An Roinn Talmhaíochta,
Bia agus Mara
Department of Agriculture,
Food and the Marine

13F442 - Cold plasma treatment of waste water

Final Report

This project was funded under the Department of Agriculture, Food and the Marine Competitive Funding Programme.

SUMMARY

The main objectives of this project were to develop and study an environmentally sustainable wastewater treatment solution aimed specifically at the food effluents. A series of prototype atmospheric plasma reactors were designed and built. The protypes developed included the optimisation of the power sources, the plasma-bubble reactors, the water vessels, and process monitoring systems. The technology was fond to be very effective for both the degradation or removal of chemical and biological contaminants in water. A particular feature of the technology is the efficacy of the technology to degrade or mineralise challenging recalcitrant compounds including pesticides, antibiotics, and endocrine disruptors. The research points to many potential applications for the technology both for agri-food applications and other industrial waste waters. The findings from this work could also assist both the agri-food sector and the water industry in identifying effective innovations for disinfection of emerging pathogens and chemical contaminants along with underpinning future risk-management and ecotoxicological studies.

KEYWORDS

pesticides, pathogens

ACRONYM	Watertreat
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Section 1 - Research Approach & Results

Start Date

01 December 2013

End Date

31 July 2016

Research Programme

Food Institutional Research Measure

TRL Scale

TRL 5: Technology validated in relevant environment

NRPE Priority area

Sustainable Food Production and Processing

Total DAFM Award

€195,038.89

Total Project Expenditure

€161,031.92

Rationale for undertaking the Research

Agriculture uses up to 70% of the world's freshwater usage, meaning everything we eat impacts the water supply. Given the growing global population and the associated demand for water its efficient use and reuse have become critical issues for all industries including the food industry.

Wastewater generated from agricultural and food processing has distinctive characteristics that set it apart from municipal wastewater managed by public or private sewage treatment plants. It is typically biodegradable and nontoxic but can have high biological oxygen demand (BOD) and suspended solids. The constituents of food and agriculture process effluents are often complex to predict due to the differences in organic matter treated, the range of BOD and pH in effluents from vegetable, fruit, dairy and meat products in addition to the seasonal nature of food processing and post-harvest processing.

Water is involved in many food processing methods and unit operations, e.g., soaking, washing, rinsing, fluming, blanching, scalding, heating, pasteurising, chilling, cooling, steam production, as an ingredient, and for general cleaning, sanitation and disinfection purposes. Processing of food from raw materials requires large volumes of high-grade water. Vegetable washing generates process effluents with high loads of particulate matter and some dissolved organics, surfactants as well as a potential variety of pesticides. Animal slaughter and processing produces process effluents highly contaminated with organic waste such as blood, gastrointestinal contents and hide washings. Such wastewater may be contaminated with significant levels of pathogens and by a variety of pesticides used to control external parasites. Pathogenic microorganisms are widely found in the wastewater released from the food Industry. The microbial load of process effluents is dependent on the type of food processing industry.

The use of pesticides in modern agricultural practices has enabled the stabilisation of crop production patterns globally. However, continual use can lead to bio-accumulation. Most pesticides are water-soluble to some extent with residuals removed during washing in water. Other concerns include; Endocrine disrupting compounds (EDCs) which are organic chemicals that are either excreted endogenously from humans and

animals or are derived from use in clinical practices. They are defined as exogenous agents that alter function(s) of the endocrine system and leading to adverse health effects in organisms.
Environmental impacts can be caused by such wastewaters if they are not effectively treated before discharging. This forms the impetus to characterize the effects of cold plasma on organic contaminants (dyes, pesticides, endocrine disruptors, antibiotics) in model food effluents (dairy, meat, vegetable).

