

Perspectives on the Interaction of Plasmas With Liquid Water for Water Purification

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Abstract—Plasma production or plasma injection in liquid water affords one the opportunity to nonthermally inject advanced oxidation processes into water for the purpose of purification or chemical processing. Such technology could potentially revolutionize the treatment of drinking water, as well as current methods of chemical processing through the elimination of physical catalysts. Presented here is an overview of current water treatment technology, its limitations, and the future, which may feature plasma-based advanced oxidation techniques. As such, this field represents an emerging and active area of research. The role that plasma-driven water chemistry can play in addressing emerging threats to the water supply is discussed using case study examples. Limitations of conventional plasma injection approaches include limited throughput capacity, electrode erosion, and reduced process volume. At the University of Michigan, we are investigating two potential approaches designed to circumvent such issues. These include direct plasma injection using an underwater DBD plasma jet and the direct production of plasmas in isolated underwater bubbles via a pulsed electric field. These approaches are presented here, along with the results.

Index Terms—Atmospheric pressure plasmas, high voltage techniques, organic compounds, plasma applications, plasma chemistry, waste water, water pollution, water pollution control.

I. INTRODUCTION

ON July 28, 2010, the United Nations passed a resolution declaring access to clean drinking water a basic human right [1]. The National Academies have listed *access to clean drinking water* as an Engineering Grand Challenge, advocating the need for the infusion of new technologies to address this worldwide problem [2]. These gestures are timely in that the projected world population is expected to grow to nearly 10 billion by the year 2050. With this increased population growth, an associated growth in industry and agriculture is anticipated—with all segments over time requiring an increasing allotment of freshwater. Such increasing demand on fresh water reserves is problematic as the reserves themselves represent a fixed quantity. In this regard, a delicate balance must be achieved between maintaining existing water reserves in order to address industrial and agricultural requirements—which are

driven in turn by development and population growth—while at the same time addressing domestic consumption needs. One method of achieving these ends is the infusion of technologies that support water recycling. Recycling, in this context, refers to the reuse of treated industrial and agricultural wastewater for the purpose of supplying water needs as well as potentially recharging aquifers. For such a recycling approach to be successful, new technologies will be required to remove harmful contaminants and to monitor the overall health of water streams. The purpose of this paper is to describe the current state of water purification technology by defining the problem, listing the shortcomings of current water treatment technologies, explaining the role of advanced oxidation methods in the future of water treatment, discussing plasmas as a source of advanced oxidation processes including example cases and ongoing related work at the University of Michigan, and suggesting prospects for the future.

II. CONVENTIONAL WATER TREATMENT TECHNOLOGIES

In order to realize large-scale wastewater reuse and thus relieve stress on freshwater reserves, wastewater must be rendered usable after processing. Existing water treatment technology for a typical city water treatment plant focuses on filtration and disinfection. Particulates are filtered from input water streams via a multistep process in which chemical coagulation agents are added to the water to encourage the formation of larger particulates, which are then removed via sedimentation and subsequent filtration. This water is then disinfected, typically with chlorine precursors, ozone or more recently UV light [3]. Fig. 1 schematically shows the inner workings of a water treatment plant. In this regard, conventional water treatment addresses only particulates and bacteria. Industrial and agriculturally derived wastewater contains a host of toxins that are not directly addressed by conventional water treatment. Of particular concern are volatile organic compounds (VOC). These organic compounds can concentrate in air as well as in water. Because of this property, VOCs can migrate into drinking water sources and persist there. These toxins are of particular concern as they can contaminate surface and aquifer water sources. These toxins have been linked to a host of human health impacts ranging from damage to the circulatory system to the digestive and nervous systems. VOCs have been detected in over 51% of all US aquifers from which drinking water is derived. The US EPA has set maximum contaminant levels for a number of these toxins [4]. These components cannot be removed from water using conventional water

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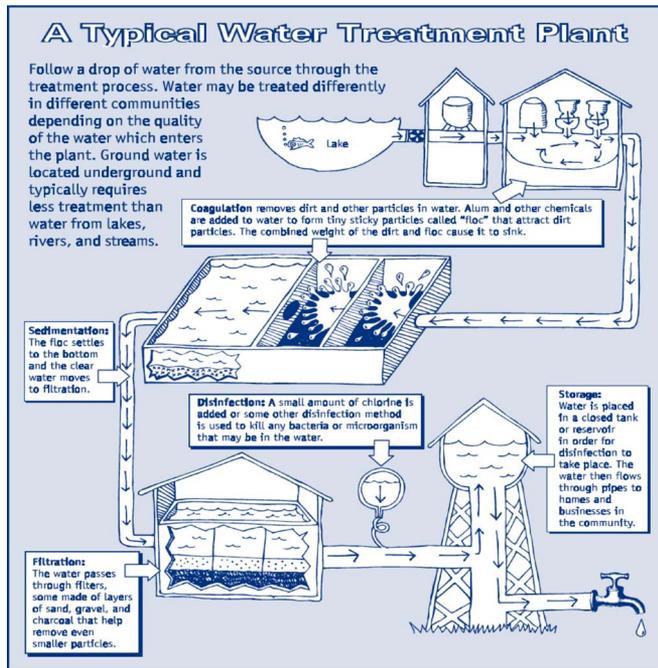


Fig. 1. Schematic depiction of water treatment plant. Courtesy of the EPA [3].

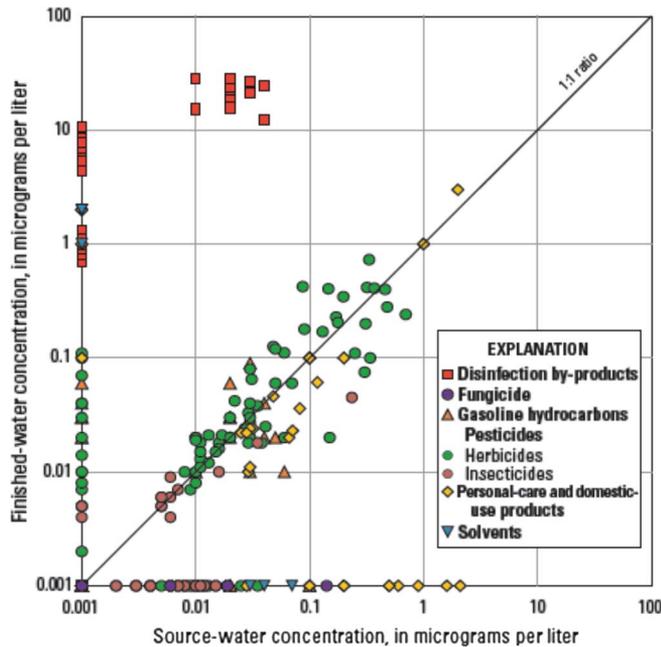


Fig. 2. Detected concentration of common contaminants in source and city water [5]. (Courtesy of U.S. Geological Survey).

