Plasma Technology for the Future of Wastewater Treatment

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Abstract *— The conventional wastewater treatment used in Puerto Rico cannot remove micropollutants, which are contaminants that occur in low concentrations and are found on Wastewater Treatment Plant effluents, and therefore, are discharged in the receiving water body. These micropollutants include drugs, pesticides, herbicides, Industrial effluent chemicals and personal care products. It has been proven that these micropollutants have negative effects on humans and the environment. This work presents the Plasma technology as an interesting and promising advanced oxidation technology capable of treating wastewater efficiently, and removing the micropollutants mentioned above. Plasma technology has the ability to generate a wide spectrum of oxidative species and processes in proximity of the wastewater, which is ideal for efficient micropollutant decomposition. The investigation has proven that the use of Plasma technology for the treatment of wastewater is a promising technology for the future of wastewater treatment.*

Key Terms *— Advanced Oxidation, Conventional Wastewater Treatment, Micropollutants, Plasma Technology.*

INTRODUCTION

Because of the increase in micropollutants found in receiving water bodies and the knowledge that those micropollutants are dangerous for human health and the environment, Plasma technology is gaining interest for the future of Wastewater Treatment. Plasma has the characteristic that it can generate a wide spectrum of oxidative species and processes in proximity of the wastewater [1]. This is particularly important for the decomposition of those micropollutants. Plasma in contact with water generates significant amounts of Ozone O_3, Hydrogen Peroxide H_2O_2, oxygen O, Hydroperoxyl HO_2, and superoxide anion O_2^-. The Hydroxyl OH is named as the most important because of its high standard oxidation potential. The presence of different types of oxidants reduces the selectivity of the Plasma oxidation method, making it unselective, which is important for the removal of all micropollutants found in effluents. Studies show that using Plasma technology for the treatment of wastewater is effective in removing micropollutants without using chemicals that are unhealthy for humans and the environment. The real challenge is to include Plasma technology in a reactor for the wastewater treatment process. In this work two types of Plasma reactors are presented further trying to understand Plasma technology as a viable technology for wastewater treatment.

JUSTIFICATION

Conventional Wastewater Treatment Plants are not designed or capable of removing micropollutants; these Plants are only capable of removing organic matter and nutrients in greater concentrations. Micropollutants are increasing because of lifestyle changes and Industrialization, therefore are more abundant in effluents and water bodies. It is proven that these micropollutants are harmful to humans and the environment, finding environmental effects like microorganism resistance due to antibiotics, feminization, masculinization and immunomodulation in fish and frogs, chronic effects in human health including cancer, and bioaccumulation in living organisms [2]. Due to these serious problems, an innovative technology should be studied and implemented as soon as possible, to improve human health and the environment, therefore improving quality of life.

The Plasma technology has the most important characteristic for the decomposition of contaminants and micropollutants, which is that it can generate a wide spectrum of oxidative species and processes in proximity of the solution under treatment. Also, Plasma does not need chemicals, and it can be of simple operation and maintenance. This makes Plasma a target to implement in the wastewater treatment process in Puerto Rico.

LITERATURE REVIEW

Conventional wastewater treatment consists of the following steps: 1) primary treatment consisting of mechanic and/or physicochemical treatment removing solids, oils and fats; 2) secondary treatment consisting of biological treatment converting colloidal and dissolved organic compounds to low energy stabilized compounds through a diverse group of microorganisms in the presence of oxygen; 3) tertiary treatment consisting of disinfection through chlorination and ultraviolet disinfection, improving the quality of the effluent and therefore improving the environment of the receiving water body receptor [3]. Figure 1 shows the complete process of a conventional Wastewater Treatment Plant.

