Part C

WATER JOINT PROGRAMMING INITIATIVE

WATER CHALLENGES FOR A CHANGING WORLD

2018 JOINT CALL
Closing the Water Cycle Gap

"Sense and Purify : Detect, Destroy and Remove Water Contaminants"

"SPy"

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1. EXCELLENCE

TECHNOLOGY: The "Sense and Purify" SPy technology (Figure 1) allows organic molecules and pathogens, that cannot be destroyed using conventional wastewater treatments, to be mineralised to carbon dioxide, ammonia and water. It does this by generating a high concentration of the powerful oxidising agent, hydroxyl radicals, *throughout a water sample volume* with very high electrical efficiency. The active agent has no persistent toxicity (radical lifetime is ≈ 5 µs), causes no residue and causes no secondary pollution. It can be implemented at source, is highly mobile/portable, is low cost, has a high throughput, ensures optimised water quality for a given application through sensing/analysis of the inlet and outlet streams, is energy efficient, environmentally friendly, broadly applicable to a wide range of waste streams (from microalgae farms to industry and municipal waste) and has low Capex and Opex.

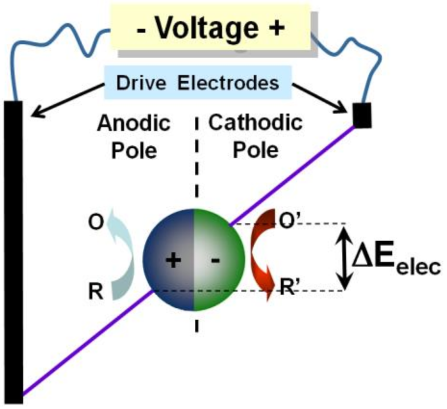

Figure 1. Wireless electrochemical cell showing linear voltage drop generated by two external, electrically isolated, drive electrodes. Either side of the conducting particle assumes a positive or negative potential and hydroxyl radicals are created from the oxidation of water and these then destroy organic contaminants.

TEAM: Dr Soares, Chair of the ecoSTP16 Conference[1] stated: "*The water sector needs to be delivering innovations now, and that means more collaboration across industry and academia and rapid progress to application, making sure the economic aspects are a constant element in new thinking and how research programmes are formulated*." The SPy team members are ***internationally recognised leaders*** in the key areas needed to deliver the required innovations, i.e., electrochemical incineration, materials chemistry, modelling, rapid prototyping and integrated sample-to-answer sensor systems. Consistent with international best practice,[2] ***SPy*** will deliver "modelling" (DCU), "experimentation" (NU, UWC, URV), "fabrication" (DCU) and field testing (Mylan, Ipsen, and French food industry, (partner agreed, but wishes to withhold identity in proposal).

1.1 INTRODUCTION. The outlook for water is sobering. The ever-expanding demand for water by the world's growing population and economy, combined with the impacts of climate change, are already causing shortages, damaging livelihoods, and compromising the health of people and ecosystems. By 2035, demand for water will be 40 percent higher than it is today. Treating and recycling wastewater, especially industrial wastewaters, needs to be a key aspect of closing the water gap. However, many wastewater streams, e.g., from the pharmaceutical and food industries as well as municipal wastewater, contain pollutants, e.g., APIs and precursors, herbicides, pesticides and, increasingly, personal care products, that cannot be efficiently removed/broken down with conventional primary, secondary (biological) and tertiary treatments. Moreover, the current practice of "pooling" wastewater from many different municipal and industrial sources and treating centrally is not optimum since the treatment method cannot be easily optimised to address the different pollutants present. There is a growing recognition that what is needed are **powerful treatments that can process diverse biological and synthetic organic compounds and can be implemented at the point of production**. For example, Dr. Ram Venkatadri, global marketing manager for Pall Corporation, (2017 Revenue $3.8 billion) has stated "*Water presents a **very serious business risk**, and **water recycling through local treatment** is becoming a huge trend in this industry because it presents a way for plants to be significantly more cost effective and become less dependent on raw water supplies*."[3]

Advanced Oxidation Processes (AOPs) are treatment technologies aimed at degrading and mineralizing recalcitrant organic matter from wastewater through reaction with hydroxyl radical (${}^{\bullet}$OH). Recently, these technologies have been recognised as a solution to treat emerging contaminants, that are recalcitrant to conventional treatments, especially herbicides, pharmaceuticals and personal care products and other contaminants such as MTBE. Overall, the worldwide market for water treatment systems in 2017 exceeded **€70 billion** and a compound annual growth rate (CAGR) of 5.0% is expected until 2021 making it a compelling market/commercialisation opportunity.[4] However, these traditional approaches have significant shortcomings. First, they **lack the oxidising power to**

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[1] http://www.ecostp2016.com/

[2] http://ec.europa.eu/research/industrial_technologies/modelling-materials_en.html

[3] http://www.waterworld.com/articles/iww/print/volume-12/issue-05/feature-editorial/water-treatment-chemical-and-pharmaceutical-industries.html

[4] *Water and Wastewater Treatment Technologies: Global Markets*, BCC Research, Wellesley, MA, USA, Report ENV008D November 2016

mineralise recalcitrant organics (convert organics to carbon dioxide, ammonia and water). Second, they either use **relatively expensive reagents** in solution that need to be removed after processing to generate the radicals required, or the **reactions only occur at electrode surfaces** making the process inefficient since transport of the organic contaminants to the electrode requires stirring. Third, there are very few reports on the design and implementation of reactors that integrate bio-chemical sensing of the inlet stream and the water during processing to optimise treatment, the generation and delivery of the radicals.

SPy Innovative Solution. The practical solution is the hydroxyl radical that has an oxidising power of 2.70 V which is second only to fluorine, 2.85 V and significantly more powerful than ozone, 2.07 V. Thus, it can rapidly (up 10^{10} $M^{-1}s^{-1}$) mineralise or electrochemically incinerate a vast array of organic compounds in a wide variety of sample types and under a wide range of conditions. Hydroxyl radical are very energy efficient compared to other AOPs, e.g., ozone or UV, and there are no vapour emissions. They can be generated using the Fenton reaction,[5] but that requires additional reagents, mixing and pH adjustment as well as chemical post-treatments to get usable water. Electrochemical generation represents the best way forward (it also opens up the possibility of using sustainable energy produced locally from wind or solar) but the problem is that pollutants are decomposed only on the Electrode Surface and must be transported, e.g., using a stirred reactor, to the electrode surface. Thus, **high throughput processing is hard to achieve**. Most importantly, in traditional approaches each electrode is physically wired back to a power supply severely limiting the ability to multiplex the electrodes.

In order to achieve high throughput processing, SPy will be a “wireless” electrochemical approach for the mineralisation of recalcitrant organics in industrial wastewater coupled with high speed sensing of the contamination level before and after treatment. Unlike all existing approaches, its key innovation is that electrochemical oxidation occurs throughout the entire volume of the wastewater sample. **The eco-innovative *SPy* technology has significant advantages over traditional treatment processes including portability/mobility, lower capital, operations and maintenance costs, reduced energy consumption, higher conversion efficiency, easier operation, better effluent water quality, and lower waste production. To accelerate and enhance its industry relevance, we will demonstrate the industrial utility of the approach by creating integrated analysis and treatment reactors optimised for the pharmaceutical and food industries as well as for treating municipal wastewater.**

1.2 STATE-OF-THE-ART AND RELATION TO THE WORK PROGRAMME. Traditional treatments,[6] e.g., settling, filtration, adsorption etc., simply concentrate toxins, producing residues that must be disposed of in landfills or incinerated. Biofilm processes can remove recalcitrant compounds, but the transformation products can be toxic. Moreover, functional operational parameters (C, N, P load, aeration, residence time, etc.) for the safe and sustainable removal of organic pollutants using biofilms have not been established. Nano-functionalised membranes are useful, but high cost, poor long term stability and mechanical fragility, hinder their widespread use.

Preliminary Data. Hydroxyl radicals can be generated electrochemically through the oxidation of water, $H_2O \Rightarrow HO^{\bullet} + H^+ + e^-$, but their extreme oxidising power means that conventional electrode materials have a short lifetime. One exciting development is **Boron Doped Diamond (BDD) *electrodes,*** that can operate stably at very positive potentials.[7,8] For example, in common with many hetero-poly-aromatic compounds, the anticancer **drug, Cabometyx**, N-(4-((6,7-Dimethoxyquinolin-4-yl)oxy)phenyl)-N’-(4-fluorophenyl)cyclopropane-1,1-dicarboxamide is extremely challenging to decompose using traditional AOP, chemical or biochemical treatment approaches. Significantly, using a 2 mm diameter BDD film electrode in contact with a solution of Cabometyx, for potentials positive of +2.55 V hydroxyl radicals are generated and mass spectroscopy reveals that significant quantities of CO_2 are produced. Moreover, following treatment Cabometyx cannot be detected by UV-Vis spectroscopy. Significantly, in the absence of an organic substrate no CO_2 is detected. Thus, BDD can mineralise

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[5] *Oxidation of Chlorinated Phenols using Fenton’s Reagent*, F. J. Potter, J. A. Roth, *Haz.Waste and Haz. Materials*, 1993, 10(2), 151.