treatment systems. An anecdotal example of the shortcomings of conventional water treatment systems is illustrated in a U.S. Geological Survey study of the Atlanta City water supply. In that study, it was found that there was a one to one concentration correspondence between the toxins found in the source water and the water sampled at the tap. This relationship is shown graphically in Fig. 2 [5], [6]. As indicated in Fig. 2, water contaminants nominally not addressed by conventional water treatment methods include halogenated hydrocarbons, aro-

matic compounds, pentachlorophenol, pesticides, herbicides, and more recently pharmaceuticals, all of which are associated with a range of human health concerns including cancer, hormone disruption, and birth defects [4], [7], [8]. Pharmaceuticals in urban waste waters represent another emerging threat to the drinking water supply. Conventional methods are not capable of removing these chemicals [9].

The textile industry is one of the largest producers of wastewater [10]. Approximately 1 million kg of dyestuffs are emitted into the environment per year [11], [12]. The dye-laden water poses a number of health concerns: (i) it affects the aesthetics of the water body; (ii) it affects the photosynthesis of water plants; (iii) it increases the biological oxygen demand in surface water sources, thereby giving rise to dead zones; (iii) some textile dyes are carcinogenic or can become carcinogenic when assimilated by microbes; and 5) at high concentrations, water is no longer potable [10], [13]. One solution to this contamination problem is to reuse wastewater for further textile mill processing. This is possible if the dye can be removed from the water. This allows the wastewater to be recycled, thereby relieving stress on freshwater reserves. Bioremediation is one method of decomposing dye in wastewater. However, there is no single bioremediation method that is capable of addressing all dyes [10], [14], [15].

Overall, new technologies and methods of water monitoring will be necessary to address the aforementioned toxins. Additionally, the implementation such new technologies would presumably follow a detailed public health and toxicity survey. It is conceivable that contaminant levels can one day be brought down to arbitrarily low levels, the concentrations of which would likely still be measurable with advanced detection techniques. One must then be faced with the public health question of how low is low enough.

III. ADVANCED OXIDATION PROCESSES AND WATER TREATMENT

Advanced oxidation techniques and processes involve those chemical reactions that utilize predominantly the OH radical for the mineralization of organic chemicals in aqueous solutions [16]–[18]. Because AOPs have the ability to significantly degrade concentration levels of organic contaminants through mineralization, they are touted as the wastewater treatment method of the future [17], [19]–[22]. Indeed, the OH radical has the second highest standard reduction potential (2.7 V) next to fluorine, which is toxic [23]. Though the OH radical is important to the advanced oxidation process, the term AOP actually refers to chemical processes and precursors that have high reduction potentials and either produce OH or attack organic molecules directly. In this regard, ozone, atomic oxygen, excited nitrogen, ultrasound, super critical water, UV light, and peroxide—in addition to OH—may all be grouped together as advanced oxidation processes. The combination of these components acting in water rapidly mineralizes contaminants in solution [16]. Specific reactions capable of producing OH radicals are numerous. For example, it is well known that the decomposition rate of ozone in water increases with pH level. The interaction of the decomposed ozone with OH involves

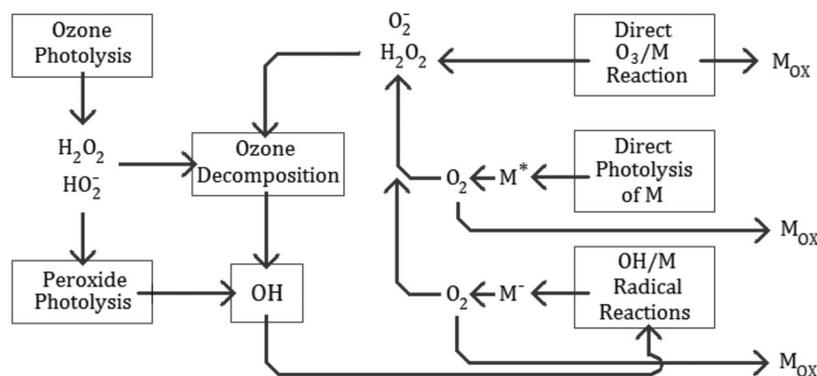
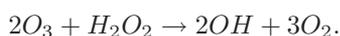
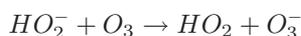


Fig. 3. Schematic depiction of UV/Ozone production of OH and subsequent oxidation and photolysis of organic contaminants (M) [16].

a series of intermediate steps that ultimately yield additional OH radicals and oxygen. This reaction conventionally requires ozone feed stock, which can currently be produced in air at a cost of ~ 30 kWh/kg



Ozone interacts with hydrogen peroxide to ultimately produce OH as well. In this case, an intermediate step involving the formation of the peroxide is necessary, with the hydroperoxyl radical (HOO) serving as the intermediate. Peroxide production costs are estimated at 7.7 kWh/kg

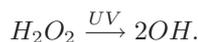


Again, several intermediate steps are involved, in which two ozone molecules reacting with peroxide yield two OH molecules. Another production mechanism of OH is the interaction of peroxide with iron ions, known as the Fenton reaction. Here, the iron serves as a catalyst for the decomposition of peroxide into OH

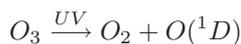


The iron ion formed in this reaction is free to interact with peroxide ions and produce additional OH radicals. The Fenton reaction is currently being investigated as a means to decompose textile dyes in wastewater.

Ultraviolet light can be used to produce OH through the direct photodecomposition of hydrogen peroxide



Additionally, OH can also be formed through the decomposition of ozone by UV irradiation and subsequent interaction of atomic oxygen with water

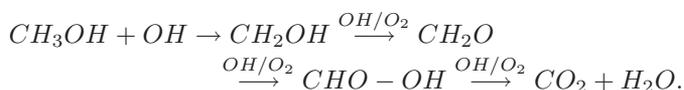


Here, $O(^1D)$ denotes metastable atomic oxygen. Also, worth noting is the formation of OH in the presence of titanium

oxide, UV light, and water. In this semiconductor reaction, electron and hole pairs formed by UV irradiation of a titanium oxide suspension (the semiconductor in this case) interacts with absorbed water, decomposing the water to OH. The OH is then free to oxidize organic contaminants. Ultrasound is still another mechanism for producing OH radicals. Ultrasound can produce cavitating bubbles. High temperatures can be reached in these bubbles leading to decomposition of water into OH and oxygen. At such high temperatures, recombination is not favored, and as a result, high concentrations of OH can be achieved [24]–[26]. Though all of the aforementioned reactions involve the production of OH, it should be pointed out that ozone, super oxides and the like are also capable of oxidizing organic contaminants [16], [17], [27], [28].