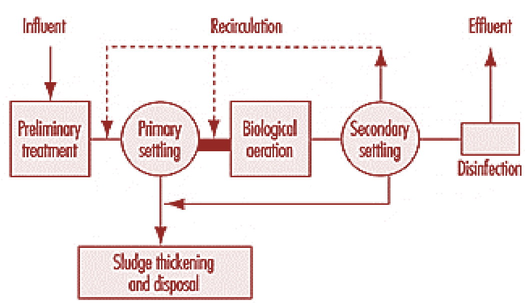

Figure 1
Conventional Wastewater Treatment Process

Micropollutants are organic or mineral substances, persistent and bioaccumulative properties may have a negative effect on the environment and/or organisms. Progress in laboratory analysis is increasingly highlighting their presence in the aquatic environment at extremely low concentrations, in the order of one nanogram per liter [4]. Some of these substances have potentially chronic direct and/or indirect effects on ecosystems and human health.

Plasma is one of the four fundamental states of matter. Plasma can be created by heating a gas and subjecting it to a strong electromagnetic field. This creates ions and dissociates molecular bonds. Plasma has charge carriers making it electrically conductive, and that's why it responds to electromagnetic fields. The ions in Plasma are unbound but not free, and when a charged particle moves, it generates an electric current with magnetic fields. Figure 2 shows a Plasma matter.

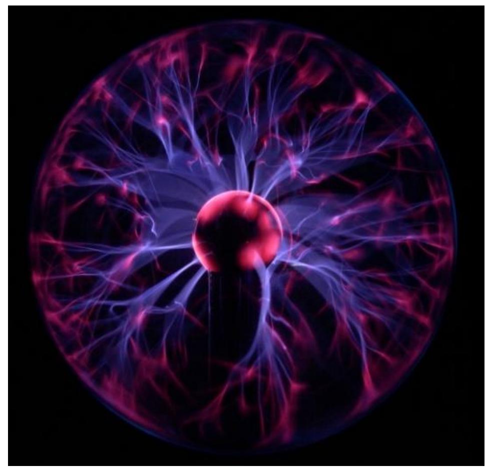

Figure 2
Plasma Matter

Plasma Research for Wastewater Treatment

The earliest studies of electrical discharges in the presence of water started with Faraday's work in 1832. Early studies showed that electrical discharge dissociates water into hydroxyl (OH^-), the most important because of its high standard oxidation potential, and hydrogen (H^+) radicals, and could lead to dissociation of OH^- into oxygen atoms (O) and H^+. Later studies showed that it produced hydrogen peroxide (H_2O_2), molecular oxygen (O_2) and hydrogen (H_2), hydroperoxyl (HO_2) and other radicals. Also, studies showed that shock waves and UV light can also be formed. Later, Clements, Sato and Davis (1987) published the first results on the chemical effects of electrical discharges formed directly in water. With that, they found that molecules inside the Plasma dissociate into highly oxidative radicals which can induce chemical changes in compounds present in the bulk liquid [5].

CASE STUDIES

Because of the Plasma ability to generate a wide spectrum of oxidative species and processes in proximity of the solution under treatment, this study is focus on two reactor types to apply Plasma in the water to be treated: electrohydraulic discharge reactors and gas phase discharge reactors.

Gas Phase Discharge Reactors (in gas phase over bulk or film)

Electrical discharge in the gas phase is more energy efficient for organic degradation than discharge in the liquid phase, i.e. electrohydraulic discharge. In this work, one subgroup of gas phase discharge reactors will be studied: corona and glow discharge over a horizontal water surface.

Corona and glow discharge over water surface has a pin-to-water configuration with a grounded water electrode, as shown in Figure 3. This type of discharge is mostly generated with pulsed power.

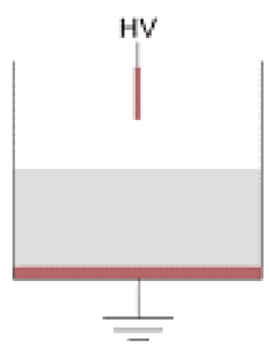

Figure 3
Corona and Glow Discharge over Water Surface Pin-to-Water Configuration with Grounded Water Electrode

Positive and negative DC (direct current) and monopolar pulsed voltage have been used for water treatment. To increase Plasma volume, high voltage pin electrode with multipoint, a brush or a horizontal wire can be used instead of a pin-to-water configuration.

Atmospheric pressure glow discharge in air produces gaseous nitrogen oxides, forming undesirable aqueous nitrates and nitrites, but DC positive corona produces ozone in air with no nitrogen oxides.

