

## PULSED POWER FOR ADVANCED WASTE WATER REMEDIATION

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### Abstract

We describe a 2-stage technology for degrading water borne chlorinated/aromatic organic pollutants, based on a pulsed power treatment in the first stage followed by bio-treatment. The combination of a strong pulsed corona/streamer discharge in the water aerosol in the first stage with inoculation of partially dechlorinated (15-30%) processed water with bacteria *Pseudomonas mendocina* KR1 in the second stage demonstrated as high as 90% dechlorination in the first 40 hours after inoculation, whereas the control (non aerosol-treated sample) had no chloride ions released, and no bacterial growth. The main features and advantages of the novel two-stage approach, and future plans for research are presented and analyzed.

### Introduction

Efficient degradation of airborne pollutants in non-thermal plasmas (NTP) generated in short electric pulses (tens-hundreds of nanoseconds) has been demonstrated for a variety of applications<sup>1</sup>. The main participants in the respective chemical reactions -are energetic and hydrated electrons, free radicals (OH-, H, O, O<sub>3</sub>, etc.) and UV<sup>2</sup>. At the same time, straight forward application of NTP techniques to bulk aqueous waste seems questionable, due to the specific properties of liquid waste water, namely: three orders higher density, high resistive losses, and an order higher electric strength. The statistical nature of streamer formation and the rapid transition of the discharge channel in the liquid water to high conductivity state usually precludes the development of a multi-channel discharge in the bulkwater<sup>3</sup> and usually results in formation of one-few spark channels with a temperature of a few eV. In such applications the bulk of the water would remain unionized, except for the layer near the discharge channel, and the energy input would be inefficiently utilized<sup>4</sup>.

Recently a novel approach was tested, which involves formation of the short pulse discharge in the water aerosol<sup>5</sup>. The technology proved to be of high efficiency for degradation of variety of water born halogenated organic pollutants (para-Nitrophenol (PNP), dichloroethylene- DCP) demonstrating dechlorination of 10-25% in one cycle from the initial 1000 ppm concentration of pollutant<sup>5</sup>.

Although chlorinated compounds may be further dechlorinated by recycling the treated sample through the aerosol discharge, the additional cost of this process would significantly decrease its commercial potential. Furthermore, the dechlorinated compound is not mineralized completely to water and carbon dioxide.

A more economical alternative, which also has the potential to mineralize pollutants, is bio-remediation. Unfortunately, bacteria such as *Pseudomonas mendocina* KR1 do not readily use highly chlorinated compounds for growth (e.g., DCP, perchloro-ethylene-PCE, etc.), although many non-halogenated compounds are metabolized (e.g. cresol, phenol, and toluene)<sup>6</sup>. This recalcitrance hinders the use of bacteria in the mineralization of the broad range of halogenated wastes. However, the advantages of both these degradation methods may be combined in a two stage

The first published data on a 2-stage approach are related with irradiation with a MeV energy DC electron beam with a large cross-section of a water waste stream from synthetic rubber plant in Russia, followed up with a biodegradation stage<sup>7</sup>. Our approach differs from Buslaeva et. al.<sup>7</sup> since the first stage rep-rate short pulsed discharge in the water aerosol<sup>8</sup>. The maturity of pulsed power technology, its inexpensiveness and customer friendliness are of high potential for

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1. REPORT DATE <b>JUN 1997</b>	2. REPORT TYPE <b>N/A</b>	3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>Pulsed Power For Advanced Waste Water Remediation</b>		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>University of California, Irvine, CA, 92697-4575</b>		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>			
13. SUPPLEMENTARY NOTES <b>See also ADM002371. 2013 IEEE Pulsed Power Conference, Digest of Technical Papers 1976-2013, and Abstracts of the 2013 IEEE International Conference on Plasma Science. Held in San Francisco, CA on 16-21 June 2013. U.S. Government or Federal Purpose Rights License.</b>			
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15. SUBJECT TERMS			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>	<b>SAR</b>
			18. NUMBER OF PAGES <b>6</b>
			19a. NAME OF RESPONSIBLE PERSON

commercial application. This paper presents description and analysis of the experiments along this innovative approach for the degradation of model aqueous compounds-DCP and PNP.