[6] *Wastewater Treatment in Chemical Industries: The Concept and Current Technologies*. M. O. Awaleh, *Hydrol. Current. Res.*, 2014, 5, 164.

[7] Tyrosinase biosensor based on a boron-doped diamond electrode modified with a polyaniline-poly (vinyl sulfonate) composite film Mangombo, Z.A., Baker, P., ***Iwuoha, E***. and Key, D., *Microchim. Acta*, 2010, 170(3-4), 267-273.

[8] *A synthetic diamond conductivity sensor: Design rules and applications*, J. B. Maxim, A. Colburn, T. P Mollart, N. Palmer, M. E Newton, J. V Macpherson, *Sensors and Actuators B: Chemical*, 2017, 238, 1128.

drugs, making them especially interesting for destruction of organic pollutants in water.[9] While these preliminary results are encouraging, there are fundamental difficulties (listed below) that make the ***SPy*** innovations essential:

1. **Mineralisation Occurs at the Electrode Surface**. Because the lifetime of the hydroxyl radical is short,[10] (2-5 μs), it does not diffuse very far into solution (20-200 nm), and the organic contaminant must be transported (e.g., using a stirred reactor) to the electrode surface. Thus, even with careful reactor design (both batch and flow) **high throughput processing is hard to achieve**.
2. **Low Overall Transformation Rates**. The overall transformation rate is controlled by the area of the electrode meaning that electrodes with large surface areas are required at very significant cost and the approach cannot be easily scaled (capital costs too high).
3. **Wiring of Electrodes**. To increase throughput and overall conversion efficiency. Multiple electrodes can be used but each needs an electrical connection making it very difficult to multiplex.

1.3 OBJECTIVES AND OVERVIEW OF THE PROPOSAL

SPy will address these issues by using **millions of Conducting Diamond Particles (CDP) as individual electrodes dispersed throughout the entire volume of a reactor**. Significantly, the **potential of these particles will be controlled by an electric field** generated by feeder electrodes located on the walls of the reactor, i.e., the **hydroxyl generating particles do not need to be wired** to a potentiostat or in contact with an electrode. Significantly, this capacitively coupled "wireless" electrochemistry approach will eliminate a long standing barrier, i.e., **transport is not an issue and the radicals are efficiently generated throughout the solution.** A custom reactor will be modelled and constructed and **chemical, biological and pathogen sensors as well as UV-Vis spectroscopy will be integrated to ensure purification** to the point where the water can be reused in the original industrial process (circular economy) or discharged into the municipal wastewater system. We will demonstrate the ability of ***SPy*** to mineralise contaminants produced by the pharmaceutical, food and municipal wastewater industries. We will communicate our findings to a range of stakeholders, disseminate our results in high impact journals and seek to exploit our findings for economic impact. Our major goal will be a technology that allows large volumes of process water to be treated quickly and at low-cost with sufficient TRL 4/5 data to make a compelling case for additional investment to support commercialisation. A broad range of education impacts will be achieved from school children to undergraduate and graduate students, as well as industry professionals, paying close attention to gender issues. The PIs will mentor the researchers in technical, entrepreneurial and project management, as well as supporting networking with academic and industry KOLs and leveraging the JPI investment through industry and European grant applications. Improved water decontamination has strong societal impacts for both environmental protection and manufacturing. Long-term progress on sustainability issues related to other industries, including drinking water, is also anticipated from the research.

OBJECTIVE 1 Sensors For Wastewater. In addition to conventional Biochemical Oxygen Demand, BOD, temperature, total dissolved solids, conductivity, and suspended sediment, we will develop rapidly responding, low cost, highly sensitive sensors for pathogens (URV, DCU, NU), and recalcitrant organics such as antibiotics and herbicides (UWC, NU, URV). Data from these sensors and UV-Vis spectroscopy will inform a machine learning algorithm to optimise the purity of the processed water in the shortest possible time and lowest running cost.

OBJECTIVE 2 Diamond Particles For Wastewater Treatment. Our objective is to convert a wide range of cellular and organic pollutants to CO_2, NH_2 and H_2O so that the treated water can be reused in industrial processes.

OBJECTIVE 3 Integrated Reactor. We will use rapid prototyping techniques, including 3D printing/additive manufacturing, to create a reactor capable of testing and treating 10 litres of wastewater per hour. Its performance, e.g., water quality at outlet, sample throughput, minimised energy costs and capital costs, will be optimised using samples whose composition reflects significant EU and global water challenges and commercial opportunities.

OBJECTIVE 4 Real World Wastewater Testing. Working closely with industry beneficiaries, the performance of the reactor that integrates sensing and wastewater treatment will be tested using water samples from the food (France, famous food company in Vendée region) and pharmaceutical (Ireland, Ipsen and Mylan) industries. Input will also be sought from the City of Cape Town Scientific Services (Drinking Water and Sanitation) on the

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[9] T. Furuta, H. Tanaka, Y. Nishiki, L. Pupunat, W. H¨anni, P. Rychen, *Diam. Rel. Mat* . **2004**, *13* , 2016–2023.

[10] *Generation mechanism of hydroxyl radical species and its lifetime prediction during the plasma-initiated ultraviolet (UV) photolysis*, P. Attri, Y. H. Kim, D. H. Park, J. H. Park, Y. J. Hong, H. S. Uhm, K.-N. Kim, A. Fridman, E. H. Choi, *Sci. Reports*, 2015, 5, 9332.

application of SPy in municipal wastewater treatment. These sample types have been carefully selected to test the performance of the technology when presented with different challenges, e.g., low concentrations of recalcitrant active pharmaceuticals or high suspended solid content and high pathogen loads in the food industry.

1.4 RESEARCH METHODOLOGY AND APPROACH

WORK PACKAGE 1: Sensors For Wastewater. We will develop sensors that address gaps in existing technology[11] so as to create an integrated, closed loop sense and purify system. In this way, the water inlet flow can be dynamically controlled to maximise wastewater throughput while minimising both the pollutant concentration in the outflow and the overall energy consumption. Forster,[12] O'Sullivan[13,14] and Iwuoha[15] have made pioneering contributions to the ultrasensitive detection of molecular and cellular targets and the development of integrated sample-to-answer analytical devices and (bio)chemical sensors, while Pellegrin is a leader in the synthesis of the transition metal complexes needed to develop sensors with the extraordinary sensitivity and selectively that prove that the concentration of specific pollutants is below the required threshold. Here, we have a three strand measurement strategy to mitigate risk and maximise progress that targets the **rapid detection of ultralow concentrations of pathogens and organics** which is essential for quality assurance of the treated water and the optimisation of the operating conditions of the *flow-through* reactor in close to real time. For example, being free of E. coli is of paramount importance for a wide variety of industries, while the concentration of organics such as benzopyrenes etc. has to be less than 0.01 µg/100 ml. **1) PATHOGENS**. The DCU team has developed a highly sensitive pathogen detection technology SepTec (www.SepTec.ie) that is capable of detecting LOD 5-10 colony forming units per ml. This sample-to-answer microfluidic device uses an array of antibodies for the selective capture of pathogens. DCU and URV will transform this disposable sample capture and analysis device into a **regenerable, multi-use device suitable for the flow-through wastewater treatment reactor**. **2) ORGANICS**. **i) Sparingly Selective Sensors.** UWC and NU will develop polymer:nanomaterial composites[16] that have a high affinity for the extraction of a broad range of organics, i.e., compounds of specific concern, herbicides, antibiotics, endocrine disruptors etc. from water. Using label-free, electrochemical ac impedance detection, this will give a rapid, quantitative measure of the total load of organics in the inlet and outlet streams. **ii) Highly Selective Sensors.** In contrast to the food production samples (NU, France) and municipal waste samples (UWC, South Africa) that contain a wide range of organics of different compositions, the pharmaceutical production samples (DCU, Ireland) will contain a much more tightly defined range of organics, but the main analytical challenge here is to achieve rapid detection at ultralow (nM and lower) concentrations. For the highly selective detection of these well-defined target molecules, we will develop antibody sandwich assays using electrochemiluminescence (ECL) detection, i.e., the generation of an optical response by applying a voltage to an electrode rather than using a light source. ECL has significant advantages over other methods, notably spectroscopy, including **insensitivity to scattering** by suspended solids, ability to **detect ultralow concentrations** of the contaminants (important for the outlet stream), **label free**, **low costs** both capital and running, **robustness**, **portability** and ability to be **multiplexed** to simultaneously detect several different analytes, e.g., active pharmaceutical ingredients, by products, precursors, reagents etc., likely to be found in a pharma wastewater stream in a single sample in **close to real time**.

Pellegrin (NU) is an expert in the creation of novel, highly intense luminescent labels that can dramatically enhance the detection sensitivity and enable the quantification of several different analytes simultaneously by engineering

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[11] *Reduced Graphene Oxide Based "Turn-On" Fluorescence Sensor for Highly Reproducible and Sensitive Detection of Small Organic Pollutants*, R. Mitra, A. Saha, *ACS Sustainable Chem. Eng.*, **2016**, ASAP article.