IV. DECOMPOSITION OF ORGANIC CONTAMINANTS VIA AOPS

As mentioned earlier, OH is a chief oxidizer. The AOPs mentioned thus far produce OH in copious amounts. The OH radical mineralizes organic compounds in solution to carbon dioxide, water, and inorganic intermediates, thereby rendering the contaminant essentially harmless. Ozone-UV pathways for producing OH are schematically illustrated in Fig. 3. This diagram shows that multiple pathways that lead to the oxidation of a contaminant, denoted as “M,” are possible including direct reaction with ozone. The action decomposition route of organic contaminants occurs by essentially two chemical pathways: (i) abstraction; and (ii) addition. In an abstraction process, OH removes hydrogen from the molecule thereby converting the molecule into a radical. Chain radical oxidation ensues further degrading of the organic molecule. In an addition process, the radical can add to double bonds in aromatic and unsaturated molecules also producing radicals that are ultimately degraded by chain oxidations. The radicals produced react not only with OH but also with oxygen and peroxide formed in solution [17], [18], [29]. These initial processes lead to the decomposition of the contaminant. A representative example of multistep oxidation of an organic compound can be seen in the mineralization of a representative organic molecule, methanol

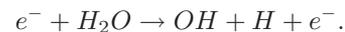


These steps again are general and act on any organic molecule. Indeed, these processes are important in the inactivation of bacteria and destruction of viral products by essentially the destruction of organic components via oxidation. In this regard, AOP approaches can be considered an alternative or supplement to conventional disinfectant approaches such as the use of chlorine, which is toxic. Chlorine reactions with organic matter in water give rise to the formation of disinfection byproducts known as trihalomethanes. These compounds are carcinogens and have been linked to a variety of cancers including bladder cancer [30]–[33]. The primary kill mechanism for chlorine acting on bacteria appears to be associated with reactions at the cell wall or membrane that inhibit normal microbial metabolic processes [34]. Because this generally does not involve the destruction of the cell wall, it is possible for bacteria and protozoa to develop resistance to chlorine if in some manner the cell wall or membrane chemical composition is altered via mutation which may does not favor the chlorine chemistry. An example of such a chlorine resistant microbe is the cryptosporidium parvum oocyst—the source of the Milwaukee outbreak in 1996, which sickened over 400 000 and was attributed to the deaths of 104 people [35]–[37]. Bacteria that forms spores (e.g., Bacillus, and enteric viruses) are also highly resistant to chlorination [38]. Herein lies the advantage of AOPs for disinfection. Advanced oxidation action leads to cell membrane and cell wall destruction. OH radicals can also diffuse into the cell, destroying or disrupting cell components, enzymes and protein synthesis. In this regard, AOPs can be applied to the disinfection of drinking water as well as foodstuffs [39]–[41]. Studies have also shown that AOP oxidation of bacterial cell membranes may allow chlorine to enter the cell and ultimately destroy it, thereby demonstrating synergistic effects with conventional disinfection methods [42]. Overall, advanced oxidation processes present a potential solution to chlorine resistant bacteria in drinking water. Bacteria and viral particles cannot develop a resistance to AOPs as the “kill” mechanism is chemical oxidation of the microbial structure itself. Finally, it should be pointed out that the effectiveness of AOPs in bacteria deactivation in a pilot plant has been demonstrated [43].

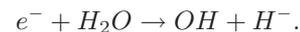
V. WATER PURIFICATION-WHY PLASMAS?

While the aforementioned AOPs can be applied conventionally to waste waters, the interaction of an ionized gas with liquid water allows for the simultaneous introduction of these processes into the water. The introduction of multiple AOPs into wastewater has the potential to give rise to synergistic effects thereby multiplying the effectiveness of the approach [22]. Plasma-induced reactivity can be introduced into wastewater by (i) formation of plasma above the liquid and (ii) direct production of plasma within the water. The latter approach can be achieved by streamer discharge propagation within either field-generated microbubbles or externally injected gas bubbles. In either approach, the plasma interacts with the water at the gas-liquid interface. The reactions at this interface and the diffusion of products from the gaseous state into the liquid state drive the chemical reactivity induced by the plasma. The plasmas produced, at atmospheric pressure in

particular, are a source of charged particles, excited species, shockwaves, ultrasound, radicals, and UV radiations—each of which are advanced oxidation techniques [44]. When the plasma is produced, localized heating of the liquid can also produce supercritical water, which can drive, high-temperature, wet oxidation. Plasma-produced radicals typically have short lifetimes (milliseconds to microseconds). Additionally, these products are generally not harmful to health or the environment [45]. Because these plasma discharges can be produced using air or vapor derived from the water itself as the feed gas, toxic disinfection consumables such as chlorine or ozone used in conventional water purification systems are not necessary. Though ozone, a powerful oxidant in its own right, is typically produced in these discharges, as described earlier, its formation is key to the subsequent formation of OH. In the presence of a plasma, additional OH production mechanisms are possible. Perhaps the most simple of these reactions to conceptualize is the direct disassociation of a water molecule by direct electron bombardment, which has a starting ground state energy of approximately 51 eV [46]



Dissociative attachment is another process that leads to OH production



In addition to these OH production mechanisms, a myriad of other reactions can also take place, including thermal disassociation, which occurs at gas temperatures greater than 2000 K, electron-ion dissociative recombination, water ion hydration, disassociation driven by interactions with radicals, metastables, and positive-negative ion recombination. Charge exchange is another mechanism that can lead to OH formation. A comprehensive tabulation of possible production mechanisms may be found elsewhere [45], [47]. In general, OH production efficiency depends on electron temperature, plasma density, working gas composition and temperature, and the excitation mechanism, which in turn depend on the mechanism by which the plasma is produced in the first place.