### 1-st Stage: Main Advantages

The main advantages of a short pulse discharge in the aerosol in the 1-st stage are:

- Absence of the sparks channels and related energy losses for media heating. With hundred nanosecond pulse duration in the replate mode of  $10^2$ - $10^3$  Hz the streamer phase of the discharge does not transit to a spark discharge.
- Increase of the air-liquid boundary surface area. In case of 10-100  $\mu\text{m}$  droplets the exposed water surface area reaches  $10^4$ - $10^5$   $\text{cm}^2$  per liter, which corresponds to  $\sim 10^4$  increase compared to bulk water
- Concentration of the pollutants near the droplet surface. In mixtures of two liquids with different surface tension coefficients, the smaller-surface tension component tends to concentrate near the surface.<sup>9</sup> Small droplet radii enhance this process, so the pollutants concentrate in the region where streamers are generated, increasing their exposure to free radicals and hydrated electrons.
- Electric field enhancement near the droplet surface. The high dielectric constant of water ( $\epsilon = 81$ ) provides electric field concentration near the surface layer during the high-voltage pulse. Thus, electron-ion avalanches will occur near the droplets' surface compared to conventional discharge degradation in a homogeneous media.
- Enhanced role of the hydrated electrons (confined at the drops surface) for dechlorination process via channel of electron dissociative sticking<sup>10</sup>, which is characterized with a very high rate, comparable to that of the scavenging of the hydrated electrons by the oxygen ( $1.3 \cdot 10^{-10} \text{ s}^{-1}$ )<sup>2</sup>.

### Experimental Apparatus

The experimental device providing pulsed corona/streamer discharge treatment of the waste water in the aerosol is illustrated at Fig. 1. The reactor chamber is Pyrex tube (25-cm diameter, 150-cm length). The intermeshed electrodes are oriented vertically to increase the transparency of the system for the atomized jet. The atomizer is located either at the top or bottom of the reactor. In the latter case the residence time of the aerosol in the discharge was enhanced. The throughput of the system is in the range of 4-10 gallons/hr.

The high-voltage pulse-generator provides pulses with regulated rep-rate frequency of  $10$ - $10^3$  Hz, voltage amplitude of 60-100 kV, and 100 ns front duration to a matched capacitive load (discharge chamber) of 180pF (measured without discharge). The generator consists of a 50 kV dc power supply, 4.5 H inductive choke, LS-189 hydrogen thyratron (operational voltage - 20 kV), trigger pulse generator (Velonex), thyratron bias supply, pulse-forming system (50 Ohm cables, 5 in parallel), and output 1:4.5 step-up pulsed transformer (wound on a 18 cm OD, 8 cm ID 2605CO, 22  $\mu\text{m}$  metglass core with 15  $\text{cm}^2$  of metal area<sup>11</sup>). When the thyratron shorts the charged pulse forming line cables to ground a high voltage pulse is applied via step-up transformer across the discharge electrodes of the reactor. The pulse duration and matching could be controlled by the cables length and their parallel number. The current through the chamber was measured by active resistor shunt of  $10^{-1}$  Ohm, placed in series with pulse forming network, the applied voltage waveforms and amplitude- by a capacitive voltage divider, placed outside at the Pyrex tube.

Analysis of the initial and final concentrations of the processed organics and composition of the intermediates was "off-line" using several techniques: UV spectroscopy for chemical-concentration analysis, pyrolytic analysis for total organic carbon (TOC) concentration, gas-chromatography with mass spectroscopy (GC/MS) for identification of chemical intermediates.

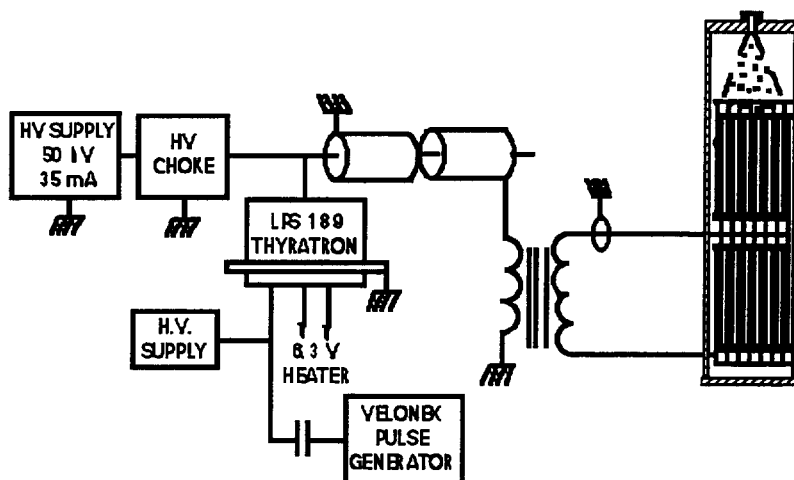


Fig.1. Schematic of the Experimental Set-up.