[12] *Label Free Sensitive Detection of Circulating Tumor Cells*, A. Venkatanarayanan, S. Roche, T. E. Keyes, R. J. Forster, *Anal. Chem.* **2013**, 19;85(4), 2216-22

[13] *Detection and quantification of the toxic marine microalgae Karlodinium veneficum and Karlodinium armiger using recombinase polymerase amplification and enzyme-linked*, A Toldrà, M Jauset-Rubio, KB Andree, M Fernández-Tejedor, J Diogène, Analytica Chimica Acta 2018, in press.

[14] *Self-assembled monolayer-based immunoassays for okadaic acid detection in seawater as monitoring tools,* S Leonardo, A Toldrà, M Rambla-Alegre, M Fernández-Tejedor, *Marine Env. Res*. 2018, 133, 6-14.

[15] Electrochemical Interrogation of G3-Poly (propylene thiophenoimine) Dendritic Star Polymer in Phenanthrene Sensing, Makelane, H.R., Tovide, O., Sunday, C.E., Waryo, T. and Iwuoha, E.I., *Sensors*, 15(9), 2015, 22343-22363.

[16] *Electrochemical nanobiosensor for glyphosate herbicide and its metabolite*. Songa, E.A., Waryo, T., Jahed, N., Baker, P.G., Kgarebe, B.V. and Iwuoha, E.I.,. *Electroanalysis:* 2009, *21*(3),671-674.

the emission wavelength. Coordination complexes based on $Ru(bpy)_3^{2+}$ and $Cu(L_\alpha)_2^+$ (where L_α is a phenanthroline ligand sterically burdened in α of the chelating nitrogen atoms) will be used as electroluminescent probes. They will be embedded in silica nanoparticles that can be decorated with antibodies and used to detect analytes in a sandwich assay. Depending on its size, the silica particle can contain several thousand metal complexes giving a brighter ECL label (higher sensitivity),[17] it acts as a protective armour[18] (minimises response to changing environmental factors such as oxygen concentration, temperature etc.) and it increases the system's durability.

WORK PACKAGE 2: Diamond Particles For Wastewater Treatment. The **composition and size of the conducting diamond particles** that will act as the "bipolar electrodes" and the electric field distribution will be optimised to maximise the rate of hydroxyl radical production. WP2 will: i) Develop a computational model that will inform the selection of conducting diamond particles. ii) Experimentally characterise and optimise the particles as well as using fast scan methods and GC product analysis to elucidate the destruction mechanism. The inset of Figure 3 shows an SEM image of 10±3 µm diameter BDD microparticles. Significantly, Figure 2 presents our *preliminary* mass spectrometry data showing that CO_2 is produced by a **suspension of these particles** when in contact with a 1 mM solution of the anticancer drug, Cabometyx and placed in an **electric field** whose strength is greater than approximately 2650 V cm^{-1}. These significant preliminary data strongly suggest that the electric field induces a potential in the individual BDD particles so that they can produce hydroxyl radicals to mineralise the Cabometyx to carbon dioxide. It is important to note that **there is no electrical connection to the BDD particle**s, i.e., the mineralisation is wirelessly driven through the electric field. Thus, while the overall efficiency is not yet known, **we have demonstrated that *wireless* electrochemical incineration of a hard to oxidise, active pharmaceutical organic molecule, is possible using BDD particles.** These preliminary data are substantially beyond the current state-of-the-art and give the team a strong position in the field both scientifically and from the perspective of creating protectable IP.

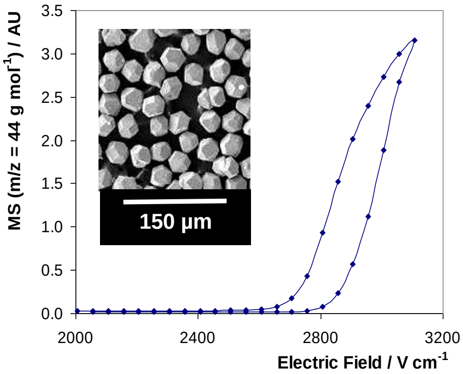

Figure 2. Wireless incineration of 1 mM solution of cabometyx using 10 µm diameter boron doped diamond particles (SEM in inset) placed in a 1 cm path length cell and exposed to an electric field. The dependence of the mass spec signal intensity at m/z = 44 g mol^{-1}, i.e., monitoring CO_2 production, on the electric field strength is shown. The inset shows the BDD microparticles used.

WORK PACKAGE 3 Integrated Reactor. The major objective of ***SPy*** is to create a technology that can mineralise/incinerate organic pollutants and demonstrate its utility for the clean-up of food, pharma and municipal wastewater streams. Informed by the electric field distribution modelling, DCU will design flow through reactors so as to optimise the destruction of organic pollutants (the optimum electric field/particle combination will be identified in WP2). COMSOL modelling will identify the optimum **electrode geometries** (number, size, position, structure) to create sufficiently intense electric fields so that the potential of the BDD particles within the reactor leads to hydroxyl generation (≈ +2.7 V). The impact of **movement** due to gas bubble formation and release, the **collection/storage of evolved CO_2, electrostatic interactions** of the charged pollutants and particles, power losses etc. on the **electric field distribution within the reactor** will also be modelled.

WORK PACKAGE 4 Real World Wastewater Testing. NU and DCU will undertake real world testing of the performance of the SPy reactor performance using food production and pharmaceutical wastewater streams, respectively. These streams have been carefully selected to have different properties from the treatment perspective including a wide range of total organic loads, different loads of pathogens, suspended solids and compounds with a

17 Variable Doping Induces Mechanism Swapping in Electrogenerated Chemiluminescence of $[Ru(bpy)_3]^{2+}$ Core–Shell Silica Nanoparticles. Valenti, G., Rampazzo, E., Bonacchi, S., Petrizza, L., Marcaccio, M., Montalti, M., Prodi, L. and Paolucci, F., *J. Am. Chem. Soc.* 2016, 138, 15935-15942.

18 Unexpected Coordination Chemistry of Bisphenanthroline Complexes within Hybrid Materials: A Mild Way to Eu2+ Containing Materials with Bright Yellow Luminescence, Raehm, L., Mehdi, A., Wickleder, C., Reye, C., Corriu, R. J. P., J. Am. Chem. Soc. *2007,* 129, *12636-12637.*

wide range of oxidation potentials. Also, the samples present different analytical challenges (concentration, number of analytes, dynamic ranges etc.) for the integrated sensing system.

1.5 ORIGINALITY AND INNOVATIVE ASPECTS OF THE RESEARCH (AMBITION)

Scientific Advancements: Our novel strategy is to use *in situ* capacitively coupled or "wireless" electrochemistry[19] to generate **hydroxyl radicals throughout the sample volume** which then attack and mineralise organic contaminants in the sample. This WWT is coupled to existing and novel sensors to give a complete picture of the improving water purity as treatment proceeds. The novel sensors are focused on specific analytes of interest to particular industries, e.g., pathogens in food wastewater streams or specific pharmaceuticals. Their distinctive features include ultrahigh sensitivity (<1 nM), rapid response/continuous readout, and high selectivity. This integrated concept enhances the treatment throughput while minimising operational costs.

Method Advancements: We will create and test integrated WWT reactors that will be modelled *in silico* using COMSOL. A key advancement will be to use rapid prototyping 3D printing/additive manufacturing to rapidly produce and optimise the prototype design. This approach will maximise progress, help to ensure that the reactors are mass manufacturable (design for manufacture in place) and provide devices for early field trials in France and Ireland.

Industrial Advancements: With the exception of a few small molecules, unlike other AOPs, hydroxyl radicals can mineralise all biological material making the SPy technology applicable in a wide range of industries, i.e., ***SPy*** will be an integrated wastewater treatment system focused initially on treating real world samples from the pharmaceutical (Ireland), food (France) and municipal waste (South Africa) industries. SPy's key innovation is that electrochemical oxidation occurs throughout the entire volume of the wastewater sample enables rapid WWT. The **eco-innovative** SPy technology has significant advantages over traditional treatment processes including **lower capital, operations and maintenance costs, reduced energy consumption, higher conversion efficiency, easier operation, better effluent water quality, and lower final solid waste production**. Ultimately, we see the pure CO_2 produced by SPy reactors being electrochemically reduced using electricity produced renewably (wind, solar etc.) into useful starting materials or fuels, e.g., methanol, **- a truly green, circular economy**.

Entrepreneurial Advancements: One of our key objectives is to develop entrepreneurial expertise in the programme's researchers. As well as specific taught modules on topics such as intellectual property identification and protection, routes to commercialisation, business plans, market analysis etc., the **cohort of researchers will develop a virtual company** based on the SPy concept and technology including marketing and business plans, VC funding and routes to commercialisation. This will develop business expertise and position the SPy programme strongly for additional investment and commercialisation.

