

Deliverable Report D2.3 Electrolyser Unit

Work package:	WP2 Treatment technology and prototype
Lead beneficiary:	UCLM
Authors:	Manuel. A. Rodrigo, C. Sáez, Miguel A. Montiel, Ismael Fernández, M. Pilar. Castro
Place, country:	Ciudad Real, Spain
Type:	Hardware
Dissemination level:	Public
Due date (in months):	Project month 13
Date finalised:	11.10.2022 (project month 14)

Version	Date	Reason for changes
1	5.10.2022	Draft
2	11.10.2022	Approved by Coordinator

Table of Contents

1	Introduction to the project SERPIC	2
2	Report summary	2
3	Deliverable description as stated in the Project Description	2
4	Introduction.....	2
5	Results	3
	5.1 Persulfates electrolyser unit.....	3
	5.2 Chlorine Dioxide production.....	5
6	Publications and other dissemination activities	7
7	Literature	7



The authors would like to thank the EU and Bundesministerium für Bildung und Forschung, Germany, Ministero dell'Università e della Ricerca, Italy, Agencia Estatal de Investigación, Spain, Fundação para a Ciência e a Tecnologia, Portugal, Norges forskningsråd, Norway, Water Research Commission, South Africa for funding, in the frame of the collaborative international consortium SERPIC financed under the ERA-NET AquaticPollutants Joint Transnational Call (GA N° 869178). This ERA-NET is an integral part of the activities developed by the Water, Oceans and AMR Joint Programming Initiatives.

1 Introduction to the project SERPIC

The project *Sustainable Electrochemical Reduction of contaminants of emerging concern and Pathogens in WWTP effluent for Irrigation of Crops – SERPIC* will develop an integral technology, based on a multi-barrier approach, to treat the effluents of wastewater treatment plants (WWTPs) to maximise the reduction of contaminants of emerging concern (CECs). The eight partners of the SERPIC consortium are funded by the European Commission and by six national funding agencies from Norway, Germany, Italy, Spain, Portugal, and South Africa. The official starting date of the SERPIC project is 1. September 2021. The project has a duration of 36 months and will end 31. August 2024.

The overall aim of the SERPIC project is to investigate and minimise the spread of CECs and antimicrobial resistant bacteria/antibiotic resistance genes (ARB/ARG) within the water cycle from households and industries to WWTPs effluents, and afterwards via irrigation into the food chain, into soil and groundwater and into river basins, estuaries, coastal areas, and oceans with a focus on additional water sources for food production.

A membrane nanofiltration (NF) technology will be applied to reduce CECs in its permeate stream by at least 90 % while retaining the nutrients. A residual disinfection using chlorine dioxide produced electrochemically will be added to the stream used for crops irrigation (Route A). The CECs in the polluted concentrate (retentate) stream will be reduced by at least 80 % by light driven electro-chemical oxidation. When discharged into the aquatic system (route B), it will contribute to the quality improvement of the surface water body.

A prototype treatment plant will be set-up and evaluated for irrigation in long-term tests with the help of agricultural test pots. A review investigation of CECs spread will be performed at four regional showcases in Europe and Africa. It will include a detailed assessment of the individual situation and surrounding condition. Transfer concepts will be developed to transfer the results of the treatment technology to other regions, especially in low- and middle-income countries.

2 Report summary

To maximize the reduction of contaminants of emerging concern (CECs), SERPIC project required some integrated technologies based on the multi-barrier approach. The electrolyzers are key to achieving this goal. One is based on the production of chlorine dioxide to treat a permeate stream from the membrane nanofiltration and the other one is based on the persulfate electro-generation. This report will define the main characteristic of each as well as the design and the key parameters to obtain the highest concentration in both.

