# Integration of filtration and advanced oxidation: development of a liquid-phase plasma membrane reactor

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ICOSSE-EPA Innovative Small Water Systems Project Review, Cincinnati, OH

# Team Background

Clarkson University is a small 'high research activity' engineering college located in Potsdam, NY

**Chris Bellona** – Assistant Professor in the Department of Civil and Environmental Engineering (CEE). Engaged in membrane related research

**Selma Mededovic** – Assistant Professor in the Department of Chemical and Biomolecular Engineering. Engaged in electrical discharge related research

**Thomas Holsen** – Professor in the CEE Department. Engaged in fate and transport research regarding legacy and emerging contaminants


The Southern Nevada Water Authority (SNWA) is is a cooperative agency formed in 1991 to address Southern Nevada's unique water needs on a regional basis. SNWA manages local water resources comprised of eight member organizations

**Eric Dickenson** – Project Manager for the Applied Research and Development Center at SNWA. Engaged in research on the treatability of organic and inorganic contaminants in water and wastewater treatment systems

# Objectives & Approach

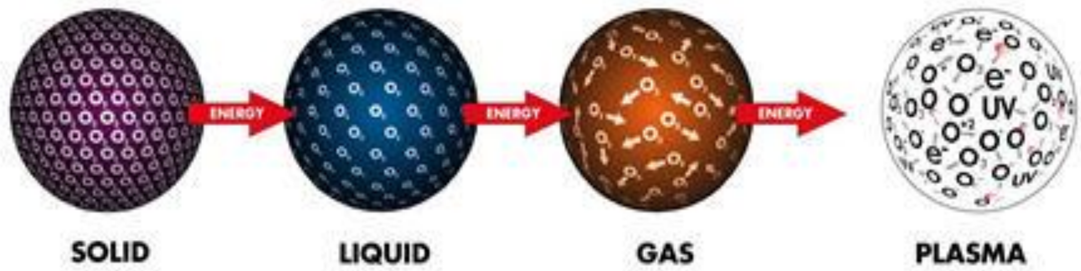
- Objectives:
  - To develop an innovative technology to potentially replace conventional treatment processes for small water systems
  - Simultaneously remove particles, pathogens and bulk organic carbon, and degrade regulated and unregulated organic contaminants
  - Demonstrate technology at a small utility

- Approach:
  - Integrate ceramic membranes with plasma advanced oxidation generated with a novel electrode material

# Project Background

- What is plasma?

"Plasma is a collection of free charged particles moving in random direction that is, on average, electrically neutral." (Lieberman and Lichtenberg, 1994)




<u>Main plasma species</u>: electrons, ions, atoms, radicals and neutral molecules

| | Thermal | Non-thermal |
|---|---|---|
| Temperature | $T_i \approx T_e \approx T_g$<br>$T_e > 10^4$ K | $T_e >> T_g$ $T_e > T_i > T_g$<br>$T_e \sim 10^4$ K,<br>$T_g$~room temp. |

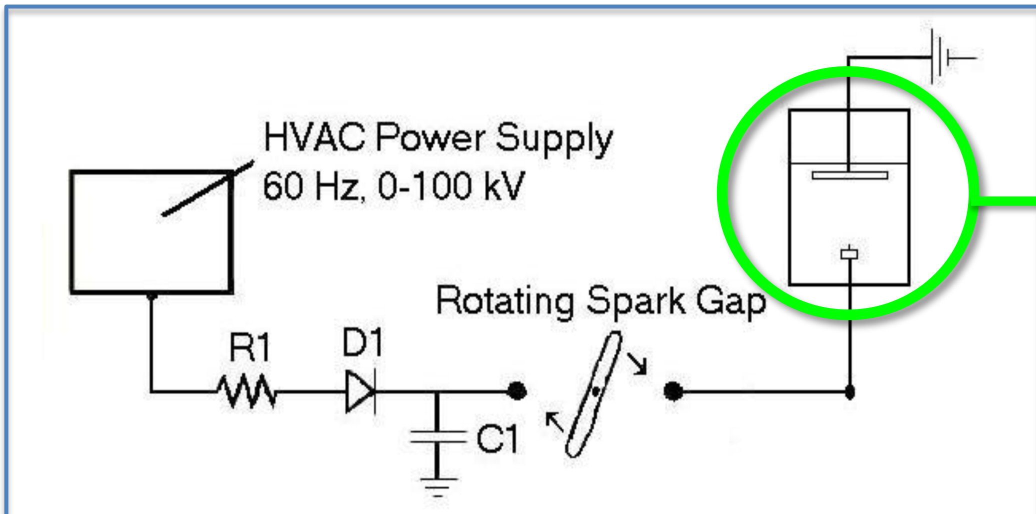
$T_i$=Ion temp.