Energy efficiency of organic decomposition is independent of the type of discharge, voltage amplitude, polarity, and amount of pin electrodes. Dimensions and movement of the water phase in corona and glow discharge reactors can affect energy efficiency. Water movement affects radial flow reactors. To enhance the oxidation process, the solution flow should be as a thin film along the discharge [6].

This type of gas phase discharge leads to the oxidation of ferrous salts. Also, in DC corona discharge with HV (high voltage), forms nitrates and nitrites. Also, NO and NO_2 are formed in the gas phase from the nitrogen in the air and, the reaction with water, hydroxyl radicals, and other oxidants in the liquid phase lead to nitrate and nitrite formation. Placing the HV (high voltage) electrode in the aqueous phase and the ground in the gas phase leads to formation of larger quantities of hydrogen peroxide. The reactions of ozone, hydrogen peroxide, and other radicals may lead to very effective degradation or organic compounds, showing that this type of discharge can be very promising for the future of wastewater treatment. This discharge also can produce ozone and hydrogen peroxide making it ideal for organic degradation, but the presence of humid air is known to decrease the efficiency of ozone generation.

Electrohydraulic Discharge Reactors (directly in the water bulk)

Electrohydraulic discharge reactors have high ratio of Plasma-water contact surface to Plasma volume and proximity of Plasma to the water surface. Because of the direct contact between Plasma and water, electrohydraulic discharge reactors are the most efficient reactors in water treatment. These reactors generate shock waves that help in the process of organic decomposition. This technology produces hydrogen peroxide, molecular oxygen and hydrogen, hydroxyl, hydroperoxyl, hydrogen, oxygen, and ozone. Because of the production of all these reactive species, this technology rapidly and efficiently degrades many organic compounds. Also, the production of all these species, chemical and mechanical mechanisms, makes it ideal for the removal of chemical and microbial contaminants, and, eliminates the need for externally supplied sources of hydrogen peroxide, ozone, and other highly reactive compounds [7].

This reactor requires additional input energy for cavitation, making it a less efficient reactor than other types of reactors for water treatment.

The treatment mechanisms generated by electrohydraulic discharge include high electric fields, radical reactions (ozone, hydrogen peroxide), UV irradiation, thermal reactions, pressure waves, electronic and ionic reactions, and electromagnetic pulses. Both electron and ion densities are proportional to the discharge current, and UV intensity, radical densities and the strength of pressure waves are proportional to the discharge power. Electrohydraulic discharge has the potential to be more efficient than either indirect or remote Plasma because they use all these mechanisms mentioned above due to direct contact with the wastewater to be treated. It has been found that electrohydraulic discharge effectively treats aqueous chemical contaminants such as atrazine, paraquinone, 4-chlorophenol, dichloroanaline, phenol, dyes, urine compounds, MTBE, and, trinitrotoluene.

Other studies found that electrohydraulic discharge produces benzoquinone and chloride as a function of cumulative power input, and 99% TNT (2,4,6-Trinitrotoluene) degradation was achieved.

Types of Electrohydraulic Discharge Reactors (directly in the water bulk)

The most common types of electrohydraulic discharge reactors are pulsed arc electrohydraulic discharge (PAED) and pulsed corona electrohydraulic discharge (PCED). Therefore, these two types of electrohydraulic discharge systems will be studied and compared.

The characteristics of pulsed corona (PCED) are summarized in Table 1.

PCED include an operating frequency of 10^2 to 10^3 Hz, current of 10^1 to 10^2 A, voltage of 10^4 to 10^6 V, voltage rise of 10^{-7} to 10^{-9} secs, weak pressure wave generation, weak UV generation.

Table 1
Pulsed Corona Electrohydraulic Discharge Characteristics

Operating Frequency	10^2 to 10^3 Hz
Current	10^1 to 10^2 A
Voltage	10^4 to 10^6 V
Voltage Rise	10^-7 to 10^-9 secs
Preassure Wave Generation	Weak
Weak UV Generation	Weak

A streamer-like corona is generated in the water when the distance between high voltage and grounded electrodes is large enough and the discharge does not cover the whole gap between electrodes. Also, weak shock waves and UV radiation are formed. Because of these weak shock waves and UV radiation generated, radicals and reactive species are formed in the narrow region close to the discharge electrodes, and bubbles are also formed.