Methodology

Prototype design and optimisation
This project designed both lab and pilot scale plasma systems aimed at wastewater treatment. The approach consisted of testing different designs and operational parameters following a series of design iterations. A Dielectric Barrier Discharge (DBD) design approach was integrated into a wastewater reactor for further testing. The developed plasma system demonstrated the required stability and efficacy during long-term operation. The modular nature of the selected design should support future scaling of the reactor.
During testing of the plasma treatment process, the system was capable of being monitored in terms of the electrical and spectroscopic outputs of the reactor. The plasma treatment process could be controlled through the regulation of electrical parameters and gas flow rate. The design supported real-time process monitoring through electrical and optical diagnostics techniques which could be integrated into the prototype.

Effluents
There is a lack of data in the literature on the degradation of organic chemical constituents in food process effluents by atmospheric plasma technologies. In order, to fill this gap, model effluents (dairy, meat) were prepared to study the effect of plasma treatment. The physical and chemical quality characteristics such as Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Total Suspended Solid (TSS), Total Dissolved Solid (TDS) of the prepared effluents were monitored by chemical and spectroscopic techniques. In order to obtain information about the plasma induced chemical changes in lipid molecules, the use of Fourier transform infrared (FTIR), Nuclear magnetic resonance spectroscopy, gas chromatography and chemometrics was explored. The optimization of plasma parameters for lipid degradation was carried out with identification of secondary oxidation products.
To study the breakdown efficacy of endocrine disruptor contaminants, model effluents from the dairy and meat sectors were made. The system parameters for endocrine disruptors degradation were studied including identification of degraded products and unravelling the plasma induced degradation mechanism of EDC's.

Emerging contaminants
In recent years, the presence of pharmaceuticals in the environment has become an emerging issue that is threatening living organisms. Among various classes of pharmaceuticals, the presence of antibiotics in aquatic environments is of major concern due to the potential development of antibiotic-resistant bacteria. Antibiotics, such as ofloxacin (OFX) and ciprofloxacin (CFX) are frequently found in significant concentrations in wastewater and surface water. The efficacy of atmospheric air plasma for the degradation of antibiotics in water and meat effluent including antibacterial activity of samples submitted to plasma process and by-products formed by the processes were evaluated.
Fresh produce and the process effluents from fruit and vegetable industries and dairy plants may contain pesticides. While the levels of such pesticides may be at ppm or ppb levels, these are very harmful to human health at such low concentrations. This work also explored the feasibility of employing cold plasma treatment for dissipation of pesticides in water and on fresh produce.
Humic acids (HAs) are heterogeneous macro molecules widely dispersed in natural waters, which display significant resistance to biodegradation and its presence may lead to chlorination disinfection by-products (DBPs) such as trihalomethanes (THMs). The developed atmospheric air plasma reactor was employed for the breakdown of HA and THMs in water.

Bacterial contamination

In addition to the organic and chemical constituents, pathogenic microorganisms are widely found in the wastewater released from the food Industry. Effluents from two different food processing plants were used for this study: meat effluent and diary effluent. Based on the predominance and resistance of bacterial pathogens found in such effluents a number of target bacteria were studied including; Enterococcus faecalis, Escherichia coli, Clostridium perfringens and Bacillus megaterium endospores were employed as a principle indicator microorganism.

Project Results

Prototype reactor developed:

The project developed both lab and pilot scale DBD-PLASMA effluent treatment systems. The Dielectric barrier discharge electrode was integrated into the plasma effluent treatment reactor. The developed plasma technology demonstrated both good system stability and efficacy during long-term operation. These systems were used at the platform prototypes for all the effluent treatment tests. The modular structure of scaled-up plasma treatment system allows the future enlargement of effluent treatment volume. During the plasma treatment process, the plasma system is capable of being monitored by the electrical and spectroscopic methods. The plasma treatment process can be controlled online through the regulation of electrical parameters and gas flow rate. The design supported real-time process monitoring through electrical and optical diagnostics techniques which could be integrated into the prototype. The output of this project provides a prototype plasma wastewater treatment system.