In conclusion, SPy will develop, test and demonstrate a prototype for an innovative wastewater treatment and monitoring system that will efficiently mineralise organic pollutants rapidly and at low cost. We believe that once the technology is qualified and demonstrated using real world samples that, following additional significant investment, it has the potential to disrupt current practice and find broad application in WWT. Significantly, the technology is scalable and can address practical volumes needed by modern industry.

1.6 CLARITY AND QUALITY OF TRANSFER OF KNOWLEDGE FOR THE DEVELOPMENT OF THE CONSORTIUM PARTNERS IN LIGHT OF THE PROPOSAL OBJECTIVES.

1. Researcher and PI Exchange. The researchers recruited will each spend time in at least one other partner location for an extended period. These researcher visits will be reinforced by PI exchanges to deliver Master Classes in particular topics **2. Specific Technical Expertise.** DCU will transfer expertise in understanding the mechanism and kinetics of electrocatalysis as well as the modelling of electrochemical systems to both NU and URV and rapid prototyping using 3D printing to UWC. NU will expand the expertise of URV and UWC in the synthesis of metal binding ligands and transition metal complexes both of which are key for the development of new sensing strategies. URV will transfer knowledge in rapid screening of samples and sensor development especially immunosensors for wastewater to both DCU and NU. Through UWC, NU and DCU will develop deep expertise in the synthesis of nanomaterials, especially microwave-enabled synthesis, for the development of electrochemical sensors. **3. Career**

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[19] *Principles of Bipolar Electrochemistry*, R. M. Crooks, *Chem. Electro. Chem*. **2016**, 3(3), 357.

Development. Developing the careers of the researchers is a key objective. Specifically, the researchers will engage in the following **Communications** training: workshops, written & oral communications, communication to scientific and public audiences, school children, social media and industry engagement. **Research Management**: Project management, information transfer, networking, team building, proposal writing, financial planning, resource management, data management (DMP, IP). **Technology Transfer.** Efficiently publishing and wide dissemination of key, impactful results to potential water and manufacturing partners coupled to oral communication in scientific and public meetings. **Professional**: Supervision of MSc and PhD students, mentoring, networking, career management, international profile, acting as EU ambassador. The best-practices established in individual partner organisations will be shared and embedded in each institution, e.g., NU organise an annual "Science Fair" and participate in "scientific popularisation conferences" where the public will learn about SPy successes, this model will be implemented by each of the partners.

1.7 QUALITY OF THE CONSORTIUM PARTNERS AND COLLABORATIVE ARRANGEMENTS. Coordinator: Prof. Robert Forster, (Dublin City University, DCU, H-Index 44, >7000 citations; Wireless electrochemistry, Electrocatalytic decomposition and Sensing); **PI: Prof. Yann Pellegrin** (University of Nantes, NU, H-Index 32, >3100 citations; electro- and photo-active materials); **PI: Prof. Emmanuel Iwuoha** (University of the Western Cape, UWC, H-Index 40, >5000 citations) and **PI: Prof. Ciara O'Sullivan** (Universitat Rovira i Virgili, URV, H-Index 43, >7000 citations) chemical, biological and pathogen sensing. **COMPANIES** including Ipsen, Mylan, Laboratoire GEnie des Procédés Environnement, GEPEA and a major French Food Processor are committed to supporting the programme, e.g., practical implementation, samples and independent performance testing and by hosting a demonstrator in their facilities once the technology has reached an appropriate stage of maturity. They are also potential early adopters and advocates within the industry for ***SPy*** going forward. The technology can be diversified to Wastewater Treatment Plants (WWTP) and priority compounds will be identified through the **EU FP7 NORMAN database**.[20] The activities and outputs of EU projects, e.g. Neptune, Poseidon, DEMEAU, DIAMOND, PREPARED, TREAT&USE, and MariaBox, have been taken into account when developing the ***SPy*** strategy to ensure synergy with the European agenda and to eliminate the risk of duplication. This core team will benefit from an **EXTERNAL ADVISORY BOARD** that includes leading industrial and academic experts (Section 3.2). This multidisciplinary team, coupled with the industry collaborators, is perfectly positioned to deliver innovative, practical solutions to the local treatment and reuse of industrial wastewater streams. Collectively, we have a significant track record of both high quality research accomplishments, (>700 papers) and **delivering practical devices** including sensors for environmental pollutants and water borne pathogens and contaminants. The team's **proven track record of delivering both industrial and oriented basic/fundamental projects** coupled with the highly innovative measurement and treatment technologies for wastewater that is strongly supported by exciting preliminary data, positions the consortium to reinforce a position of leadership in the of integrated, high performance WWT reactors.

2. IMPACT

2.1. IMPACT OF THE PROPOSAL. Our ultimate objective is to see the SPy technology commercialised and widely deployed in a range of industries. For some applications, e.g., pharmaceutical production streams, it is likely to be the only treatment needed while others, e.g., food waste, may require additional bioprocessing. To move the technology towards commercialisation, significant additional investment will be required that will initially be sought through Angel and then Venture Capital investors with a view to either spinning out a manufacturing company or establishing a distribution deal with one of the major distributors.

This programme directly addresses UN SDG **Goal 6: Ensure access to water and sanitation for all**. The innovative Sense and Purify programme will create a custom reactor with integrated electrochemical sensors that is suitable for the local production of clean water for industry or drinking at low capital and operating cost. To **enhance innovation capacity and integration of new knowledge** prototype reactors will be demonstrated for the treatment of production wastewaters from the food (NU) as well as pharmaceutical industries (DCU). Moreover, because of the oxidising power of the hydroxyl radicals produced, the technology will find fruitful application in the environmental remediation of brown field sites since the feeder electrodes generating the electric field could be inserted into contaminated soil and the organic pollutants, e.g., fuel oil, PAHs etc. destroyed. The expertise of the

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[20] http://www.norman-network.net/

team are high complementary with each partner having distinct, autonomous tasks that link directly to the overall objective, e.g., BDD particles synthesis and reactor fabrication at DCU, synthesis of Ru and Cu sensors at NU, sensor device development at URV and UWC *as well as* highly co-operative linked work, e.g. testing of the sensors in the reactor, (all partners), reactor design for multiple applications, NU, DCU, UWC, reactor field testing, DCU, NU. The mid-term benefits include the translation of basic research into practical application, e.g., the NU metal complexes into sensors (URV, UWC), new bilateral partnerships, NU and URV, trained researchers and significant dissemination and communication of the project. Longer term, the team plan to leverage this investment and work together to commercialise the technology most likely through a distribution deal with a major supplier or a spin-out company (also see Section 2.2).

2.2. EXPECTED OUTPUTS

IMPACT/Year	1	2	3	4	5	5-10 Yr
Scientific:						
•Novel wireless electrochemical approach to oxidative electrocatalysis.			X			
•Insights into the rates and mechanism of organic pollutant oxidation					X	
•Novel sensors for rapid and sensitive assessment of water quality.						
Economic						
•Integrated sense and purify reactor with decreased wastewater treatment costs.					X	
•Enhanced removal of recalcitrant organic pollutants from industrial wastewater streams					X	
Social						
•Enhanced public awareness of water resource issues				X		
Education and Outreach						
•Researchers with the necessary multidisciplinary skills for future industrial, policy, academic and start-up employment			X	X	X	X

Specific Outputs: Publications: Minimum of 10 peer reviewed papers in leading journals (Impact Factor >5) such as J. Am. Chem. Soc., Langmuir, Anal. Chem., ChemElectroChem, Water Research, Env. Sci. and Technol. etc. **Oral and Poster Conference Presentations**: Minimum of five presentations at leading conferences such as European Water and Wastewater Treatment Conference and Leading Edge Conference on WWT. **Events**: A one day meeting on Integrated Wastewater Sensing and Treatment to be organised with >100 participants.

2.3. EXPLOITATION AND COMMUNICATION ACTIVITIES

Dissemination: The findings will be published in leading scientific and engineering journals (>10 publications with >3 joint with industry over project's lifetime). These will be complemented by opinion and review articles for in ecological publications and media. Presentations at major conferences attended by academics, regulators and industry as well as industry seminars will help ensure stakeholder engagement. Participation in state-of-the-science workshops will also be actively pursued. Additionally, the team's extensive network of collaborators will be used to disseminate findings to relevant national and international committees and organisations including OECD, European Environment Agency, USDA and WHO. Research results will also be included in the courses in which the academics of this project are involved (Teaching of MSc or PhD). Towards the end of the project, the research team will initiate a range of activities aimed at informing different stakeholders of the issues around water quality and its cost-effective, sustainable treatment. This will include webinars to share recommended best practice.

Communication and Public Engagement Strategy: The entire research team will communicate with non-expert audiences through the use of on- and off-line social networks. The research team will optimize communication efficiency for sharing project performances by utilizing internet social media tools. **Blogging** on Twitter and other social platforms such as **Facebook** will be used to communicate findings and results in real time to the public. Furthermore, blogging will highlight current events, news stories and other impactful research publications. The blog forum will also allow for controlled interaction with readers through comments or message board. The important findings will also be presented on the project **web site**, which can help general public and policy-makers understand the importance water treatment by AOP and its role in an integrated WWT, energy and CO_2 reduction strategy. The **community** will be engaged through participation in campus wide and city-wide events (e.g., Café Scientifique events). The research team will publish articles in non-expert **magazines** and an interactive module will be developed for primary **school** classrooms. The goal of these modules will be to educate in a fun and hands-on manner. Examples include, **Case Studies**, e.g., real-world polluted water, **Practicals**, e.g., impurity removal using carbon and battery electrolysis, **Round Table Discussion**, **Post It Parade** describing pollution problems and solutions, **Peer to Peer Review** where students provide their peers with feedback and **Debates**. Finally, the results will be reported in **press releases** to provide information to the wider public in Europe or other countries about research outputs on this topic.