Released chloride ions (in the form of HCl) dissolved in water were measured by either a selective ion probe<sup>12</sup> or spectrophotometric method of Bergman and Sanik<sup>13</sup>, which measures the colored ferric thiocyanate complex, that strongly absorbs at  $\lambda = 460$  nm and is formed by  $\text{Cl}^-$  and  $\text{Hg}(\text{SCN})_2$  in the presence of ferric ion. Samples of treated 2,4-dichlorophenol (DCP) were extracted with pentane, then analyzed using a Varian 3600 gas chromatography system equipped with a 1% SP1240-DA, 100/120 mesh Supelcoport packed column from Supelco (column temperature 170 °C, FID temperature 210 °C, injector temperature 210 °C,  $\text{N}_2$  flow rate 30 mL/min). The measurement of DCP degradation was also corroborated using a gas chromatograph equipped with a flame ionization detector.

#### 1-st Stage: Results and Analysis

The scaling studies with PNP starting from a concentration of 800 ppm, at pulsed discharge of 60-70 kV amplitude and frequency of 385 Hz showed, that nearly 40% of PNP could be degraded in 4 sequential cycles, and the estimate of the average total specific energy cost based on the wall voltage utilization gives a value roughly 150-200 eV/mol. This figure is significantly lower than reported for sono-hydraulic technology<sup>4,14</sup>. Concurrently with PNP mineralization GC/MS data for higher number of treatment cycles indicated on the formation of intermediates with bigger molecular weights than that of PNP (possibly due to phenol rings polymerization).

Several tests with 1000 ppm 2,4-dichlorophenol (DCP) were performed at the same pulse parameters and frequency. The maximum of 62% of the total possible chloride was removed after six cycles at a rate of 10% of the total possible chloride removed per cycle. For  $V_0 = 70$  kV and  $f = 385$  Hz, the estimated specific energy cost based on the wall voltage utilization was 400-600 eV/ $\text{Cl}^-$  which is 2-3 times higher than in the case of PNP treatment.

These data on degradation were also corroborated using a gas chromatograph equipped with a flame ionization detector. It was found that for a 1000 ppm DCP sample in which 56% of the total possible chloride was released, over 90% of the initial DCP was degraded. This indicates that the treatment of DCP releases one chloride ion per molecule of DCP rather than removing both chlorine atoms for roughly 50% of the DCP molecules.

Upon treatment of DCP with the aerosol reactor, the color change of the sample appeared to be related to the extent of dechlorination. After the initial, untreated, colorless DCP was

processed, the sample was observed to change from a light yellow-orange color (10 - 20% dechlorination) to an aqua green hue (50 - 70% dechlorination). This increase in color is probably indicative of polymerization of the oxidized, dechlorinated phenol to form quinones as has been reported in other high-energy systems<sup>15</sup>. It was found that for 1000 ppm DCP sample in which 56% of the total possible Cl<sup>-</sup> was released, over 90% of the initial DCP was degraded. This indicates that the treatment of DCP releases in average one chloride ion per molecule of DCP rather than removing both chlorine atoms for roughly 50% of the DCP molecules. Using MS/GC these breakdown intermediates of DCP were identified as hexanedioic acid diocetyl ester and 1,2- benzene-dicarboxylic acid.

The APED was also able to degrade successfully 2,4,6-trichlorophenol (TCP). After one cycle 70% of the TCP was removed from 200 ppm solution, while 2 cycles destroyed 93%. These results were corroborated by the independent detection of 50-60% of the chlorine atoms of TCP as free chloride.

### 2-nd Stage: Results and Analysis

To prove that biodegradation is indeed accelerated by first treating DCP in the Aerosol Pulsed Electric Discharge (APED-treated), we provided several partially de-chlorinated APED-treated DCP samples with different residual chlorination degree ( from 65 to 85% of total initial 1000 ppm ), and used them as the sole carbon and energy source for growth of the bacterium *Pseudomonas mendocina* KR1. The same bacteria as it was proven in simultaneous experimental run could not grow on 1000 ppm solution of DCP. The results of these tests are illustrated at Fig. 2 and Fig. 3. for several operational conditions in the first stage (voltage, frequency of the pulse and number of treatment cycles).