It has been found that electrohydraulic discharge effectively treats aqueous chemical contaminants such as atrazine, paraquinone, 4-chlorophenol, dichloroanaline, phenol, dyes, urine compounds, MTBE, and, trinitrotoluene, however, organic compound treatment by PCED requires the addition of activated carbon.

Pulsed corona (PCED) is good for removing microorganisms, urine components, and VOCS, and is partial in removing algae and adequate in removing inorganic compounds.

Pulsed arc (PAED) is summarized in Table 2.

Table 2
Pulsed Arc Electrohydraulic Discharge Characteristics

Operating Frequency	10^-2 to 10^2 Hz
Current	10^3 to 10^4 A
Voltage	10^3 to 10^4 V
Voltage Rise	10^-5 to 10^-6 secs
Preassure Wave Generation	Strong
Weak UV Generation	Strong

PAED has an operating frequency of 10^{-2} to 10^2 Hz, current of 10^3 to 10^4 A, voltage of 10^3 to 10^4 V, voltage rise of 10^{-5} to 10^{-6} secs, strong pressure wave generation, and strong UV generation. PAED makes rapid discharge of stored electrical charge across a pair of submerged electrodes to generate electrohydraulic discharges forming a local Plasma region. PAED also generates Plasma bubbles because of strong shock waves. Because of its strong UV radiation, PAED generates high radical densities, which are short-lived in the cavitation zone. A common PAED configuration is the rod-to-rod electrode configuration, where high voltage and ground electrodes are placed directly in the water to be treated (refer to Figure 4).

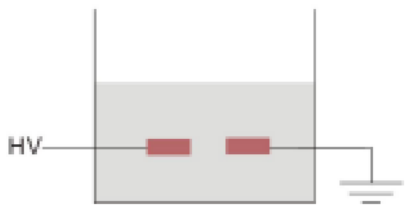

Figure 4
Pulsed Arc (PAED) Reactor Rod-to-Rod Electrode

Figure 5 shows PAED mechanisms in water treatment.

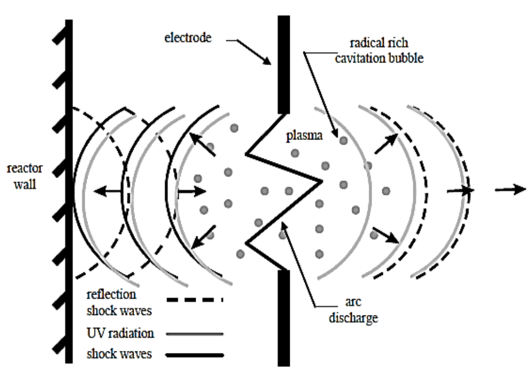

Figure 5
Pulsed arc (PAED) Mechanisms in Water Treatment

Pulsed arc (PAED) is good in removing microorganisms, algae, and urine components, and adequate in removing VOCS and inorganic compounds. PAED offers effective treatment for broader contaminants, including micropollutants, than conventional treatment. PAED is also more effective than indirect plasma in removing microorganisms, algae, VOCS, nitrogenous municipal waste compounds, and inorganics. All these treatments can be available with PAED as opposed to different treatments employed. Other good characteristic about PAED is that it uses less than 50% of KW/hr required by other Plasma technologies for effective water treatment.

Analysis and Comparison of the Two Types of Plasma Reactors

Electrical discharge in the gas phase is more energy efficient for organic degradation than discharge in the liquid phase, i.e. electrohydraulic discharge. Corona and glow discharge over water surface has a pin-to-water configuration with a grounded water electrode, meaning that the Plasma is not in direct contact with the wastewater to be treated. Atmospheric pressure glow discharge in air can produce gaseous nitrogen oxides, forming undesirable aqueous nitrates and nitrites, which must be controlled.