IP and Exploitation: Our focus is on delivering a TRL 4/5 device that is ultimately capable of meeting the needs of European and global markets. This device will be built on key IP created and patents (>3 expected) will be sought to protect key aspects such as optimised BDD particle size, composition and shape, the shaping of the electric field to enhance treatment efficiency and speed as well as a range of highly sensitive, rapid sensor technologies. All beneficiaries own the background IP. Specific agreements will be made in case of collaborations between a beneficiary and associate partners. However, if in the course of carrying out work within the project, a joint invention, design or work is made - and more than one partner is a contributor - and if the features of such joint invention design or work are such that it is not possible to separate them for the purpose of applying for obtaining and/or maintaining the relevant patent protection or any other IP, the partners concerned agree that they may jointly apply to obtain and/or maintain the relevant right together with any other partners. In order to clarify such Protection of Knowledge issues as well as exclusion of access-rights to pre-existing know-how and grant of access-rights outside the consortium, the partners will sign the a PEDR and Data management Plan at the Consortium Agreement. Sense and Purify will strengthen the green/circular economy by allowing water to be treated and reused locally, driving growth in income and employment. Increasing the efficiency of use of non-energy resources is a key goal. Electrochemiluminescence is an area where SPy will contribute significant new knowledge and create protectable IP to support the ultimate commercialisation of the technology. It is important to note that compounds that contain secondary and tertiary amines, such as APIs and their metabolites found in wastewater, can be detected directly using ECL without the need for an antibody. We will promote rapid market penetration by closely collaborating with WWTP operators and make the results from demonstrations easily accessible to support their decision-making. To foster this communication, an **Advisory Board** (Section 1.1) will be established in which stakeholders, including the public, water companies, representatives of industry sectors and end-users will be informed about our findings and used as an Advocacy Group for Sense and Purify.

2.4. MARKET KNOWLEDGE AND ECONOMIC ADVANTAGES/RETURN OF INVESTMENT

Market Potential: In developing the SPy proposal, we have carefully considered key recent market reports.[21,22] The overall **market for water supply/sanitation/water efficiency is significant, €185 billion**, but will increase markedly to €480 billion by 2020. The SPy approach will also reduce costs for industry, e.g., by avoiding thermal incinerations costs, thus increasing competitiveness, reduce overall carbon emissions and pollution, e.g., by dramatically decreasing wastewater transport costs. It will also prevent the loss of biodiversity and ecosystems by avoiding contamination or, where contamination does occur, allowing a rapid corrective response to be implemented. Advanced Oxidation Processes, AOPs,[23] including ozone (O_3, market leader €650 million worldwide market in 2015 hydrogen peroxide (H_2O_2), ultraviolet (UV), high energy electron beam (E-beam) irradiation, ultrasonic and hydrodynamic cavitation and titanium dioxide (TiO_2) catalysis, can decompose contaminants, but even ozone typically needs biological polishing, requires separate units for Biological Oxygen Demand, BOD, nitrogen and phosphorus removal. The global market for **advanced oxidation processes will be around $10 billion by 2025 with a CAGR of 9.8 %.** The market size for AOPs in water and wastewater treatment is growing rapidly due to the drive towards water reuse and stricter regulations for wastewater discharge. Overall, the high destruction efficiency, lower capex and Opex, smaller footprint and lower energy/voltage consumption will give SPy a strong position in the marketplace and allow us to rapidly penetrate key markets in the pharma, food and municipal waste treatment markets. We would expect to capture between **5 and 10 % of the market within 5 years of commercialising SPy.** SPy can destroy micropollutants, or contaminants of emerging concern, further enhancing its commercialisation possibilities. We are fully committed to commercialising the technology once appropriately matured and our Advisory Board can provide key insights into market niches that should be targeted first as well as acting as advocates.

Competitors: Our competitors are companies that generate hydroxyl radicals using either chemical or electrochemical means. Other AOPs, e.g., ozone, lack the oxidising power to tackle recalcitrant organics. The

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[21] *Global Advanced Oxidation Technologies Market Analysis & Trends-Technology, Forecast to 2025*, ReportLinker, 2016, ID: 4366640.

[22] *Advanced Oxidation Technologies: Global Markets*, 2016, BCCResearch,N. Thomopoulos, ENV034A.

[23] *Advanced Oxidation Processes (AOPs) in Wastewater Treatment*, Y. Deng, R. Zhao, *Curr. Pollution. Rep.* 2015, 1, 167.

current state-of the-art hydroxyl radical generating systems, e.g., Condias, use complex electrode designs (metal and diamond) as well as forced aeration and additives such as sulphate/persulfate to try to achieve a 3D distribution of hydroxyl radicals (max. efficiency 80%). In contrast, SPy employs particles distributed throughout the sample volume to dramatically enhance the destruction efficiency (>90%) and to allow industrial scale systems to be developed. Moreover, it uses chemical sensors to measure the contamination levels at the inlet and as the treatment proceeds to maximise throughput and can inform an AI module that optimises the treatment protocol to minimise Opex. SPy will also reduce/eliminate the volume of residual sludge produced.

Partner ROI. The return to the partner team is deep integration of core technologies and expertise into a functioning wastewater measurement and treatment system that moves from TRL level 2/3 to TRL 4/5 by the end of the project. This partnership will then seek additional investment through angel investors, venture capitalists and industry joint ventures/distribution deals to commercialise the technology and bring it to the market. Significantly, URV are participating fully in the programme on a no cost basis because of their belief in closed loop monitoring of wastewater treatment using aspects of their sensor technology.

3. IMPLEMENTATION

3.1. OVERALL COHERENCE AND EFFECTIVENESS OF THE WORK PLAN

WORK PACKAGE 1: SENSORS FOR WASTEWATER. TASK 1.1 In Reactor *Pathogen* Sensing. DCU has developed SepTec (www.SepTec.ie) which is a highly sensitive sample-to-answer microfluidic device capable of detecting and categorising (Gram positive, Gram negative, Fungal) 5-10 pathogens per ml within 10 minutes. DCU and URV will transform the *single shot* SepTec platform into a device capable of repeated/continuous analysis. Specifically, URV and DCU will investigate the ability to regenerate the capture surface by triggering a reversible conformational change in the cell membrane protein of the bound pathogen by controlling the voltage applied or flowing an electrolyte solution across the capture surface As well as label free electrochemical impedance, NU will develop novel high brightness electrochemiluminescent labels for immunoassay based pathogen detection coupled with wireless electrochemiluminescence (DCU, UWC, URV).

TASK 1.2 In Reactor Sensing *Organics*. Knowledge of the “organic load” within the wastewater will inform the optimisation of the WWT protocol. **i) Sparingly Selective Sensors.** Polymer films of super-absorbers of organics, UWC: conducting polymers and co-polymers. NU, URV: Crosslinked lipophilic polyacrylates doped with tetra-alkylammonium salts (polyelectrolyte gels) will be deposited as thin films on electrodes and their impedance measured as organic pollutants partition into the film. The total volume of the film is ≈10 nl generating a sensitive response even when the concentration of organics in the water (e.g., after treatment) is below admissible thresholds. **ii) UV-Vis Spectroscopy**. (NU, DCU) NU develop UV-Vis spectroscopy within the reactor as a cost effective, real time approach to monitoring effective TOC and develop an algorithm to minimise the treatment time.

At the end of Year 1, the optimum performing technology, i or ii, will be selected based on its overall analytical performance. The selection criteria will be: *1. Limit of Detection 2. Dynamic Range. 3. Broad Applicability*.

TASK 1.3 High Performance Electrochemiluminescent (ECL) Sensors. Specific compounds, e.g. APIs for pharma, will be detected with ultrahigh sensitivity so as to prove they have been adequately removed. Many of the pharmaceuticals of interest can be detected directly using electrochemiluminescence, i.e., the generation of light using a voltage rather optical excitation. Equally, antibodies or aptamers exist for many of the pollutants allowing highly sensitive electrochemiluminescent sensors to be developed based on sandwich immunoassays.

i) High Brightness Labels. NU will deliver ultrahigh sensitivity (<1nM) ECL active nanoparticles that incorporate many high brightness dyes within a silica shell (higher detection sensitivity). Hybrid nanoparticles **Ru-Si** (luminophore = $Ru(bpy)_3^{2+}$) and **Cu-Si** (luminophore = $Cu(L_\alpha)_2^+$) will be created. While silica embedded ruthenium based ECL sensors are known, the switch to copper is hugely significant in terms of cost and toxicity and, for the first time, will be enabled by co-condensing silane bearing copper complexes with silica precursors, leading to copper based luminophores encapsulated inside a silica matrix. This will enable: i) **complexes that are stable** even in the hostile wastewater and in presence of strong competitor ligands since ligand scrambling due to the well-known lability of the $Cu\text{-}L_\alpha$ coordination sphere is blocked; ii) **intense ECL** since quenching by exciplex formation and photo-induced flattening of the coordination sphere are prevented.