$T_e$=Electron temp.

$T_g$=Gas temp.

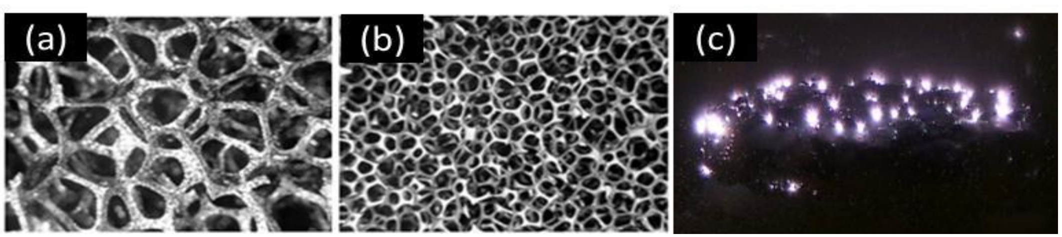
# Liquid-phase Plasmas

<u>High Voltage Power Supply System</u>

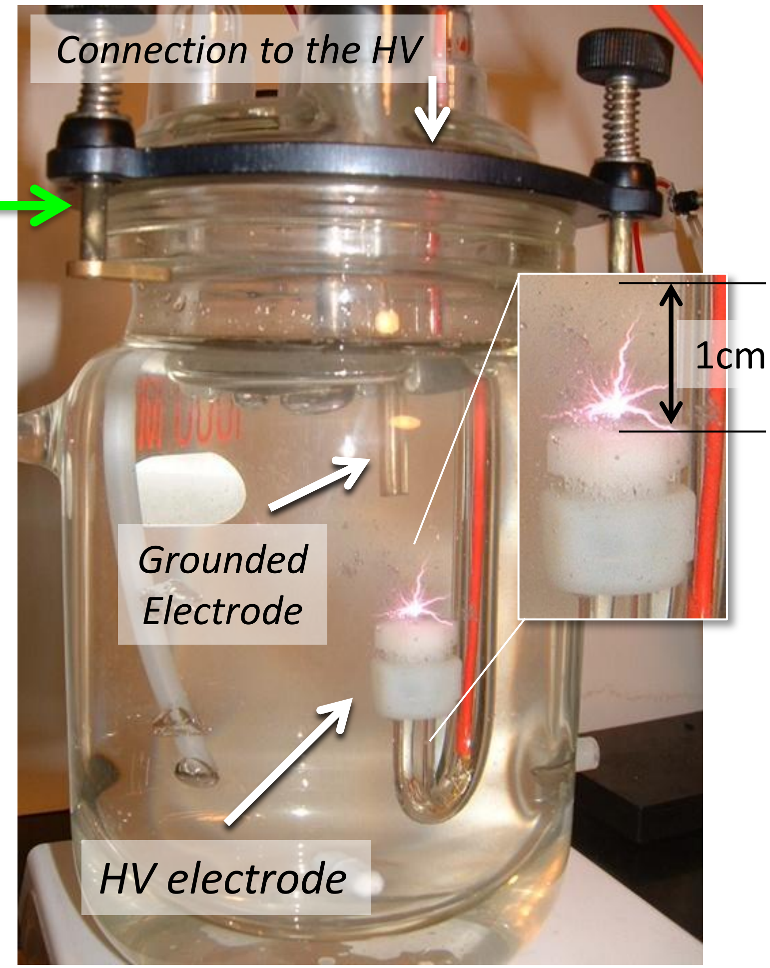



HVAC = 0-100 kV, 0-28 mA
R1 = 333 kΩ

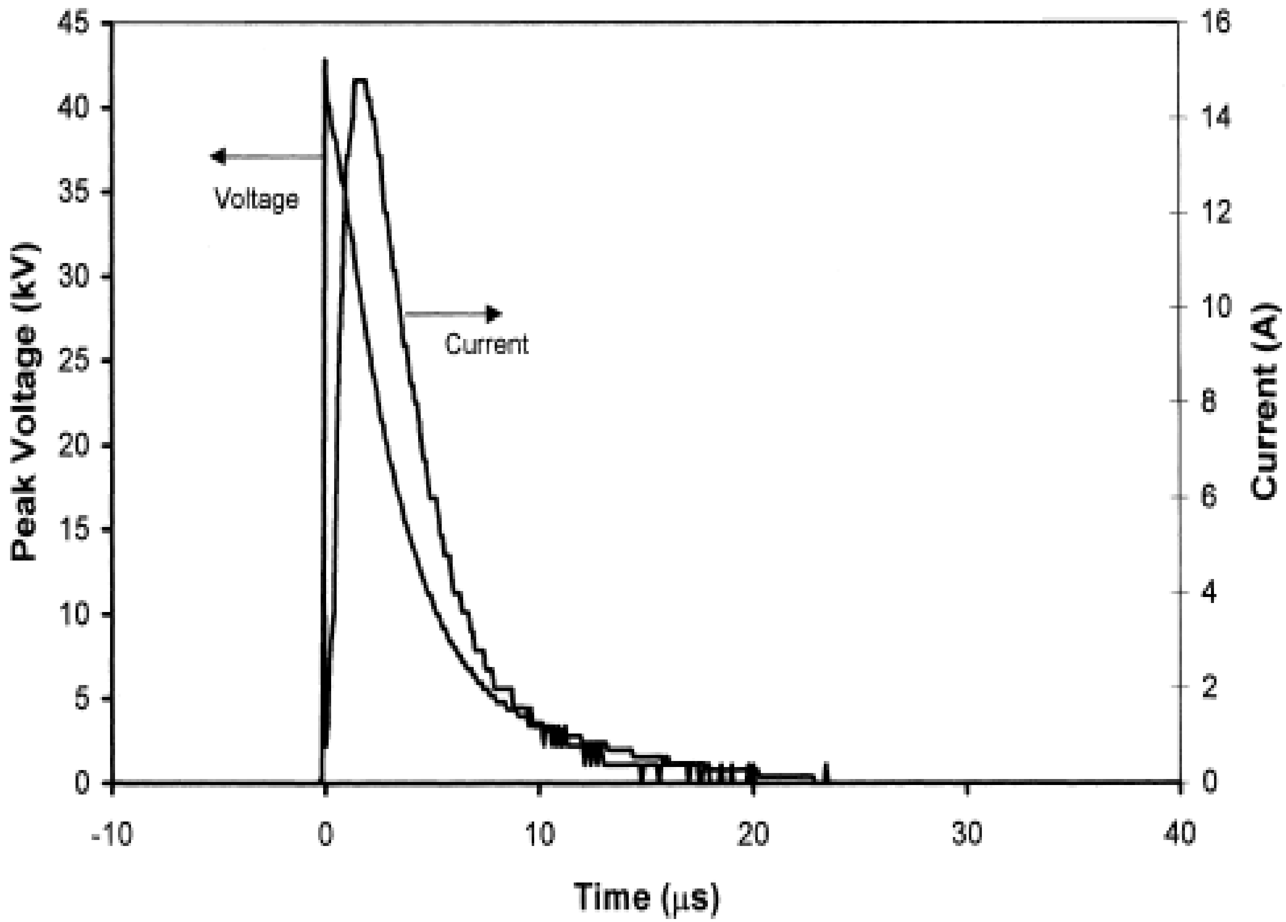
D1 = 60 kV, 12 A
C1 = 2000 pF
Frequency = 60 Hz