A. Generating the Plasma-Liquid Water Interaction

As mentioned earlier, it is through the interaction of the plasma with the liquid water that reactivity within the liquid is induced. This occurs via direct diffusion of gas phase products into the liquid or by direct interaction of the plasma with the liquid. For example, electron bombardment of water molecules can lead to disassociations, and in a likewise manner, simple electron attachment to a water molecule can lead to disassociation. A plethora of discharge approaches are possible. A comprehensive review of these approaches of plasma produced in liquid water may be found elsewhere [48]–[50]. Here, we review briefly the generalities of such approaches. Plasma produced over the liquid surface relies on gas phase interactions with the liquid surface. This approach can be carried out in essentially three ways: (i) glow discharge electrolysis [51], [52]; (ii) dielectric barrier discharge (DBD) [53], [54]; and

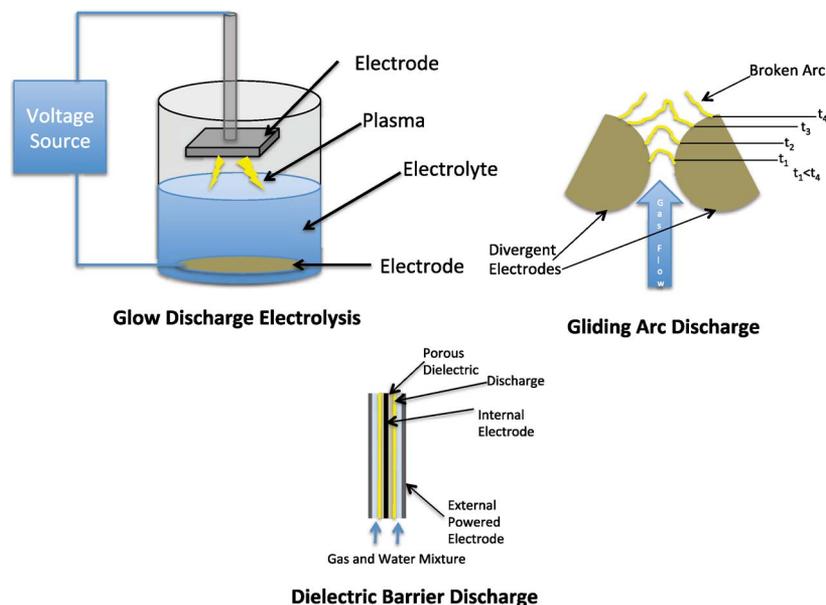


Fig. 4. Surface-water plasma interaction approaches.

(iii) Gliding arc discharge [55]–[58]. In glow discharge electrolysis, as illustrated in Fig. 4, a discharge is initiated between the surface of the liquid and an external electrode. The discharge current actually flows through the electrolytic solution. As current flows, chemical reactions, such as radical production can take place in both the liquid and the gas phase. In the DBD approach, the plasma is produced in general proximity to the surface of the liquid. In this manner, reactive species produced in the gas phase can interact with the liquid at the surface region thereby affecting reactivity within the water. The gliding arc discharge features the striking, subsequent formation and rise of an arc discharge between two divergent electrodes in the presence of a high-speed gas flow. The flow field essentially drags the discharge upward as depicted in Fig. 4. The discharge extends laterally as it rises, ultimately extinguishing at large electrode spacing. The discharge possesses arc and nonthermal glow-like properties owing to its transient nature and the variation of plasma properties as it rises. Water can be introduced along with the feed gas forming a spray. Radicals and plasma particles produced in the arc interact with the water, decomposing organic contaminants therein. It has been shown that gliding arc discharges are a very efficient means of decomposing contaminants in liquid water [59].

Another method of achieving the interaction of plasma with liquid water is to produce the discharge within the liquid itself. This so-called direct injection method typically involves the application of a fast, high-voltage pulse between submerged electrodes. Upon application of the voltage pulse, evidence suggests that microbubbles actually form local to the electrode, presumably due to localized field-driven heating or gas desorption from the surface of the immersed electrode [50], [60]–[64]. The field is amplified at the water-air interface (dielectric constant ~ 80 for deionized water) leading to the formation of a streamer discharge. The streamer then propagates in the bubble and perhaps jumps from bubble to bubble as a propagation mechanism [65]–[70]. In either case, the discharge forms

in the bubble. Radicals are formed both within the bubble and at the water/gas interface. Bubbling affords the opportunity to vary the gas mix and thus the chemistry of the plasma produced. Perhaps, the most common method of direct injection is the point to plane geometry. The concentrated electric field at the pointed electrode drives localized bubble formation and subsequent breakdown. Fig. 5 shows a typical point to plane geometry without and with bubbling. These atmospheric pressure discharges are streamer driven, which produces copious amounts of radicals. The short duration of the streamer discharge, typically $\sim ns$, limits the amount of heating to the heavy particles and the liquid medium, essentially assuring a nonthermal and efficient discharge. A complete review of underwater discharge approaches is given by Locke [49]. A comparative study of the relative efficiency of various discharge approaches has also been carried out [59], [71]. These studies suggest that there may be an advantage to methods involving the production of plasma above the liquid water. In any event, the study of plasma in liquid water is compelling in that it stands as an advanced water treatment solution that can potentially address the emerging threats to drinking water. Even so, additional research will be required before this science can truly become a technology. Key areas of focus involve (i) quantifying conversion efficiency; (ii) quantifying electrical efficiency and comparing to conventional methods; (iii) quantifying lifetime of the plasma applicator; (iv) improving throughput (increasing process volume); and (v) assessing toxicity of treated samples. Work in these areas is necessary to bridge the gap between laboratory demonstrations and engineering practice.

While the aforementioned approaches may be applied to conventional water treatment systems—either pretreatment or direct treatment—the approaches are equally applicable for point-of-use applications. By point-of-use, we refer to those systems capable of purifying water at the source itself. This is to be contrasted with centralized, conventional water treatment methods. A point-of-use approach featuring plasma-based