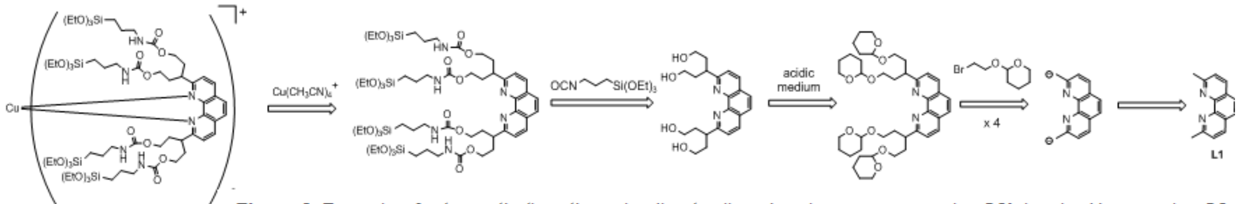

Figure 3. Example of retrosynthetic pathway leading to silane bearing copper complex **C2'**, inspired by complex **C2**.

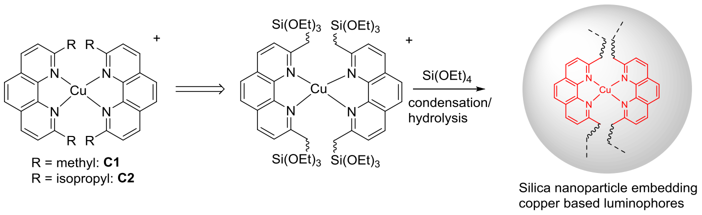

Figure 4. Copper(I) complexes that will be synthesised and immobilised in silicate nanoparticles.

Figure 3 shows a silane bearing ligand that will be synthesised while Figure 4 shows two representative copper(I) complexes. These complexes have been chosen for ease of synthesis, cost, and maximising ECL intensity, e.g., **C2** is highly luminescent due to significant steric bulk. Synthesis of the complexes involves mixing precursor $Cu(CH_3CN)_4^+$, X^- ($X = PF_6^-$, ClO_4^-, SO_4^{2-}) with the appropriate ligand at room temperature for a few minutes.

ii) ECL Biosensors. ***A) Direct Detection.*** NU will alter the peripheral ligands to tune the redox potential so as to optimise light generated in the presence of specific APIs that act as a co-reactant. Targets include: **IPSEN**: Cabometyx (poly aromatic/heterocyclic), Dysport (botulinum toxin). **JANSSEN**: Haldol (fluorinated and chlorinated aromatic), Ergamisol (Fused heterocycle, tendency to polymerise), Risperdal (fused rings, high nitrogen content). **MYLAN**: Methotrexate (multiple fused rings high nitrogen content). ***B) Immunoassays.*** URV and DCU will develop sandwich immunoassay sensors for key pollutants in which the secondary antibody is labelled (EDC coupling of pendant amine/carboxylic acid to antibody) with an ECL active metal complex (NU, Task 1.3). **Targets** will be selected from: 2-(2,4,5-trichlorophenoxy)propionic acid, 3-phenoxybenozic acid, alachlor, atrazine, azoxystrobin, , diazinon, diuron, endosulfan, fenthion, forchlorfenuron, imidacloprid, malathion, pentachlorophenol, pyraclostrobin, sulfasalazine, and triclosan for which antibodies exist.

WORK PACKAGE 2: OPTIMISED PARTICLES FOR WASTEWATER TREATMENT. **TASK 2.1 Modelling of Electric Field Distribution.** The potential distribution between drive electrodes (Figure 5) located within a flow through reactor will be modelled using COMSOL Multiphysics to identify the optimal conditions (especially electrode size and placement, conducting diamond particle size and composition/conductivity) for optimised hydroxyl generation and minimised energy costs.

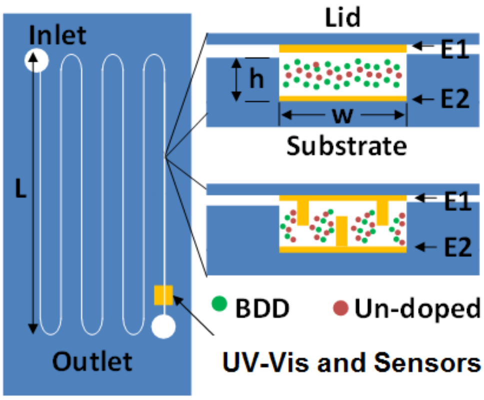

Figure 5. Prototype reactor capable of processing 1-10 litre hr^{-1} wastewater. Two alternative electrode configurations are shown (configuration will be optimised in Task 2.1).

TASK 2.2. Optimised Particles For Wireless Wastewater Treatment. The optimum source of Boron Doped Diamond, BDD particles for use in the reactor will be identified (e.g. US Research Nanomaterials, Inc., Element Six Ltd (discussions have taken place with Dr. Tim Mollart, Applications Engineer)), and ultrananocrystalline diamond (UNCD) (Advanced Diamond Technologies, Grafen). Specifically, we will quantify the electrochemical performance, lifetime and costs for wastewater treatment/destruction. Characterisation of the particles (all partners): HRSEM, STM, solid state NMR, DLS, Zeta potential, voltammetry, FTIR, fluorescence and Raman spectroscopy. The BDD particle selection process (DCU) will use **solutions of single target molecules before moving to mixtures relevant to our target industries.** Mineralisation rate: GC (CO_2, NH_3, O_2) as well as HPLC and LCMS (residual compounds). The long term stability of the conducting diamond particles will be assessed by running the incineration cell continuously for extended periods.

WORK PACKAGE 3 INTEGRATED REACTOR. **Task 3.1. Reactor Design.** Figure 5 shows a schematic of the proposed flow-through reactor design. DCU: COMSOL Multiphysics fluidic dynamics to simulate different mesochannel designs with varying length (L), height (h) and width (w), respectively, to estimate linear velocities, retention time (of unretained species) and volumetric flow rate through the channels. Different diameters of conducting and non-conducting diamond particles (included to prevent shorting between electrode E1 and E2) and theoretical changes in pressures will be calculated. **Reactor electric field strengths and configurations** will be modelled for different electrode designs E1 and E2 shown schematically (RHS panels) in Figure 5.

TASK 3.2 Reactor Fabrication. The small (1-10 litre per hour flow through) ***prototype reactors*** incorporating the optimised sensors will be rapidly prototyped using 3D printing techniques (NU (3Dnewprint) and DCU) initially using ABS. These will be used to confirm the validity of the COMSOL modelling. It is important to note that the ***SPy*** approach is intrinsically scalable since the voltage difference generated, V, is controlled by the particle radius, r, i.e., V = Field Strength (V cm^{-1}) x 2r, ***not*** the channel size of the reactor. Equally, dielectric breakdown dictates the maximum field strength and initial measurements on *wastewater* suggest that dielectric breakdown is observed only at field strengths greater than 60,000 V m^{-1}. Thus, industrial scale reactors, hundreds of litres per minute, are perfectly achievable with our approach.

WORK PACKAGE 4 REAL WORLD WASTEWATER TESTING. Task 4.1 Pharmaceutical Production Plant, Dublin, Ireland: DCU will test SPy performance using the production wastewater stream of a full scale pharmaceutical production facility (Ipsen, Dublin). Currently, the treatment cycle used is: Flow EQualisation (EQ), Aerobic Digestion (AD), Membrane BioReactor (MBR), Ozonation (OZ) and DeGassification (DG). Based on the Chemical Oxygen Demand this reduces the loading from 600 mg/l at the inlet to 15 mg/l at the outlet (97.5% efficiency). Two types of testing will be undertaken. First, the SPy technology will replace the ozonation step (AOP) and its efficiency and throughput evaluated using COD. Second, the possibility of replacing the entire five step process with the SPy technology by treating the wastewater stream directly will be assessed. Testing will be against the European Pharmacopoeia (Ph. Eur).

Task 4.2 Food Production Facility, Nantes, France. NU: SPy treated wastewater from a food production facility (in Vendée region, France) will be tested using the EU standards (S.I. No. 464/2017 - EU (Drinking Water) Regulations 2014 & 2017). These are High-Strength Industrial Wastewaters with the following characteristics, BOD 18-30 g/l, Fats (FOG) 1-3 g/l, COD 30-50 g/l and total suspended solids (TSS) of 5-50 g/l. Currently, the waste is treated by Mechanical Pre-Treatment (MPT), Oil/Water Separation (OW),Flow Equalization (EQ), Anaerobic Biological Treatment (AND), Anaerobic Membrane Bioreactor (AnMBR). BOD, FOG and TSS results indicate >99% removal of contaminants before the wastewater is sent off site for municipal wastewater treatment. The performance of the SPy reactor following mechanical pre-treatment alone will be investigated.