Efficacy demonstration:

The research has shown that atmospheric air plasma can be used as an Advanced Oxidation Process (AOP) for wastewater treatment. In this task it has shown efficacy as a secondary treatment with reductions in BOD, COD and fats. Along with successful degradation of all key parameters tested, the system was optimised for food wastewaters with high BOD contents namely dairy, fresh-produce and meat. This work demonstrates that atmospheric air plasma can effectively degrade pesticides in water and endocrine disruptors in a model dairy effluent. Based on the intermediates formed a degradation mechanism was proposed for three different pesticides and EDC's. Importantly, the products identified showed lower estrogenic levels when compared to the parent compounds and less toxic than parent compound. The use of atmospheric air as the treatment gas and the low energy inputs make this technology a potential approach for industrial application. This work provides an efficient method for detoxification of contaminants in water and has the potential in leading to novel applications for environmental protection.

ACP treatment was shown as a promising technology for reduction and complete inactivation of principle indicator microorganisms in both model dairy and meat wastewater effluents. Depending on the microorganism target, 5 min of ACP treatment at 80 kV with 10 min of PTRT was sufficient for effective elimination of monoculture bacteria while mixed culture bacteria showed greater resistance to ACP treatment. However, prolonging the treatment time was able to effectively eliminate all bacterial strains from the model effluent. The findings show that ACP could be adapted to disinfect wastewater at varying process parameters.

System control:

Electrical diagnostics of the developed plasma systems, namely current-voltage waveforms, were found to be successful for monitoring the plasma conditions employed. Electrical characteristics of the micro discharge depends on operating parameters like voltage, gap width, gas flow rate, frequency.

Optical diagnostics using Optical Emission Spectroscopy (OES) was capable of identifying distinct peaks obtained in the UV region. From these results it is evident that nonthermal plasma is source of Reactive oxygen species (ROS) and Nitrogen species (RNS) Electro-acoustic signals were also capable of monitoring the variable control parameters of the plasma conditions evaluated in the studies. A simple process control platform was also tested in this experiment.

Overall, the research showed that it is feasible to use relatively simple techniques as process control systems for these plasma water treatment technologies.

Section 2 - Research Outputs

Summary of Benefits / Improvements of Project Findings

The research points to many potential applications for the technology both for agri-food applications and other industrial waste waters. In particular the technology has applications in difficult to treat contaminants such as pesticides and EDCs. Based upon this it is also feasible that the design could be used for other chemicals such as pharmaceuticals. The findings from this work could also assist the water industry in identifying effective innovations for disinfection of emerging pathogens along with underpinning future risk-management and ecotoxicological studies.

Ensuring Ireland's water quality is paramount for our environment and public health. There are numerous policy and regulatory guidelines on wastewater treatment. These include Guidance Notes on Best Available Techniques for specific food sectors such the slaughtering sector, Brewing, Malting & Distilling Sector and dairy sector. The outputs of WaterTreat may address an identified industrial need stemming from regulatory requirements for process effluent treatment and public demand for clean water treated in an environmentally sustainable manner. The outcomes will also enable Irish companies to address and deliver a sustainable and efficient solution for treatment of process water. The technology developed in this project has the potential to provide effective intervention strategies for the treatment of such wastewaters.

Collaborative links developed with:

- Martin Danaher, Teagasc: A collaboration on the pesticide and other chemical residues work outlined in the project was setup with Martin Danaher, Teagasc. A number of meetings and student training sessions were held between TUDublin and Teagasc on this area. The collaboration led to publication of a high impact paper on the degradation of ECDs in the journal of Chemical Engineering.
- Amit K. Jaiswal, TUDublin: A collaboration on using the developed reactor was undertaken to use the design for improving the enzymatic hydrolysis of brewer spent grain. This collaboration resulted in a joint publication in Bioresource Technology

Summary of Staff Outputs

Research Output	Male	Female	Total Number
PhD Students	1	0	1
Post Doctorates	2	0	2

Summary of Academic Outputs

Research Outputs	Total Number	Details
Publications in Peer Reviewed Scientific Journals	9	The peer review papers published between 2016 and 2019 are listed in the publication section of this report.
PhD Theses	1	Chaitanya Sarangapani, May 2018. Thesis title: Cold Plasma Interactions with Chemical Contaminants
Peer Reviewed Conference Papers	6	The full list of the Popular non-scientific publications and abstracts including those presented at conferences by members of this project are listed in the publication section of this report.