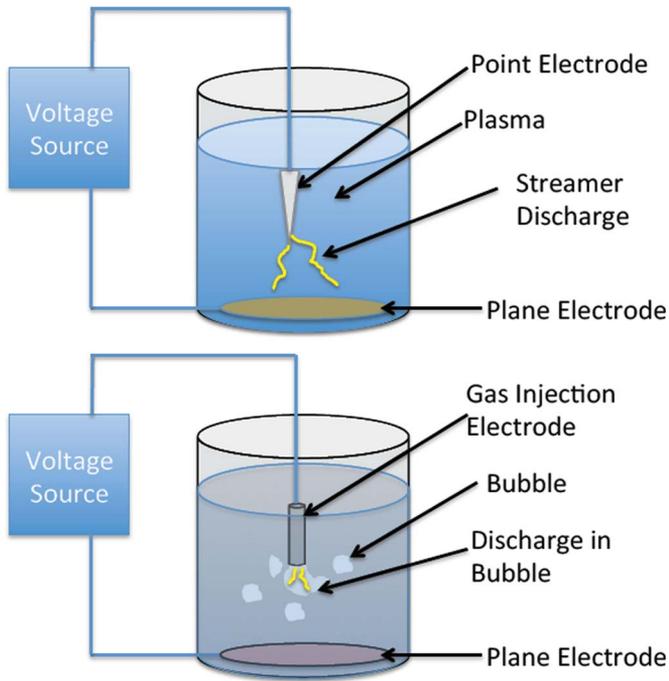


Fig. 5. Direct plasma injection approaches.

methods is applicable in particular to underdeveloped countries or remote locations where purification infrastructure simply does not exist [72]. Indeed, nearly 1 billion people lack access to clean drinking water. As a result some 80% of all childhood deaths are attributable to water-borne illness. The situation is made even more dire in underdeveloped regions where there is also a lack of regulation and oversight of the release of industrial toxins or agricultural runoff—both of which lead to contamination of drinking water. A plasma-based point-of-use technology would be well poised to address this societal issue. Point-of-use technology is also directly applicable in industrial settings such as textile mills where wastewater streams must be treated directly before expulsion into a nearby river or stream.

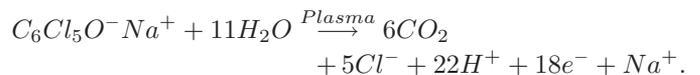
VI. CASE STUDIES DEMONSTRATING THE WATER PURIFICATION CAPACITY OF PLASMAS

The ability of plasmas to introduce AOPs on demand in liquid water is appealing from a water purification standpoint. Because of this ability, many of the research demonstrations involving plasma-based water purification have focused on the decomposition of organic compounds—key contaminants in source water [54], [73]–[76]. Of particular interest is the ability of plasmas to treat water contaminated with herbicides/pesticides, VOCs, bacteria, and textile dyes. While not an exhaustive list, these contaminants are representative of a portion of emerging threats to source waters. Here, we provide anecdotal research case studies, demonstrating the ability of plasmas to address such contaminants.

A. Pesticides

The U.S. alone uses over 1 billion pounds of pesticides each year. The result of such use is the intrusion of these

compounds into surface and ground sources [77]. These contaminants are also detectable in aquatic species such as fish. The existence of pesticide contaminants in the water shed is tied in particular to urbanization and agriculture. While the use of pesticides have definite societal benefits such as reduction of insect borne illness and improved crop yields, the presence of these contaminants still raises public health concerns. Pesticide intrusion into ground water and surface water sources is a potential threat to drinking water quality. The levels of such contaminants are monitored and limits are established by the EPA [5], [8]. Pesticides tend to be recalcitrant; the environment does not readily decompose them [78]. These compounds can therefore persist in the environment. Plasma-based approaches offer a potential solution to the mineralization of such contaminants. Pentachlorophenol (PCP) in particular is a carcinogenic compound found in pesticides and is difficult to decompose conventionally. Sharma *et al.* demonstrated high-level decomposition of PCP in an aqueous solution using glow discharge electrolysis. The glow discharge was generated at reduced pressure (50 Torr of oxygen or argon) above a solution containing 30–50 ppm of PCP. Reduction of PCP below detection limits (0.01 ppm) was achieved for process times ~ 0.5 h. The best decomposition rates were observed with air or oxygen, suggesting that ozone chemistry played an important role. The decomposition mechanism for the complete mineralization of the PCP salt was summarized



The study also found that the power cost of decomposition using this approach was competitive with conventional advanced oxidation methods such as UV/peroxide or UV/ozone [79]. More recently, it has been demonstrated that plasma-based methods of producing peroxide in liquid state is also competitive with conventional methods from an energy cost standpoint [80]. Plasma decomposition of the common herbicide atrazine has also been demonstrated using a pulsed corona discharge in the presence of an electrolyte [81].

B. Sterilization

While conventional water treatment filters and disinfects input source water, such systems may not adequately address all microbial threats. For example, as mentioned earlier, chlorine resistant bacteria spores and protozoa are not currently addressed by conventional means. AOPs can decompose these contaminants, and in this regard, such processes may be used in conjunction with conventional methods. Here, we present two representative cases illustrating the interaction of a plasma with liquid water for the purpose of bacteria inactivation. In one approach, Dors *et al.* utilized a pulsed corona discharge to disinfect *E. coli* bacteria in river water [82]. In this experiment, untreated water entered a control volume through a hollow needle electrode. The needle electrode was pulsed with high voltage relative to a larger “plane” electrode also immersed in the liquid. In this experiment, a 56 kV pulse was applied at 50 Hz to the needle electrode. In this approach, contaminated water to be processed was forced through the needle electrode,

thereby directly interacting with the pulsed corona discharge. The exponential decrease in colony forming units was documented as a function of discharge pulse number and treatment time achieving 99.8% inactivation.

A study featuring a dc plasma jet capable of operating underwater also demonstrated high levels of bacteria inactivation. In this paper, carried out by Liu *et al.*, the dc plasma jet was immersed in a solution of *S. aureus* bacteria [83]. It was observed that inactivation was not immediate; rather, there was a time delay before appreciable inactivation was observed. This delay was correlated with pH changes. When pH was sufficiently low, significant inactivation was observed. It was speculated that the time delay was attributed to the build up of the hydroperoxyl radical HOO, whose production is favored at low pH. It should be pointed out that acidification of plasma treated aqueous solutions has been observed in general. Treatment of the solution with plasmas therefore favors the production of the hydroperoxyl radical [70]. The hydroperoxyl radicals formed under these conditions oxidize the fatty acids in the cell membrane, thereby leading to membrane degradation and ultimately cell death. The synergistic antimicrobial effects of plasma produced oxidants and increased acidity have been observed elsewhere as well [84]. The exact deactivation mechanism, however, remains unresolved.