3.2. APPROPRIATENESS OF THE MANAGEMENT STRUCTURE AND PROCEDURES, INCLUDING QUALITY MANAGEMENT. The decision making process is based on the **DESCA model consortium agreement for H2020**. The **General Assembly** (GA) will comprise one representative from each signing organisation and will meet annually (extraordinary GA as required). It is responsible for: the institutional agreement for **Project Board** (PB) plans where necessary; approving and signing the **Project Consortium Agreement** (PCA) and dispute resolution. The protocols for summoning GA and extraordinary GA, and their decision making will be detailed in the PCA. The **Project Coordinator** (PC) will be **Prof. Robert Forster, DCU** (highly experienced in managing complex multi-partner projects), responsible for **overall management** and **scientific coordination**. He will chair the GA and PB, ensure that costs, deliverables and milestones are met, and that any significant deviations are reported to the GA, PB and EU project officer. The Research Support Office at DCU, which is experienced in administration of EU grants, will lead preparation of all non-technical documents, legal affairs, deal with all financial transfers, monitor budgets and administer any central funds. It will also arrange and run project technical and management meetings. **The PB comprising the Coordinator and WP Leaders is responsible for strategic management and direction of *SPy*.** It will ensure that the project remains on schedule, communication between WPs is maintained, and that quality and ethical standards are met. It will resolve conflicts that cannot be resolved at WP level. **WP Leaders** will: plan, coordinate and monitor the execution of the work within the WP, ensure deliverables appear on time, and escalate issues that cannot be resolved at the work package level to the PB. **An Advisory Board (AB)** will be established comprising **industrial and public sectors representatives-**scientific, technology transfer, policy KOLs including **Prof. Richard Compton** (University of Oxford, electrochemistry, H Index:99), **Prof. Gordon Wallace** (University of Wollongong, rapid prototyping of reactors, H Index:103), **Tom O'Dwyer** (Analog Devices, Director of Technology, electric field power supply), **Dr.**

Declan Moran (Manufacturing Director, Ipsen Pharmaceuticals), **Dr. Tommy Cussen** Abbott Nutritionals and **Prof. Fiona Regan**, Director, DCU Water Institute. This Board has informed our understanding of sample composition, volumes and other performance criteria, market scale and opportunities, and cost models.

Effective collaboration will be achieved by annual meetings, regular exchange of researchers and ad-hoc teleconferences (small sub-groups). The secure area of the programme website will be the central deposit of data and results. All partners are involved in Dissemination and Exploitation.

MILESTONES AND DELIVERABLES

WORK PACKAGE 1: SENSORS FOR WASTEWATER

Milestone	**Description**	**M**
M1.1	Reversible release of captured pathogens within existing SepTec device	12
M1.2	Selection of spectroscopic or sensor approach for the determination of organic load to define treatment protocol.	12
M1.3	Strategy identified for the encapsulation of ECL dyes within silicate nanoparticles.	18
Deliverable	**Description**	
D1.1	Device for highly sensitive pathogen detection (<1000 CFU/ml) device in water.	18
D1.2	100 mg of dye loaded silicate nanoparticles with ECL efficiency >80%.	24
D1.3	ECL based immunoassay for detection of priority pollutant in pharmaceutical wastewater.	24
D1.4	Minimum of five public engagement events including school visits, Café Scientifique and debates (see Section 2.2).	36

WORK PACKAGE 2: OPTIMISED PARTICLES FOR WASTEWATER TREATMENT

Milestone	**Description**	**M**
M2.1	Fully characterised conducting diamond particles.	6
M2.2	Model of electric field distribution in the presence of organic pollutants accounting for solution composition, electrode size, number and placement within the reactor.	12
M2.3	Rate of hydroxyl radical and oxygen generation measured and optimised for a suspension of CDPs within an electric field.	18
Deliverable	**Description**	
D2.1	>100 mg of BDD particles capable of wirelessly mineralising single APIs at an industry relevant rate.	12
D2.2	*In silico* model that replicates experimental results on wireless electrochemical incineration of recalcitrant organics.	12
D2.3	Invention Disclosure Form filed on the use of BDD particles for wireless incineration of recalcitrant organics.	36
D2.4	Following IP protection, minimum of two publications in high impact journals on CDP properties, hydroxyl radical generation and wireless mineralisation of recalcitrant organics.	36
D2.5	Minimum of five public engagement events including school visits, Café Scientifique and debates (see Section 2.2).	36

WORK PACKAGE 3: INTEGRATED REACTOR

Milestone	**Description**	**M**
M3.1	Model of electric field distribution within reactor correlates with experimental results.	18
M3.2	Reactor design finalised that incorporates electric field modelling, rates of electron transfer and coupled chemical reactions as well as mass transport of the BDD particles and organic pollutants.	24
M3.3	UV-Vis spectroscopy protocol correlating with TOC established.	18
M3.4	Reactor performance optimised for wireless incineration of *single pollutants* relevant to pharma and food industries.	20
M3.5	Reactor performance optimised for wireless incineration of *multiple pollutants* relevant to pharma and food industries.	24
Deliverable	**Description**	
D3.1	*In silico* model of reactor.	18
D3.2	Reactor fabricated using rapid prototyping incorporating design features identified by *in silico* model.	30
D3.3	UV-vis sensing system directly coupled to reactor.	30
D3.4	(Bio)Chemical sensors integrated into reactor.	30
D3.5	Minimum of five demonstrations of the integrated reactor to industry and relevant stakeholders as well as students.	36

WORK PACKAGE 4: REAL WORLD WASTEWATER TESTING

Milestone	**Description**	**M**
M4.1	Prototype reactors deployed in Dublin and Nantes.	30
M4.2	Correlation between reactor performance in lab and field established.	36
M4.3	Understanding of well-defined application domains of SPy technology in pharma and food industries.	36
Deliverable	**Description**	
D4.1	Report on performance and use issues surrounding SPy technology in an industrial setting.	36
D4.2	Report on market possibilities for technology and initial assessment of route to market.	36
D4.3	Delivery of minimum of two business focused Masters projects looking at the route to commercialisation.	36

GANTT CHART (Example with work packages, events, dissemination, public engagement activities, deliverables, milestones or others. Delete rows and columns that do not apply).

Month/ Description	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
WP1	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
Milestones												M1.1, M1.2						M1.3																		
Deliverables																		D1.1						D1.2, D1.3												D1.4
WP2	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
Milestones						M2.1						M2.2						M2.3																		
Deliverables												D2.1, D2.2																								D2.3, D2.4
WP3							🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦						
Milestones																		M3.1, M3.3		M3.4				M3.2, M3.5												
Deliverables																		D3.1												D3.2, D3.3, D3.4, D3.5						D3.5
WP4																															🟦	🟦	🟦	🟦	🟦	🟦
Milestones																														M4.1						M4.2, M4.3
Deliverables																																				D4.1, D4.2, D4.3
Progress Monitoring						🟩						🟩						🟩						🟩						🟩						🟩
Mobility Schemes												🟨						🟨						🟨												
Risk Management						🟥						🟥						🟥						🟥						🟥						
Others																																				

3.3. RISK MANAGEMENT

SCIENTIFIC/TECHNICAL: R1:QUALITY OF THE PROCESSED WATER: We will develop continuous monitoring approaches based on UV-Vis spectroscopy, electrochemical sensors as well as electrochemiluminescence detection strategies. The most promising approach will be selected at the end of **Year 1**. The sensing strategies will be benchmarked against gold standard measurements that will quantify the concentration of individual components in the post-treatment water samples. Moreover, bioluminescent bacteria (e.g., Microtox) will be used to detect the relative toxicity of the samples. TOC (total organic carbon) is considered as the most relevant parameter for quantifying the organics in water. **R2: COMBINATION WWT**. Our objective is to develop the SPy technology so that it can convert a wide range of pollutants to CO_2, H_2O and NH_3. However, if the most recalcitrant molecules cannot be fully mineralised, we will test the ability of conventional biological polishing techniques to remove the final traces of pollutant, i.e., even conversion of recalcitrant organics into simpler compounds that are compatible with biological processing would be a significant accomplishment. **R3: STABILITY OF REACTOR MATERIALS.** While there would be issues using these 3D ABS reactors long term, our "rapid prototyping" approach will allow the optimal internal geometries to be achieved quickly due to efficient interactions between modelling/simulation, prototype production and wireless electrochemical experiments. However, the team has an extended network of engineering contacts who can produce reactors in Teflon or stainless steel, part of which could act as the electric field generating electrodes.