<u>Plasma Reactor</u>



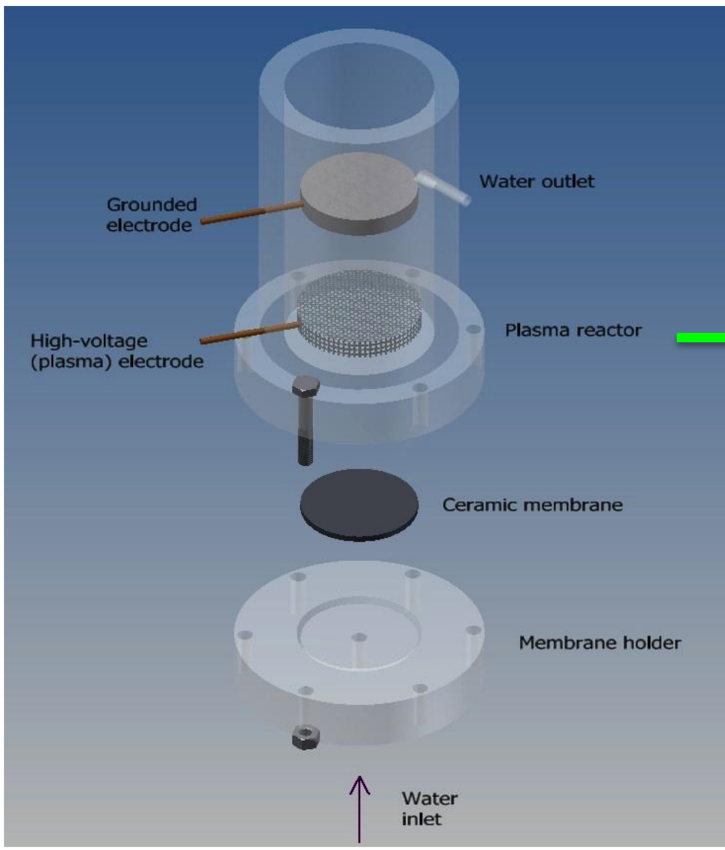
# Pulse Discharge

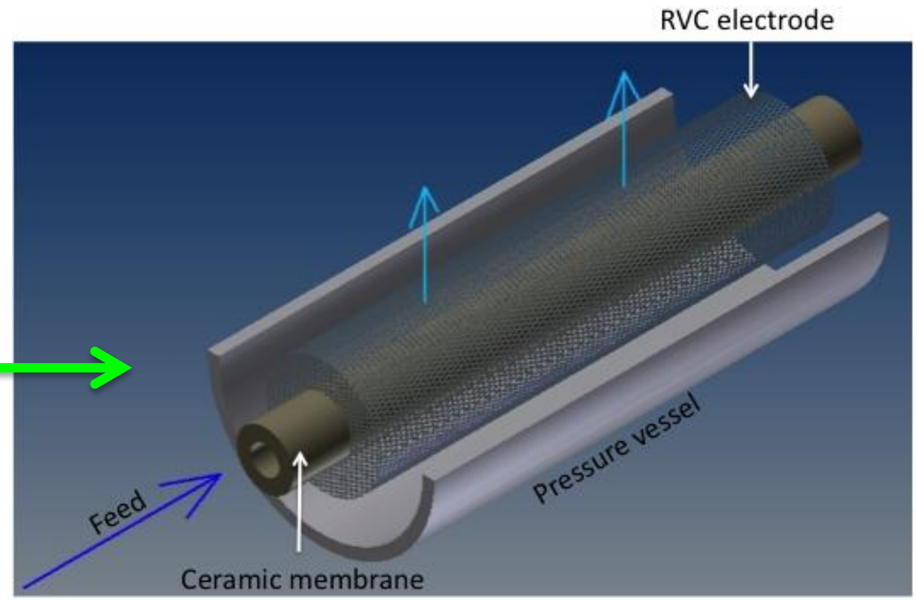



*- Pulsed plasma prevents energy being wasted on the acceleration of ions*

# Project Background

- Project was initiated as an internal collaboration to integrate membrane filtration with advanced oxidation




<u>Goal</u>: Integrate the membrane/plasma technology into a scalable and small footprint system

# Project Overview

- <u>Task 1:</u>
  - Selection of contaminants for technology development and demonstration
- <u>Task 2:</u>
  - Evaluate and optimize the plasma system at the bench-scale
  - Develop and evaluate the integrated membrane/plasma system at the bench-scale
- <u>Task 3:</u>
  - Development of prototype for demonstration
- <u>Task 4:</u>
  - Prototype demonstration at a small utility

# Current Work: Task 1 – Selection of Contaminants

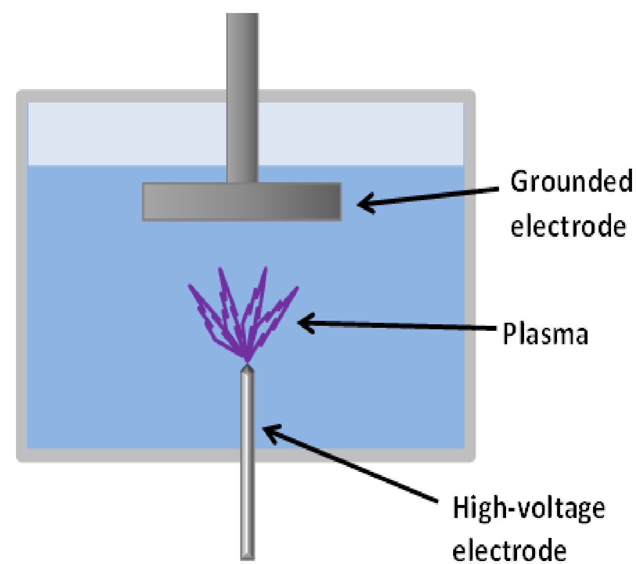
- Goal:
  - Develop list of contaminants of concern that allows an unbiased evaluation of the developed technology
- Approach:
  - Screened ~260 contaminants of concern
  - Binned compounds based on published reaction rates with ozone ($O_3$) and hydroxyl radicals (OH•)
  - Selected 10 - 15 compounds from each bin based on likelihood of occurrence, current and future regulations, and analytical capabilities