C. Textile mill dyes

Some 20% of industrial water pollution can be attributed to textile mill wastewater effluent, making this industry one of the largest producers of wastewater [10]. This amounts to approximately one million kilograms of dyestuff deposited into rivers and streams [11], [12]. The deposited textile wastewater affects the general aesthetics of the water body as well as photosynthesis processes of water plants. Some of the dyes are carcinogenic or can become carcinogenic when metabolized by microorganisms, thereby leading to food chain contamination. The dye stuffs can be toxic to fish and other aquatic life. Because microbes need oxygen to metabolize dye molecules, the presence of dye in water increases the biological oxygen demand, thereby generating regions lacking oxygen—dead zones [10], [13]. At high concentrations, the dye wastewater is not potable. The treatment of textile mill effluent is complicated by the fact that there are over 100 000 different types of dyes [85]. Additionally, these dyes are designed to resist fading and thus degradation. Traditional water treatment methods cannot remove such dyes [86]. Conventional methods, such as sorption, which produces solid sludge waste—which in turn requires disposal or biodegradation—which rely on microbial action, are not capable of removing all dyes from wastewater streams [10], [14], [15], [87]. Advanced oxidation methods show great promise in complete mineralization of organic dyes [10], [16], [24], [86], [88]–[90]. With advanced oxidation methods, the prospect of complete removal of dyes from wastewater, allowing for textile mill recycling of spent water streams, becomes a real possibility.

Plasma-based degradation of organic dyes in solution using atmospheric pressure, nonthermal discharge has been demonstrated in a number of studies [52], [66], [91]–[93], [94].

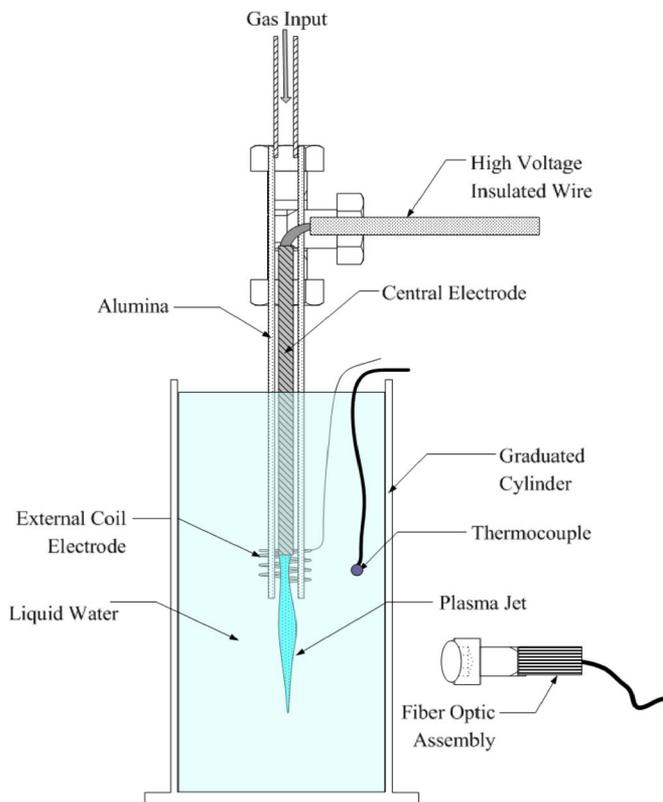


Fig. 6. Underwater DBD plasma jet.

Indeed, many investigations involving plasma interaction with liquid water tout observed decolorization of dye solutions as a demonstration of plasma-induced reactivity. For textile mill applications, one major concern is throughput and process time. A plasma-based approach must be capable of either inline processing or in-volume processing. One such method currently being investigated at the University of Michigan Plasma Science and Technology Laboratory and in collaborative efforts with NASA Glenn Research Center involves the direct insertion of the plasma applicator into the liquid medium [70], [95]. This approach features an underwater DBD shown schematically in Fig. 6. The discharge applicator consists of a centrally powered electrode with an intervening gas-fed dielectric tube separating a return coil electrode. In this approach, the discharge tube is excited with ac or fast voltage pulses, giving rise to the formation of a discharge plasma within the tube and within gas the bubble formed at the dielectric tube exit. Discharge initiation occurs only when the tube is submerged in liquid water. Vacuum field simulations suggest that field amplification just downstream of the central electrode tip occurs in the presence of the water, thereby making conditions favorable for breakdown. The amplification is derived from field refraction owing to the large difference in dielectric permittivity between the water and the air. This amplification is illustrated in simulations results shown in Fig. 7. The interaction of the discharge jet with the water-air interface contributes to the production of radicals and associated reactivity. At low frequency excitation < 5 kHz, the discharge may be considered the supposition of microdischarges and an arclike discharge, the appearance of which depends on polarity [70]. Discharge

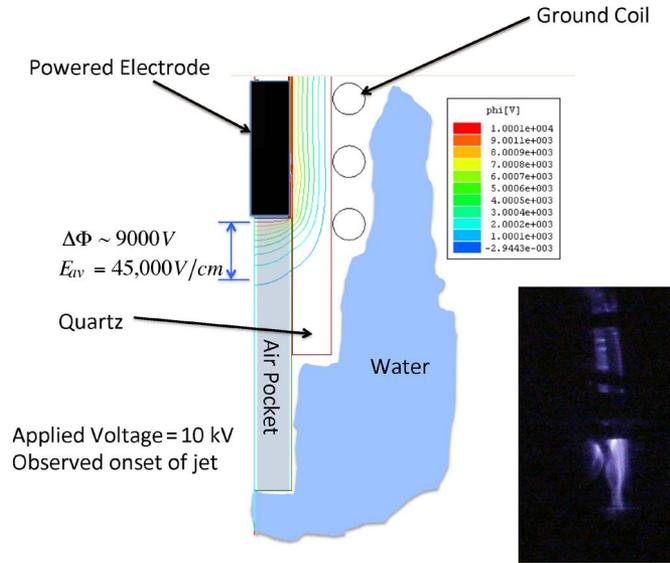


Fig. 7. Simulation results indicating electric field amplification downstream of electrode tip. Inset shows multimode operation.



Fig. 8. Plasma driven decomposition of dye.