MANGEMENT: R4: DELAY IN RECRUITMENT. Sufficient lead time has been allowed, full engagement of beneficiaries and partner organizations of the different countries, use of tools such as Euraxess, a specific group at LinkedIn, networks, emails to contacts, specialized webpages, etc. **R5: EARLY DEPARTURE OF RESEARCHER.** An exceptional PB meeting will adopt measures such as task re-distribution to recruitment of a new researcher (a prioritized list of candidates will be maintained). **R6: WITHDRAWAL OF PARTNER/PI.** Would be promptly addressed by an exceptional GA meeting to quickly re-assign/accelerate tasks prior to withdrawal. Each partner organisation has identified co-supervisors (Section 4) who would become full supervisors if needed. **R7: UNFORESEEN COSTS.** Appropriate decisions will be taken in the GA, including modifications to the distribution of the management budget allocated to partners**. R8: TASK INCOMPLETE/DELAYS.** DCU will closely monitor the execution of the project. Close project follow-up will be set up by a project manager who will support the consortium, will gather the information and encourage all participant's engagement. The GA will deal with any project conflicts generally by consensus decision making. However, one partner, one vote can be implemented if needed with the Coordinating Institution having a casting vote if ever required.

3.4. POTENTIAL AND COMMITMENT OF THE CONSORTIUM TO REALISE THE PROJECT.

DCU	**NU**	**UWC**	**URV**
Coordinator General Assembly, GA and Project Board (PB) Chair Leader of WP2, WP3 and Management. Research in WP1, WP2, WP3 & WP4. Supervise PD researcher. Hosting incoming researchers from NU and UWC Outgoing researcher to NU and UWC. PI visit to URV. Organises electrochemistry workshop and meeting. Organizes Main Training Event. Delivers outreach, dissemination and communication activities.	Leader of WP4 Member of PB. Research in WP1 and WP3 Supervise PD researcher. Hosting incoming researcher from DCU. Hosting Coordinator secondment. Hosts PB meeting. Technical course on dye development and UV-Vis spectroscopy. Delivers outreach, dissemination and communication activities.	Member of PB. Research in WP1 and WP2. Supervise researcher. Hosting secondments of DCU researcher. Delivers outreach, dissemination and communication activities.	Leader of WP1 Member of PB. Research in WP1 and WP3. Hosting secondments of DCU researcher. Hosting Coordinator visit. Delivering Masterclass on biosensing at DCU. Hosts PB meeting. Delivers outreach, dissemination and communication activities.

EXPERTISE: The SPy team has the multidisciplinary expertise, advanced (nano)(bio)materials, electrochemistry, physical chemistry, (bio)sensors, analysis, rapid prototyping and industrial deployment, needed to deliver practical, industry relevant next-generation WWT devices. (**INDUSTRY) EXPERIENCE**: The team has deep experience in working with MNCs and SMEs delivering key projects in sensors, energy, coatings and device development. The Coordinator has spun out a company, SepTec.ie, and all PIs have translated research from the bench to practical application. C**OMMITMENT:** All members see tremendous value in SPy and are fully committed to delivering it, e.g., URV are covering their own costs of participating. **INFRASTRUCTURE:** All required instrumentation and infrastructure is available for the production, characterisation, testing and deployment of the sensors, BDD particles and reactor.

4. DESCRIPTION OF THE PARTICIPATING RESEARCHERS

Partner Number, according to Part A	Research Team Members (for personnel include name, position and affiliation)	General Description
Partner 1, Prof. Robert Forster, Dublin City University, DCU	**1 Coordinator and PI Prof. Robert Forster**, Full Chair, and Director of the National Centre for Sensor Research, Dublin City University, DCU	H-Index 44, >7000 citations; Wireless electrochemistry, electrocatalytic decomposition, sensing, modelling of electrochemical systems, rapid prototyping, microfluidics.
	2 Prof. Mary Pryce, Professor of Inorganic Chemistry, Dublin City University	H-Index 20, >2000 citations, Nanomaterials, electrochemical reactor design and fabrication, field deployable systems.
Partner 2 , Dr, Yann Pellegrin, Nantes University NU	**1 (PI) Dr. Yann Pellegrin,** CNRS Research Fellow, Nantes University (NU)	H-Index 32, >3100 citations; synthesis and photochemistry of custom ligands and metal complexes designed for sensing and energy applications. Winner of the Bronze Medal of the CNRS (2014). 96 publications
	2: Dr. N. Blart, Senior Lecturer, NU	H-Index 41 (65 joint publications with Pellegrin). Organic chemistry for molecular engineering of ligands.
	3: Dr. Clemence Queffelec, lecturer, NU	H-Index 8 22 publications, organic chemistry, nanoparticles. Recipient of the ADEME Innovation Trophy.
	4: François-Xavier Lefevre, engineer, NU	Expert in microscopy (AFM, SEM, TEM, atomic absorption)
Partner 3, Prof. Emmanuel Iwuoha, University of the Western Cape UWC	**1: (PI) Prof. Emmanuel Iwuoha,** Prof. of Chem. & SA Research Chair (TIER 1) for NanoElectrochemistry & Sensor Technology, University of the Western Cape.	H-Index 40, >5000 citations, Materials characterisation, sensing of pollutants and the application of SPy to municipal wastewater samples.
	2: D. Keegan Pokpas, Lecturer, Dept. of Chem. UWC	Sensor platforms for the determination of pollutants in water samples.
	3: Dr. Samantha Douman, PD Fellow, UWC	Contactless/wireless electrochemistry and electrochemiluminescence
	4: Dr. Hlamulo Makelane, Researcher, UWC	Sensing and degradation of polyaromatic hydrocarbons using AC Voltammetry and polymer modified electrodes
Partner 4, Prof. Ciara O'Sullivan, Universitat Rovira i Virgili URV	**1: (PI) Prof. Ciara O'Sullivan,** ICREA Research Professor, Engineering Sciences Universitat Rovira i Virgili (URV)	H-Index 43, >7000 citations, chemical, biological and pathogen sensing, electrochemical and optical transduction, aptamers and engineered bio-components.
	2. Prof. Ioanis Katakis, Prof. Chemical Engineering, URV	H-Index 24, 2197 citations, co-author of 85 publications, co-inventor on 6 patents (3 exploited) that led to products in glucose diagnostics (Therasense/Abbott) and pathogen detection (iMicroQ S.L.

5. CAPACITY OF THE CONSORTIUM ORGANISATIONS

Partner Number (Organisation Name)		General Description
Partner 1 (Dublin City University, DCU)	**Role and main responsibilities in the project**	**Coordinator**, Chair of GA and PB, Research in WP1, WP2, WP3, WP4 and Management. Organises main training event. Financial and progress reporting to JPI.
	Key research facilities, infrastructure, equipment	WWW.NCSR.ie, http://www.nanoresearchfacility.org/facilities/ Electrochemistry, HRSEM, confocal and super-resolution microscopy, synthetic labs, 3D printing and additive manufacture, micromilling of plastics, COMSOL and custom simulations
	Relevant publications/research/innovation products	**PRODUCT:** www.SepTec.ie, ultrasensitive, rapid device for the detection of pathogens. **INNOVATION:** On-going collaborations with Mylan, Ipsen, Janssen, Abbott, Crescent Diagnostics and TheraDep.
Partner 2 (Nantes University, NU)	**Role and main responsibilities in the project**	Member of PB involved in research activities of WP1 and WP2, hosting secondments of DCU researcher and relating with stakeholders and research result communications.
	Key research facilities, infrastructure, equipment	Synthetic labs for molecular and nano-materials and their characterisation. HPLC, GC-MS, UV-Vis, fluorescence, NMR, Raman and NIR spectroscopies. SEM, AFM and DLS.
	Relevant publications/research/innovation products	**Advanced Optical (Nano)Materials or practical applications**: *New luminescent copper(I) complexes with extended π-conjugation*, Polyhedron, 2018, 140, 42-50. NU is involved with EUROFINS, company providing reliable analysis of samples including water (https://www.eurofins.fr/environnement/)
Partner 3 (University of the Western Cape, UWC)	**Role and main responsibilities in the project**	Member of PB involved in research activities of WP1 and WP2, hosting secondments of DCU researcher and relating with stakeholders and research result communications.
	Key research facilities, infrastructure, equipment	Small angle X-ray scattering spectrometer (SAXS) for determining particle size distribution, 500 MHz solid state NMR with triple resonance, a suite of single and multichannel electrochemical workstations, as well as spectroelectrochemical and electrochemical microscopy instruments.
	Relevant publications/research/innovation products	**NanoMaterials For Pollutant Sensors**: *Synthesis and electrochemical characterization of nanostructured magnetic molecularly imprinted polymers for 17-β-Estradiol determination*. Sensors and Actuators B: Chemical, 2017, 241, 698-705. *AC voltammetric transductions and sensor application of a novel dendritic poly (propylene thiophenoimine)-co-poly (3-hexylthiophene) star co-polymer*. Sensors and Actuators B: Chemical, 2017, 227, pp.320-327.
	Role and main responsibilities in the project	Member of PB involved in research activities of WP1 and WP2, hosting secondments of DCU researcher and relating with stakeholders and research result communications. Immunosensors for monitoring of pathogens and recalcitrant pollutants
Partner 4, Universitat Rovira i Virgili URV	**Key research facilities, infrastructure, equipment**	http://www.etseq.urv.es/nbg/Interfibio/?page_id=34
	Relevant publications/research/innovation products	http://www.etseq.urv.es/nbg/Interfibio/?page_id=469