Energy efficiency of organic decomposition in gas phase is independent of the type of discharge, voltage amplitude, polarity, and amount of pin electrodes, but dimensions and movement of the water phase in corona and glow discharge reactors can affect energy efficiency. This means that the reactor can be very energy efficient and therefore improve the wastewater system that uses this type of gas phase reactor.

In this type of gas phase discharge, it has been proven that it leads to the oxidation of ferrous salts, the formation of nitrates and nitrites, NO and NO_2, and the reaction with water, hydroxyl radicals, and other oxidants in the liquid phase lead to nitrate and nitrite formation. Also, placing the HV electrode in the aqueous phase and the ground in the gas phase leads to formation of larger quantities of hydrogen peroxide. The reactions of ozone, hydrogen peroxide, and other radicals in such cases may lead to very effective degradation or organic compounds, showing that this type of discharge can be very promising for the future of wastewater treatment. This discharge also can produce both ozone and hydrogen peroxide making it ideal for organic degradation, but the presence of humid air is known to decrease the efficiency of ozone generation.

Electrohydraulic discharge reactors, on the other hand, have high ratio of Plasma-water contact surface to Plasma volume and proximity of Plasma to the water surface. Because of the direct contact between Plasma and water, electrohydraulic discharge reactors are the most efficient reactors in water treatment. These reactors generate shock waves that help in the process of organic decomposition. This technology produces hydrogen peroxide, molecular oxygen and hydrogen, hydroxyl, hydroperoxyl, hydrogen, oxygen, and ozone. Because of the production of all these reactive species, this technology rapidly and efficiently degrades many organic compounds. Also, the production of all these species, chemical and mechanical mechanisms, makes it ideal for the removal of chemical and microbial contaminants, and also, eliminates the need for externally supplied sources of hydrogen peroxide, ozone, and other highly reactive compounds.

On the bad side, electrohydraulic discharge reactor requires additional input energy for cavitation, making it a less efficient reactor than gas phase and other types of reactors for wastewater treatment.

The treatment mechanisms generated by electrohydraulic discharge include high electric fields, radical reactions (ozone, hydrogen peroxide), UV irradiation, thermal reactions, pressure waves, electronic and ionic reactions, and electromagnetic pulses. Both electron and ion densities are proportional to the discharge current, and UV intensity, radical densities and the strength of pressure waves are proportional to the discharge power, which can be controlled and can be a great factor for the future design of Wastewater Treatment Plants.

Electrohydraulic discharge has the potential to be more efficient in the treatment of wastewater than either indirect or remote Plasma because they use all these mechanisms mentioned above due to direct contact with the wastewater to be treated. It has been found that electrohydraulic discharge effectively treats aqueous chemical contaminants such as atrazine, paraquinone, 4-chlorophenol, dichloroanaline, phenol, dyes, urine compounds, MTBE, and, trinitrotoluene.

Other studies found that electrohydraulic discharge produces benzoquinone and chloride as a function of cumulative power input, and 99% TNT (2,4,6-Trinitrotoluene) degradation was achieved.

Table 3 shows a summary of the comparisons between electrohydraulic discharge and gas phase discharge.

Table 3
Electrohydraulic Discharge and Gas Phase Discharge Comparison

Energy efficiency	Low	High
Plasma contact with water	High	Low
Treatment efficiency	High	Medium
Sock wave generation	High	Medium
Reactive species production	High	Low
Need of external supply source (chemicals)	None	None
Chloride production	Yes	No

Based on the analysis made and the Table 3 comparisons, Electrohydraulic Discharge reactors are more efficient in wastewater treatment and therefore should be implemented in Wastewater Treatment Plants in Puerto Rico. But future studies must concentrate also in how to make this reactor more energy efficient so that it can be commercialized and used as a conventional wastewater treatment system.

Between the two types of electrohydraulic discharge reactors shown in this study (Pulsed Corona and Pulse Arc), as Tables 1 and 2 show, Pulsed Arc Electrohydraulic Discharge (PAED) is the more wastewater treatment efficient of the two.