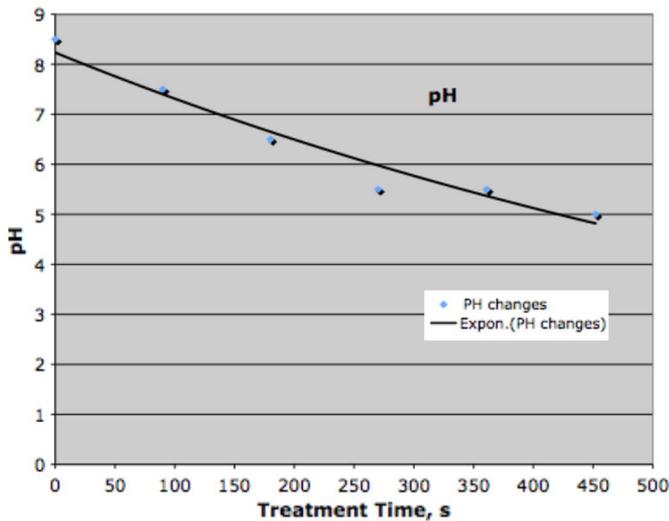


Fig. 9. pH variation with time of MB treated solution.

appearance is shown in the inset of Fig. 7. When excited with ns voltage pulses, the discharge produced is a combination of a background corona glow and streamers. The interaction of the plasma with the liquid as well as radicals and ozone produced in the tube itself contribute to the decomposition of the dye. Rapid decoloration of the methylene blue textile simulant was observed as shown in Fig. 8. Decomposition was verified using both spectrophotometric methods and a high-pressure liquid chromatograph. Fig. 8 shows results from a demonstration

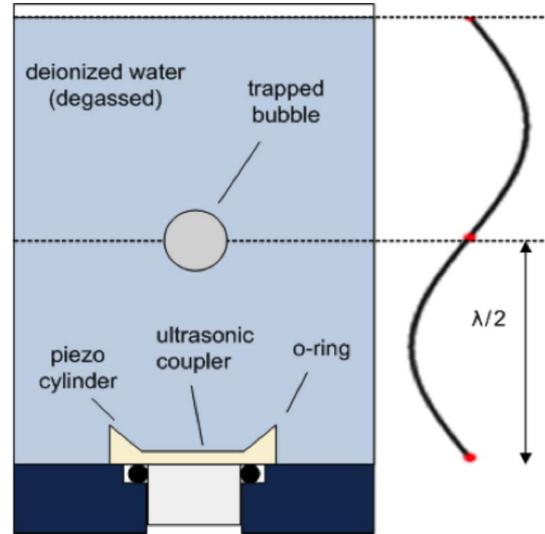


Fig. 10. Ultrasonic levitation chamber.

experiment in which a 100-ml solution of 4.3 mg of methylene blue dye in deionized water was processed. Here, the molarity of the methylene blue solution decreased from $1.7 \times 10^{-4} M$ at $t = 0 s$ to $1.2 \times 10^{-5} M$ over a treatment time of just over 7 min. The treated samples were observed to be acidic after treatment as indicated in Fig. 9. To put the acidity in context, a pH of 2 is typical of lemon juice. The acidity may be related to organic acid formation during dye decomposition [96]. Recent studies suggest that the acidity itself plays an important role in the decomposition of organic compounds in solutions [84], [97]. In those works, it is suggested that the nitrogen in the feed gas (air) gives rise to the formation of nitrogen-based acid. If the end goal is to re-introduce treated water back into the plant to repeat the dyeing cycle or if it's a once through process where treated water is returned to rivers, lakes, and streams, then the chemical state of the processed liquid must satisfy certain requirements. For the case of reintroduction into the environment, the toxicity of treated water must be carefully assessed. In this regard, a toxicity assessment must be an important aspect of plasma in liquid water research. In an effort to make a preliminary assessment of the toxicity of treated solutions, living cells were exposed to the plasma-treated methylene blue solution. This study involved growing the melanoma cells in a pH-adjusted solution of the plasma-treated liquid. All samples showed negligible toxicity with a greater than 90% cell survival rate. This preliminary work suggests that the solutions are not toxic at least for cancer cells. Future work will involve healthy cells.

D. Towards Plasma Production in Isolated Bubbles

Nearly all of the plasma injection methods investigated to date have involved electrodes either above or immersed in the liquid water. The presence of the electrodes in water increases the probability of contamination derived from electrode erosion. Such erosion also limits applicator lifetime. To achieve the necessary electric fields for breakdown, interelectrode spacing must be minimized, which means process volume is inherently small. An alternative approach that could improve in-volume

processing rates and eliminate electrode erosion and subsequent liquid contamination is to produce the discharge in free bubbles detached from the electrode. Plasma formation in free bubbles is ideal for in volume processing. Such an approach requires sufficient coupling of the applied field to the bubble. For in-volume processing, bubbles must be produced in multiplicity. Under such conditions, streamer hopping, whereby the initiating discharge can seed a discharge in adjacent bubbles via photoionization, can assure a multiplicity of discharge breakdowns in a large number of bubbles [65]. Streamer hopping therefore allows for the prospect of large volume processing.

At the University of Michigan's Plasma Science and Technology Laboratory, the study of plasma production in an isolated bubble is being investigated. This study involves first generating conditions necessary to isolate and stabilize a single bubble for study. Air bubbles are isolated by levitating them in an underwater ultrasonic acoustic field, shown in Fig. 10. Electric field pulses from unattached electrodes can then be used to excite the bubble. Applied electric fields create an effective pressure on the electrical charge residing on the gas liquid interface. This charge is composed of bound charge created by the permittivity gradient at the dielectric boundary and free charge deposited there by the ions present in solution owing to water's finite conductivity. If the stress is sufficiently large, the bubble can undergo extreme changes to both its shape and volume.

When the bubble changes shape, its internal gas pressure changes as well. In addition, the distortion of the bubble shape can sharpen the curvature of the dielectric boundary, locally enhancing the electric field. Both effects combine to alter the E/N within the bubble. In this manner, the E/N commensurate with breakdown can be achieved either by driving the bubble distortions with an applied electric field or by driving the bubbles through various shape modes and applying a high-voltage pulse near the optimal E/N . This approach holds promise for the possibility of achieving breakdown at reduced applied voltage and in isolated bubbles. By ultrasonically isolating bubbles, one can excite deformations and document the resulting change in shape and volume using a controlled repeatable, procedure. Using this technique, we can study bubble deformations over a variety of parameters such as applied field strength, field frequency, bubble size, and field shape. The response of the bubble to applied voltage has been documented using a fast camera with an acquisition rate of 5000 frames/sec. To date mm-sized bubbles have been driven in volume modes with documented cross sectional area changes of 120% above nominal size. An example of an ultrasonically levitated bubble driven by ac electric fields is shown in Fig. 11. As the electric field strength increases in the vertical direction, the bubble stretches in response to the electrical stress. As the field reduces to zero, the bubble returns to its original shape.