3 Deliverable description as stated in the Project Description

Based on task T2.4 “Build up and test electrolyzers”, the selected electrolyzers prototypes will be manufactured, preferentially using a 3-D printer, and delivered to UP. The two cells selected will include the best coating formulation of anode and cathode according to previous results and mechanical design will include the best consideration from the fluid dynamic point of view and from the necessities of temperature and pressure to warrant a high production of each of the two targeted oxidants.

4 Introduction

SERPIC project requires several technologies to maximize the reduction of contaminants of emerging concern (CECs) from wastewater treatment plants. Membrane nanofiltration is applied and its permeate stream is treated by residual disinfection with chlorine dioxide for irrigation of

crops. Chlorine dioxide is a powerful disinfectant because of its strong capacity as an oxidant and wide use in the disinfection of drinking water. On the other hand, the CECs in the polluted concentrate stream from nanofiltration units are treated by a photoreactor where longer lifetime oxidants called persulfates are activated by ultraviolet light.

This project is focused on the production of two different oxidants by electrochemical technologies. The first one is chlorine dioxide whose electrogeneration is based on two electrochemical processes, the combination of electrochemically produced hydrogen peroxide and chlorates. In the case of persulfates, they can be generated from sulfate ions in combination with a strongly reactive oxygen species called hydroxyl radicals ($\text{OH}\cdot$). The massive generation of these species is favored at the surface of doped-boron diamond electrodes (BDD). These types of electrodes present higher chemical and electrochemical stability than other electrode materials, making them a good choice for persulfate generation.

The design of the electrochemical reactor plays a major role in the efficiency of the process of electrogeneration of chlorine dioxide and persulfates, directly affecting energy consumption and hydrodynamic behavior. In this sense, CAD design and CFD modelling pair to offer an impressive tool to prototype an electrochemical reactor. Afterward, 3D printing comes into the scene, fast producing the designed reactor to be tested in real conditions. The iteration between CAD design, CFD modelling, and 3D printing leads to a fast production of an extremely process-adapted electrochemical reactor with important savings in terms of time and resources. Furthermore, electrochemical parameters are key in achieving maximum efficiency. Therefore, an exhaustive study of the best conditions in terms of electrode type, temperature, pH, current density, and concentration or type of electrolyte used has been carried out.

5 Results

5.1 Persulfates electrolyser unit

The electrosynthesis of persulfates was carried out on a bench scale set up in a single compartment electrochemical home-designed flow cell made by 3D printing, as shown in **Figure 2**, consisting of two parallel electrodes (5 cm x 5 cm) of BDD and stainless steel as anode and cathode, respectively. Near the liquid inlet, several fins are deployed to help proper liquid distribution all along the cell. Electric contact to the electrodes is made using cold welding on the rear part of the compartments, right in the exposed electrode. For the persulfate synthesis experiments, under galvanostatic conditions and batch operation mode., a Delta Elektronika ES030-10 power supply (0-30 V, 0-10 A) was employed. A jacketed electrolyte tank of 1L, a peristaltic pump with a $47 \text{ L}\cdot\text{h}^{-1}$ flow, and a thermostat with a heat exchanger were used. Due to the heat generated by the electrochemical reactor, the thermostat is mandatory to hold the desired temperature.

The necessary BDD anode required to produce persulfate efficiently was manufactured at Fraunhofer IST from a square-shaped Niobium plate with 2 mm thickness and 50 mm both width and length (**Figure 1**). The diamond was deposited in a self-designed hot-filament-activated chemical vapor deposition reactor with a coating area of 500 mm times 1000 mm. The precursor gas was methane, used in a concentration of 1.8 % in an excess of hydrogen. The diamond film was doped during deposition using trimethyl borane in a concentration of $5\cdot 10^{-5}$ in the gas phase leading to boron concentrations of about 2000 ppm in the diamond film. The film thickness was seven μm . The crystallinity was microcrystalline.