# Current Work: Task 1 – Selection of Contaminants

| Reacts quickly with $O_3$ and OH• | | Reacts slowly with $O_3$ and quickly with OH• | | Reacts slowly with $O_3$ and OH• | |
|---|---|---|---|---|---|
| Compound | Type | Compound | Type | Compound | Type |
| Carbamazepine | Pharmaceutical | Diazepam | Pharmaceutical | Chloroacetic Acid | Regulated DBP |
| Sulfamethoazole | Pharmaceutical | Iopromide | X-ray contrast agent | Chloroform | Regulated DBP |
| Trimethoprim | Pharmaceutical | Ibuprofen | Pharmaceutical | TCEP | Flame retardant |
| Caffeine | Stimulant | 1,4-dioxane | Industrial use | PFOA | Industrial use, CCL3 |
| Fluoxetine | Pharmaceutical | Meprobamate | Pharmaceutical | PFOS | Industrial use, CCL3 |
| Naproxen | Pharmaceutical | Dilantin | Pharmaceutical | PFHxA | Industrial use |
| Triclosan | Pharmaceutical | DEET | Insecticide | PFHxS | Industrial use |
| Acetaminophen | Pharmaceutical | Primidone | Pharmaceutical | PFBA | Industrial use |
| Triclocarban | Pharmaceutical | Simazine | Herbicide | PFBS | Industrial use |
| Atenolol | Pharmaceutical | Atrazine | Herbicide | NDMA | DBP, CCL3 |
| Gemfibrozil | Pharmaceutical | MTBE | CCL3 | Sucralose | Artificial sweetener |
| Bisphenol-A | EDC | | | Musk Ketone | Fragrance |
| 17b-Estradiol | EDC, CCL3 | | | Diatrizoate | X-ray contrast agent |
| 17a-Ethinylestradiol | EDC, CCL3 | | | Trichloronitromethane (chloropicrin) | DBP |
| Nitrobenzene | EDC, CCL3 | | | | |

# Current Work: Task 2 – Plasma Optimization

- Conventional plasma reactors are relatively inefficient for contaminant degradation
- Currently working through an experimental matrix to identify main parameters controlling plasma efficiency:
  - Reactor type and geometry
  - Voltage, frequency and polarity
  - Aqueous chemistry