Intellectual Property

The reactors developed during this project were shown to be very effective and should have real potential in industry. The potential for IP capture was discussed however it was difficult to define a clear inventive step for a technology patent and it is established on the literature, meaning that a process patent was not possible.

Summary of other Project Outputs

Project Outputs	Details	Total No.
New Technology	A prototype atmospheric plasma reactor was designed and built. This protype included the optimisation of the power source, the plasma bubble reactor, the water vessel and process monitoring system.	1

Potential Impact related to Policy, Practice and Other Impacts

Impact	Details
Industry	The research points to many potential applications for the technology both for agri-food applications and other industrial waste waters. In particular the technology has applications in difficult to treat contaminants such as pesticides and EDCs. Based upon this it is also feasible that the design could be used for other chemicals such as pharmaceuticals. The findings from this work could also assist the water industry in identifying effective innovations for disinfection of emerging pathogens along with underpinning future risk-management and ecotoxicological studies.
Environmental Sustainability	The outputs of WaterTreat may address an identified industrial need stemming from regulatory requirements for process effluent treatment and public demand for clean water treated in an environmentally sustainable manner. The outcomes will also enable Irish companies to address and deliver a sustainable and efficient solution for treatment of process water. The technology developed in this project has the potential to provide effective intervention strategies for the treatment of such wastewaters.

Dissemination Activities

Activity	Details
Seminars at which results were presented	1. IWA International water conference, Cincinnati, Ohio, USA, April 20-24th, 2015 (Oral) 2. Environ 2016, University of Limerick, March 22-24th, 2016. (Oral) 3. Two posters presented at IUFOST- 18th World congress of Food Science and Technology, Dublin, Ireland 2125 August 2016. (Poster) 4. One poster at 6th Annual Graduate Research Symposium Dublin Institute of Technology. 25th November 2015, Dublin, Ireland. (Poster)

Knowledge Transfer Activities

Identify knowledge outputs generated during this project.	The major knowledge out for this project was the importance of bubbles in the developed technology. By combining atmospheric plasma discharges with bubble technology an effective means of interfacing the reactive species of plasma with water was found.
Identify any knowledge transfer activities executed within the project.	We published a number of papers on efficacy of plasma and plasma-water interactions to degrade chemical and biological contaminants. It is clear that this area is gaining interest globally from both researchers and industry. Challenges remain in terms of scaleup.
List any impacts resulting from the knowledge transferred during the project.	The knowledge transferred from this project has led to new plasma reactors which can effectively interface plasma with liquids, opening up research areas beyond water treatment into green energy storage and biomass conversion.

Section 3 – Leveraging, Future Strategies & Reference

Leveraging Metrics

Type of Funding Resource	Funding €	Summary
n/a	€0.00	n/a

Future Strategies

The potential of atmospheric plasma as a water treatment technology is now established. The project's PI (PJ Cullen) set up a start-up to develop plasma-based technology for environmental applications (PlasmaLeap Technologies). Through this company a prototype water treatment reactor (pilot scale) has been designed, although the design of the reactor is different than the approach taken in this project the efficacy of plasma for water treatment was established.

