadsorption, photolysis, photocatalysis, and germicidal sterilization. Depending on the contaminant compound, these processes have varying contributions. For heavy metals, photocatalytic reduction of the metals contributes to photoadsorption onto the mesh. For certain organic molecules, photolysis is a significant contributor to photodegradation. However, photocatalysis is the principal photodegradation process for organics, effectively removing >90% of all materials tested at flow rates of 1 liter per minute independent of starting concentration. Degradation rates of organic contaminants generally follow the predicted Langmuir Hinshelwood degradation curves, but at much higher degradation rates than previously reported. Figure 3 below shows reactor-normalized results for some of the contaminants tested in this study.

The tests also show that the PCO process acts to reduce the population of microorganisms in treated water through multiple kill mechanisms, and that the dual wavelengths act synergistically to achieve a higher kill rate. **Figure 3** on the opposite page shows that significant germicidal results are achieved with UVA illumination alone. Note that these UVA germicidal rates are more than an order of magnitude greater than reported with slurry systems (14). With modest added UVC illumination flux in the reactor, 4-log reduction of viruses and 6-log reduction of bacteria is readily achieved (not shown).

CONCLUSIONS

A novel water treatment system has been demonstrated that incorporates a photo-activated advanced oxidation process. This new AOP process combines an improved high-surface-area, stationary substrate photocatalyst system and optimized LED sources to achieve unprecedented performance on a broad range of contaminants in a low maintenance, self cleaning system. The technology allows the potential for scaling the reactor capacity and performance for different requirements in POU/POE commercial, residential, and industrial water purification applications. Addition of a UVC germicidal process within

the photoreactor synergistically increases the disinfection and photolysis performance of the treatment system.

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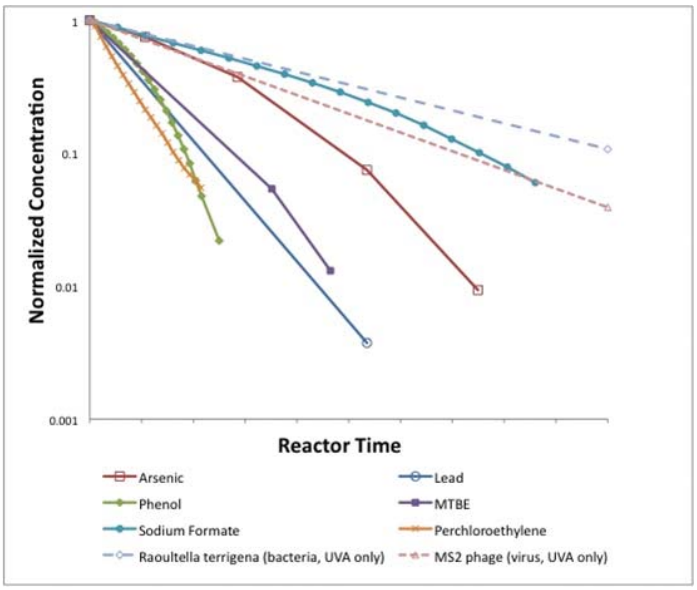

Figure 3: Observed Puralytics process contaminant removal.

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