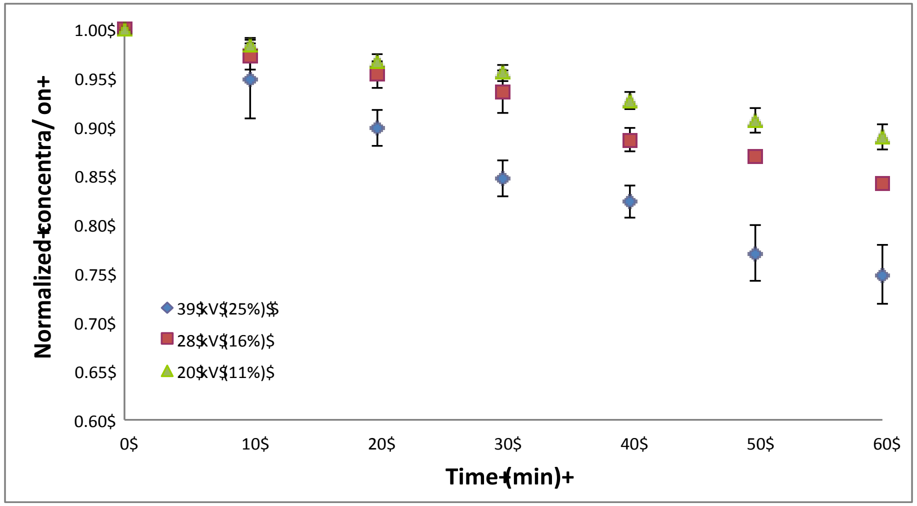


# Experimental Matrix

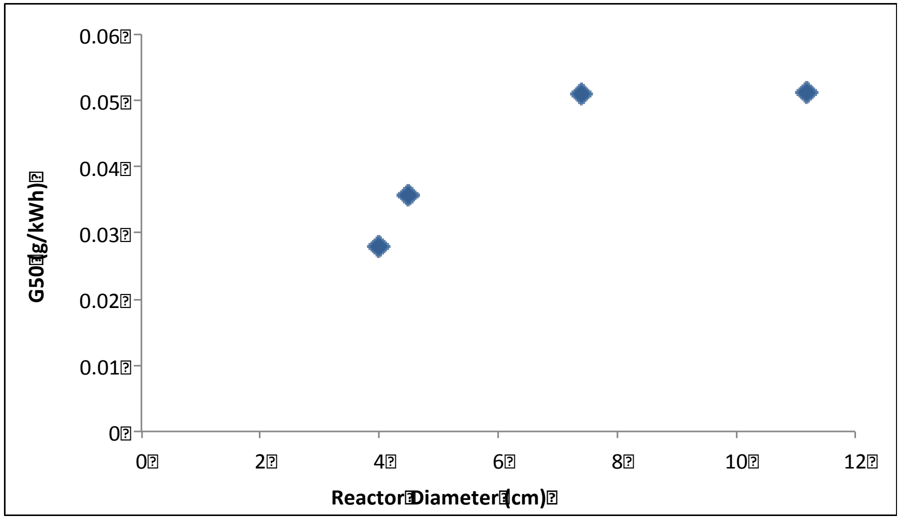
| Factor | Selected parameter |
|---|---|
| Compound | Bisphenol A, nitrobenzene, DEET |
| Voltage | 39, 28 and 20 kV |
| Initial compound concentration | 5, 2.5, 1, 0.5 mg/L |
| Solution conductivity | 150, 250, 350, 450, and 550 µS/cm |
| Flow rate in the recirculation loop | 1 and 1.5 L/min |
| Reactor type | Standard point-to-plane reactor<br>Hybrid series reactor |
| Reactor diameter | 4.5, 7.4 and 11.2 cm |
| Grounded electrode plate area | 1.75, 3.15, 4.5 and 7.8 $cm^2$ |