Project Publications

Publications in Peer Reviewed Scientific Journals

1. Pesticide degradation in water using atmospheric air cold plasma. 2016. C. Sarangapani, N.N. Misra, Vladimir Milosavljevic, Paula Bourke, Finbarr O'Regan, P.J. Cullen. Journal of Water Process Engineering, 9, 225-232.
2. Optimization of atmospheric air plasma for degradation of organic dyes in wastewater. 2017. Chaitanya Sarangapani, Y. Dixit, Paula Bourke, Carl Sullivan, P.J. Cullen. Water Science and Technology, 75 (1), 207-219
3. Characterization of cold plasma treated beef and dairy lipids using spectroscopic and chromatographic methods. 2017.ChaitanyaSarangapani, David Ryan Keogh, Julie Dunne, Paula Bourke, P.J. Cullen. Food Chemistry. 235, Pages 324-333
4. Efficacy and mechanistic insights into Endocrine Disruptor degradation using atmospheric air plasma. 2017. C. Sarangapani, M. Danaher, Brijesh Tiwari, Peng Lu, Paula Bourke, P.J. Cullen. Chemical Engineering. 326, 700-714.
5. Degradation kinetics of cold plasma-treated antibiotics and their antimicrobial activity. 2019. Chaitanya Sarangapani, Dana Ziuzina, Patrice Behan, Daniela Boehm, Brendan F. Gilmore, PJ Cullen, Paula Bourke. Scientific Reports 8;9(1):3955
6. Improving enzymatic hydrolysis of brewer spent grain with nonthermal plasma. 2019. R Ravindran, C Sarangapani, S Jaiswal, P Lu, PJ Cullen, P Bourke, Amit K Jaiswal. Bioresource technology, 282, 520-524
7. Humic acid and trihalomethane breakdown with potential by-product formations for atmospheric air plasma water treatment. 2018. Chaitanya Sarangapani, Peng Lu, Patrice Behan, Paula Bourke, P.J. Cullen. Journal of Industrial and Engineering Chemistry. Volume 59, 25, 350-361
8. Assessment of the disinfection capacity and eco-toxicological impact of atmospheric cold plasma for treatment of food industry effluents. 2018. Apurva Patange, Daniela Boehm, Michelle Giltrap, Peng Lu, P.J. Cullen and Paula Bourke. Science of the Total Environment, 631–632, 298-307
9. Ferric chloride assisted plasma pre-treatment of lignocellulose. 2017. Rajeev Ravindran, Chaitanya Sarangapani, Swarna Jaiswal, P. J. Cullen, Amit K. Jaiswal. Bioresource Technology, 243, 327-334

Popular non-scientific publications and abstracts including those presented at conferences:

1. Sarangapani, C., Misra, N. N., Milosavljevic, V., Bourke, P., O'Regan, F., & Cullen, P. J. Pesticide degradation in water using atmospheric air cold plasma. IWA International water conference, Cincinnati, Ohio, USA, April 20-24th, 2015.
2. Sarangapani, C., Peng lu , Bourke, P., Cullen, P. J. (2016) "Degradation of Organic Pollutants Using a Novel Dielectric Barrier Discharge Plasma in Water", Environ 2016, University of Limerick, March 22-24th , 2016.

3. Sarangapani, C., Martin,D, Tiwari, B.K., Bourke, P., Cullen, P. J. Dissipation efficiency of non-thermal plasma against endocrine disruptors. IUFOST- 18th World congress of Food Science and Technology, Dublin, Ireland 21-25 August 2016.
4. Apurva Patange, Daniela Boehm, P.J. Cullen, Paula Bourke. Inactivation of spore forming bacteria and spores by atmospheric cold plasma. Poster at IUFoST 18th World Congress of Food Science and Technology. 21st - 25th August 2016, Dublin, Ireland.
5. Apurva Patange, Daniela Boehm, P.J. Cullen, Paula Bourke. Atmospheric cold plasma treatment of organic constituents and bacterial pathogens in dairy wastewater. Poster at IUFoST 18th World Congress of Food Science and Technology. 21st - 25th August 2016, Dublin, Ireland.
6. Apurva Patange, Daniela Boehm, Paula Bourke, P.J. Cullen. Atmospheric cold plasma treatment of organic constituents and bacterial pathogens in dairy wastewater. Poster at 6th Annual Graduate Research Symposium Dublin Institute of Technology. 25th November 2015, Dublin, Ireland.