The curvature at the bubble's surface during these oscillations is of particular interest as mentioned earlier because it determines the distortion of the external electric field, which under certain conditions can be focused and locally increased. The most convenient model for these shape oscillations is the spherical harmonics with azimuthal symmetry ($m = 0$). In this specific example shown in Fig. 11, the oscillation is dominated

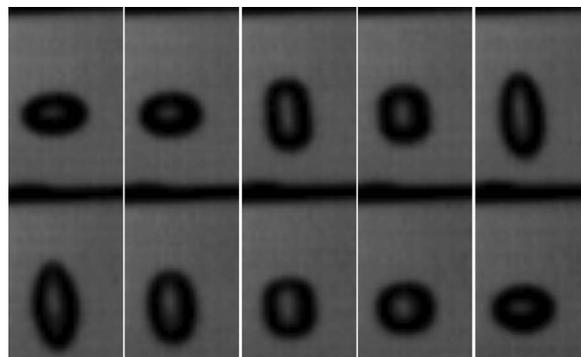


Fig. 11. Electric field-driven oscillations of an acoustically levitated air bubble in water. (190 ms per frame, 2.3-mm interelectrode gap).

by the $n = 2$ mode. However, when the bubble enters its most extreme rarefaction, the bubble tips undergo drastic distortion, forming a “cone tip,” suggesting the presence of many higher order harmonics. These cone tips should experience dramatic increases in the local electric field.

In a separate experiment, the formation of streamers in a bubble has been observed to severely distort the air-bubble interface, due in large part to the intense field strength at the tip of the streamer. These local spikes in electrical pressure are observed to excite the propagation of surface capillary waves [98]. These localized distortions, depicted in Fig. 12 amplify the applied electric field making conditions favorable for the formation of subsequent breakdowns.

VII. CONCLUDING REMARKS

The field of plasma interactions with liquid water is growing rapidly. Plasmas offer a novel method of introducing advanced oxidation processes into liquid water. This method can be applied to the purification of drinking water as well as the treatment of industrially derived wastewaters. The plasma-based water treatment technology also holds promise for the development of point-of-use water treatment capacity for those underdeveloped areas where a centralized conventional water treatment system is absent. In this regard, the promise of solidifying this research into practical technologies is high. In many respects it addresses societal needs. On the other hand, the field is highly interdisciplinary, merging physics with chemistry and environmental science. Rich physics abounds at the water-air interface. Basic questions still remain: (i) How does reactivity transfer to the liquid state; (ii) What is the state of matter at the water-air interface in the presence of the plasma? These questions require the development of new diagnostics to better understand the physics and chemistry of the interface and the role of the plasma there. Diagnostics in need include better chemical probes for the liquid state, modified Schlieren methods to image the discharges underwater, and electrochemical probes analogous to Langmuir probes to better assess plasma in bubbles and at the interface. High-speed optical diagnostics continue to be developed and will play key roles in understanding the mechanics of plasma discharge-liquid water interactions. Much has been learned to date but for practical implementation, issues such as throughput, conversion

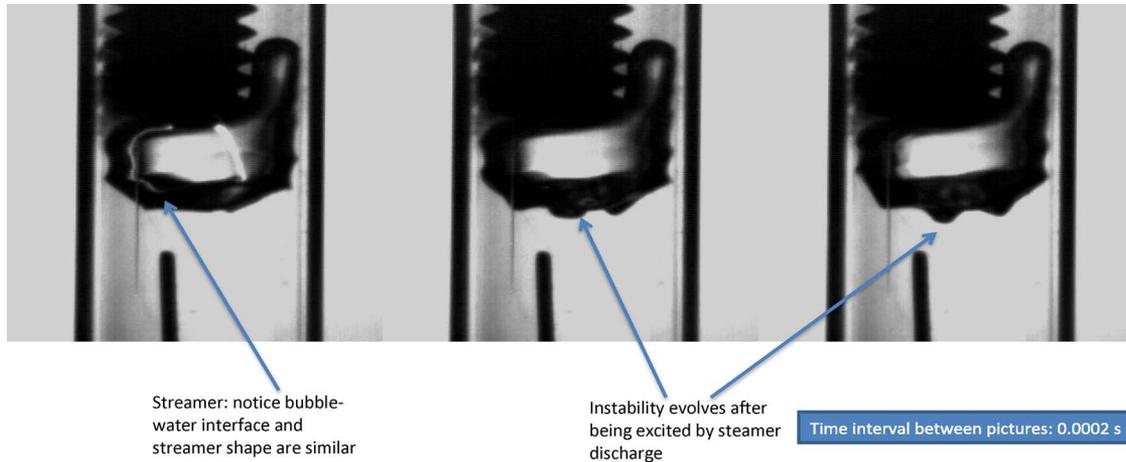


Fig. 12. Capillary wave oscillations induced by streamer formation.

efficiency, applicator lifetime, and processed liquid toxicity must be thoroughly assessed.

Scaling up plasma-based water treatment methods demonstrated in the laboratory to the level of a pilot plant is a key technical challenge. The aforementioned methods of plasma-based AOPs typically feature localized plasma injection or interaction. Such localization is inherently limiting from a throughput and process time standpoint. The challenge is therefore to considerably increase the volume per unit time processing capacity. One such approach involves the parallel operation of multiple plasma applicators. Promising results featuring multiple applicators have been reported by others and investigated by the authors as well. Another possible approach is the implementation of a “plasma array.” Here, a spatially, dense array of plasma discharges form effectively a virtual “membrane” through which water must pass. Such a geometry would accommodate high throughput systems. Resonantly driving isolated bubbles at their natural frequency with an applied electric field to achieve breakdown conditions at reduced voltages is still another potential pathway to large volume processing. Research into such approaches and variants will be necessary for practical implementation. Additionally, it has been suggested that effective implementation of advanced water treatment methods might involve a combination of AOP pretreatment followed by bioremediation stage. Here, the goal of the AOPs would be to transform waste effluent into a biodegradable variant [99]. This approach is attractive from an economic standpoint in that the energy cost is split between energy consuming plasma-based treatment methods and the lower cost biological oxidation methods [100]. Under such an implementation however, care must be taken to assure that plasma-produced intermediates are not toxic to biological decomposition agents. From a scale-up perspective, standalone plasma-based methods in comparison to conventional AOP methods, involve multiple oxidation processes that are created at once, thereby potentially reducing treatment times as compared with a single advanced oxidation process method. Research into these areas is important in that the results and findings will form the basis of the bridge that will merge the plasma laboratory demonstrations to practice, bringing to bear the promise of plasma-based AOPs for the future of water purification.

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