# Current Work: Task 2 – Plasma Optimization – Bisphenol A

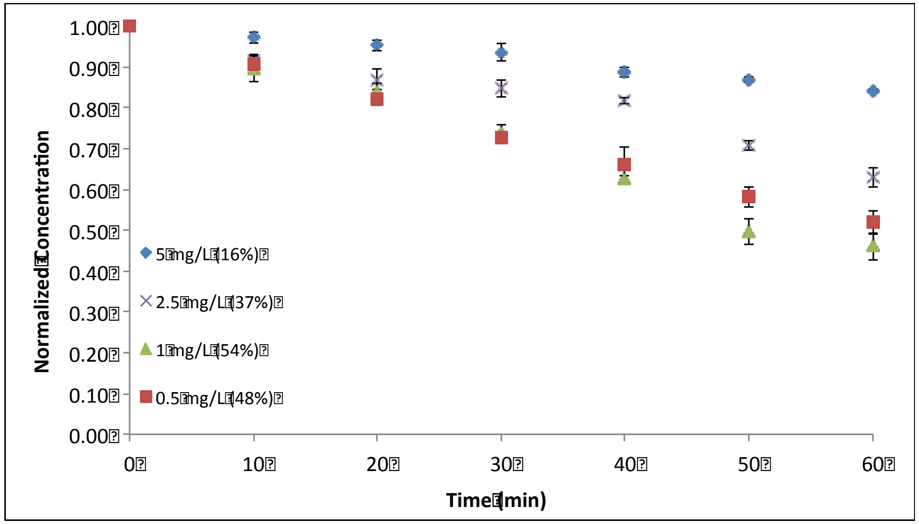
## Voltage



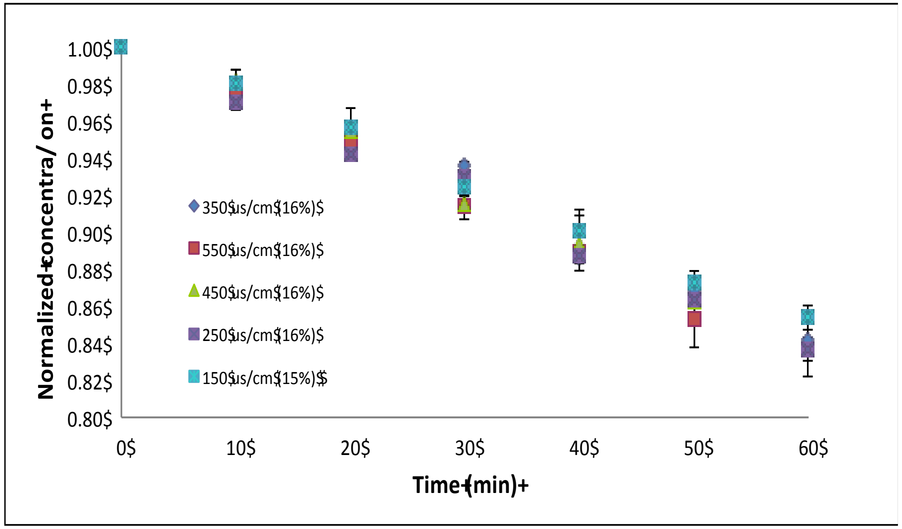

## Geometry



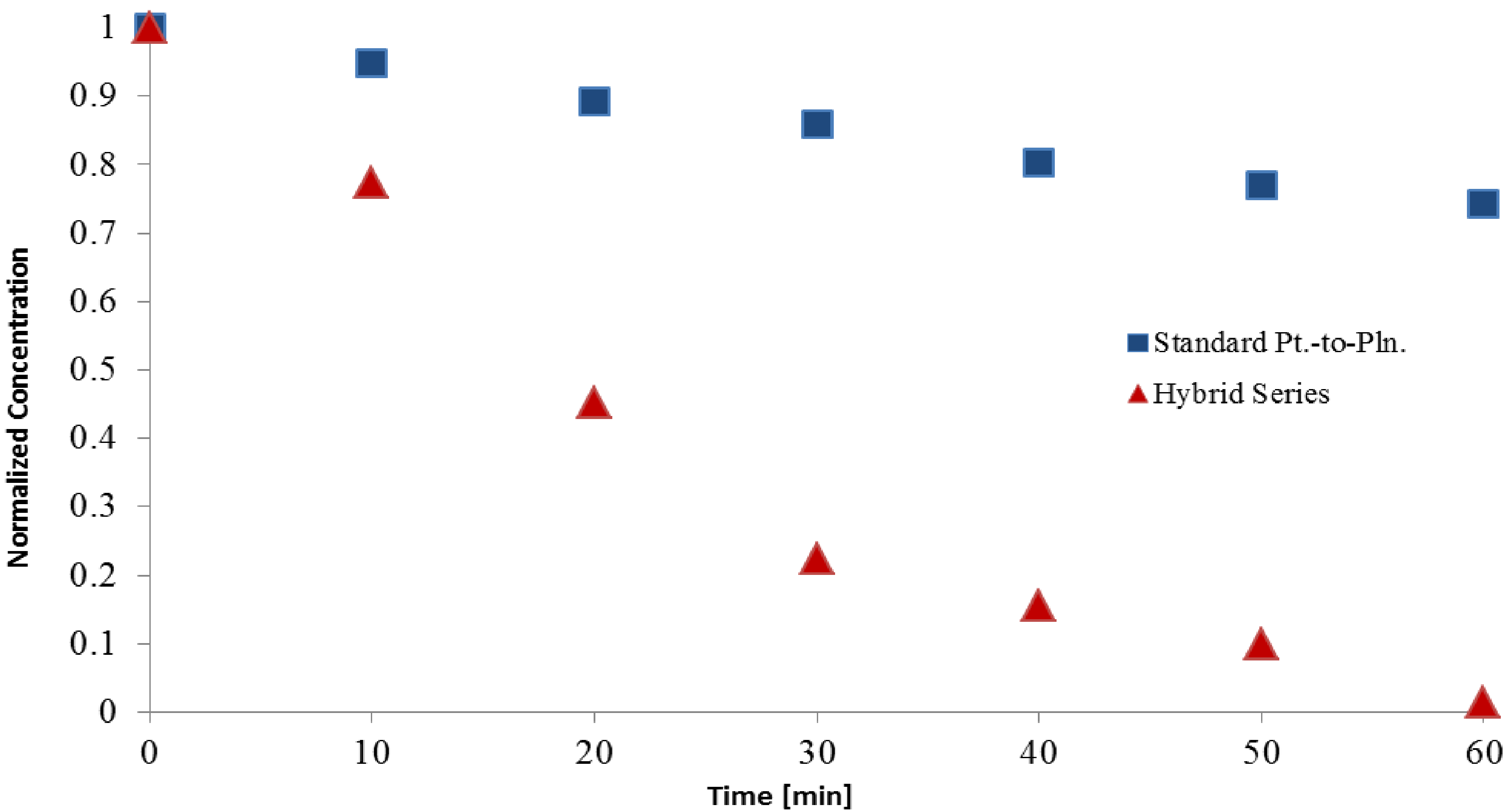

## Initial BPA concentration




## Conductivity



# Current Work: Task 2 – Plasma Optimization



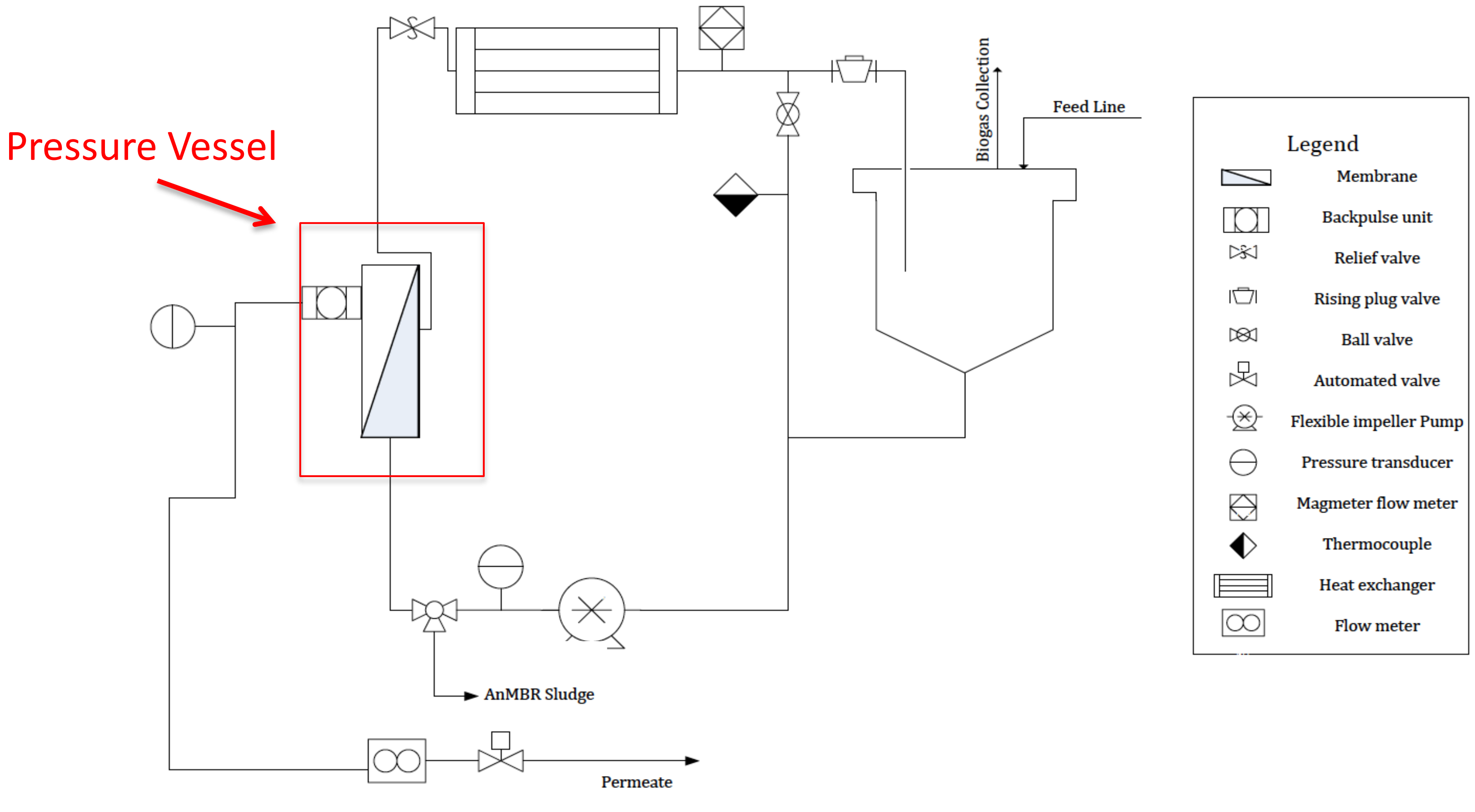

Degradation of Bisphenol-A

# Ongoing and Future Work

- Evaluate optimized plasma system with a suite of contaminants at environmentally relevant concentrations
- Integrate plasma system with ceramic membrane and evaluate performance with different source waters and membrane types
- Develop prototype system

# Current Work: Task 3 – Prototype Development

- An automated ceramic membrane system has been built



# Future Work: Task 4 – Prototype Demonstration

- System to be demonstrated at Big Bend Water District water treatment plant in Laughlin, NV
- Serves 8,800 customers
- Source water impacted by upstream wastewater discharges
- Provides a challenging source water for demonstration testing

# Acknowledgements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  - Fei Dai
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