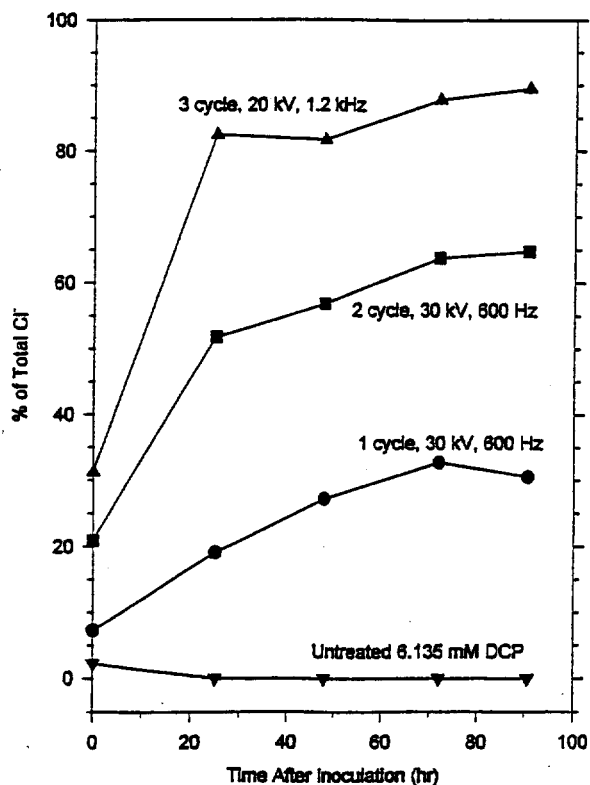


Fig. 2 Chloride concentration released by the bacterium *P. Mendocina* KR1 after 1 st stage APED treatment of DCP at various conditions as function of time after innoculation.

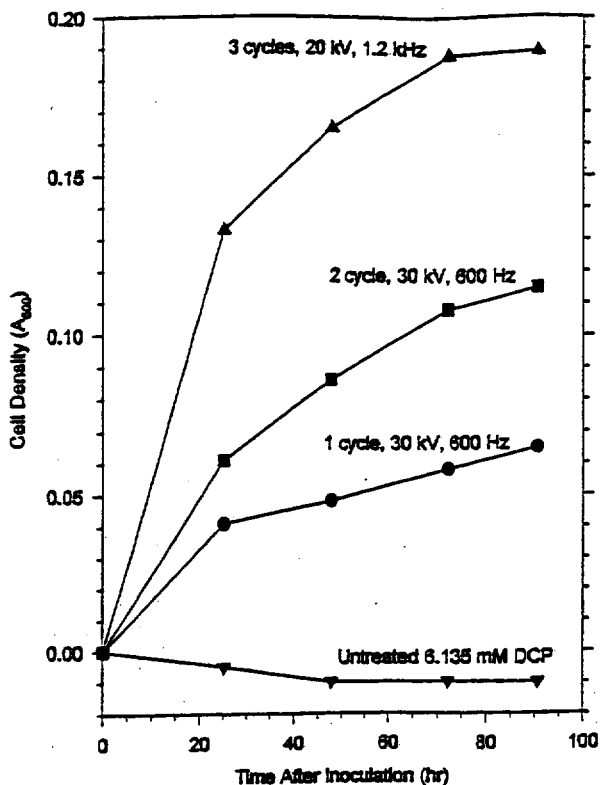


Fig. 3 Cell Density of the bacterium *P. Mendocina KRI* after DCP 1 st stage APED treatment at various conditions as function of time after inoculation

As it is clear from these figures for the APED-treated samples, the results clearly demonstrate growth of the bacteria and mineralization of the DCP: as high as 90% of chlorine atoms present in the initial DCP were released in the first 40 hours after inoculation, whereas the control (non PED-treated sample) had no chloride released and no bacterial growth. Our initial tests also indicated that PCE ( $C_2Cl_4$ ) may be efficiently and rapidly de-chlorinated using the same 2-stage technology. This result is very important in that no aerobic bacterium can biodegrade PCE; but, once treated with PED, the less-chlorinated compounds may be rapidly treated with bacteria which convert aerobically TCE, DCE, and vinyl chloride to carbon monoxides and chloride ions.

### Summary

We have demonstrated a means to degrade waste water containing various organic pollutants, including nitro and chlorinated compounds (PNP, DCP, PCE) using a two stage technology combining medium voltage, repetitive, short pulsed discharge in the aerosol for the first stage and bio-degradation as the second. The technique is based on mature and customer friendly low voltage pulsed power discharge in the aerosol, followed with ecologically benign and inexpensive bioremediation. This combination is very attractive for a variety of applications, including industrial-scale. Future studies are planned to optimize the first stage treatment parameters and the bacterium consortium in the second stage for specific types of recalcitrant pollutants (TCE, PCE, TCP, as well as higher chlorinated compounds, PCB, etc.) to provide total final mineralization of the latter.

### Acknowledgments

This paper has benefited from numerous useful discussions with Prof. C. Kulpa, (University of Notre Dame), and Dr. L. Rosocha (Los Alamos National Laboratory). The work was supported by the Los Alamos National Laboratories LACOR Program (grant 415U0015-3A), a Notre Dame University consulting agreement, and the Army Research Office (grant DAAL03-92-G-0398).

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