PCED has an operating frequency of 10^2 to 10^3 Hz, where PAED has an operating frequency of 10^{-2} to 10^2 Hz; PAED needing less frequency. PCED uses current of 10^1 to 10^2 A, PAED needing less current of 10^3 to 10^4 A. PAED uses less voltage than PCED, having also a lowest voltage rise than PCED. PCED has weak pressure wave generation and weak UV generation, whereas PAED has strong pressure wave generation and strong UV generation.

PAED also generates Plasma bubbles because of strong shock waves. PCED produces low Plasma bubbles. Because of its strong UV radiation, PAED generates high radical densities (as shown in Figure 5).

PAED is good in removing microorganisms, algae, and urine components, and adequate in removing VOCS and inorganic compounds. PAED offers effective treatment for broader contaminants, including micropollutants, than PCED and conventional treatment. PAED is also more effective than indirect Plasma in removing microorganisms, algae, VOCS, nitrogenous municipal waste compounds, and inorganics. All these treatments can be available with PAED as opposed to different treatments employed. Other good characteristic about PAED is that it uses less than 50% of KW/hr required by other Plasma technologies for effective water treatment.

Based on the analysis between PAED and PCED, PAED is much more effective in removing contaminants and micropollutants, and is more energy efficient, which makes it more appeal for a conventional wastewater treatment system is Puerto Rico.

CONCLUSIONS AND FUTURE WORK

Conventional Wastewater Treatment Plants Recent do not remove the majority of the hazardous micropollutants. These micropollutants are hazardous both for the environment and humans. Therefore, new technologies are being studied worldwide. From all techniques studied as future wastewater treatments, advanced oxidation techniques are the most effective available for the removal of micropollutants from wastewater. One disadvantage though, is the high energy costs, making these techniques difficult for large scale, but viable for small scale like Industries and Hospitals.

One of the most promising advanced oxidation techniques, Plasma technology, is gaining interest because of its characteristics. From the two reactor types studied, electrohydraulic discharge and gas phase discharge, electrohydraulic discharge is the most efficient to remove contaminants and micropollutants from wastewaters.

Electrohydraulic discharge has the most important characteristic for micropollutant decomposition; it generates a wide spectrum of oxidative species (both mechanical and chemical), creating low selectivity of the degradation process and suitable for removing both chemical and microbial contaminants. These treatment mechanisms generated by electrohydraulic discharge include high electric fields, radical reactions (ozone, hydrogen peroxide), UV irradiation, thermal reactions, pressure waves, electronic and ionic reactions, and electromagnetic pulses. Both electron and ion densities are proportional to the discharge current, and UV intensity, radical densities and the strength of pressure waves are proportional to the discharge power, which can be controlled and can be a great factor for the future design of Wastewater Treatment Plants. Also, eliminates the need for externally supplied sources of hydrogen peroxide, ozone, and other highly reactive compounds. It is proven that electrohydraulic discharge is potentially as effective and even more efficient in the treatment of contaminants and micropollutants than conventional treatment technologies.

According to the study, Pulsed Arc Electrohydraulic Discharge (PAED) is the most efficient type. PAED is more energy efficient and more treatment efficient, producing more UV and pressure wave. Pulsed arc (PAED) is good in removing microorganisms, algae, and urine components, and adequate in removing VOCS and inorganic compounds. PAED offers effective treatment for broader contaminants, including micropollutants, than Pulsed Corona (PCED) and conventional treatment. PAED is also more effective than indirect Plasma in removing microorganisms, algae, VOCS, nitrogenous municipal waste compounds, and inorganics.

Further optimization of Plasma technology can be achieved by combining it with other advanced treatment methods. There has been reports about it, but requires additional attention. Application of Plasma discharge for wastewater treatment will depend not only on efficiency of contaminant removal, but also on energy efficiency compared to conventional treatment and other technologies. Since the energy is at an all-time high in Puerto Rico, energy efficiency will be an important factor for evaluation. Optimization of the reactor for a range of operating conditions, range of contaminants that could be treated effectively, potential additives and catalysts to the reactions initiated, possible hazardous by-product formation, sustainability, ease of operation, capital costs, and maintenance costs will determine if the technology will be used on a large-scale in Puerto Rico and the world.

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