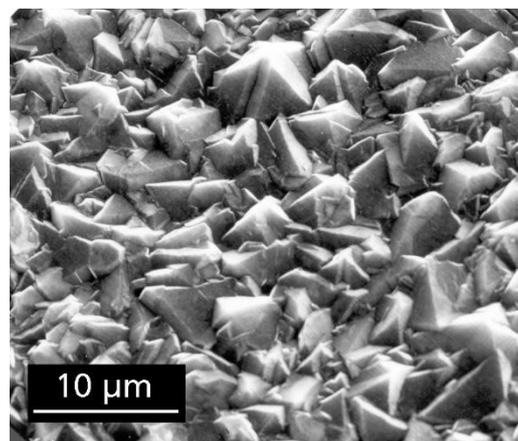


Figure 1: Electrode 50 mm x 50 mm, coated with boron-doped diamond by Fraunhofer IST: photo (left) and SEM image of surface topography (right).

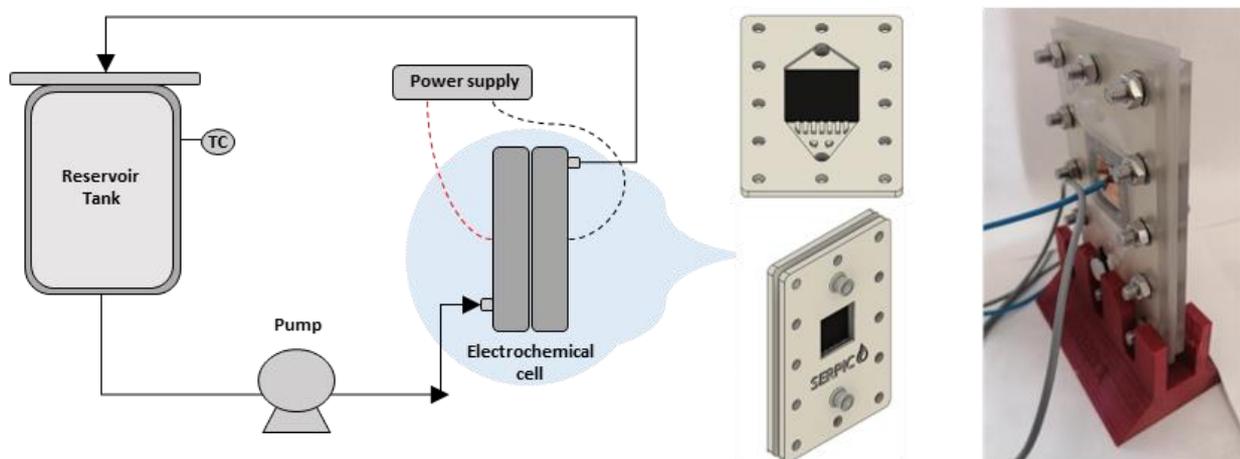


Figure 2: Left: Bench scale experimental setup in batch mode. Right: Electrochemical reactor used in the persulfate generation with BDD electrodes. CAD image of the reactor with the BDD electrode (left) and photo of the printed 3D reactor with the electrical connections.

All BDD electrodes supplied by Fraunhofer IST were tested under the same operating conditions: current density of 300 mAcm^{-2} , $25 \text{ }^\circ\text{C}$ as well as the supplied electrolyte itself. At the light of the obtained results, it can be concluded that the electrodes supplied by Fraunhofer IST can be satisfactorily used to produce persulfate from H_2SO_4 solutions. In this way, under the tested conditions of 300 mAcm^{-2} and $25 \text{ }^\circ\text{C}$ up to 200 mM persulfate with 17 % of energy efficiency can be reached, which improves the values found in the literature. Persulfate concentrations were quantified by reaction with potassium iodide and followed by the thiosulfate titration method using a Metrohm titrator unit. These four electrodes show similar behaviour with a standard deviation lower than 8 %.

To optimize the electrochemical generation of persulfates, different experiments were carried out where the main parameters of the electrochemical systems: current density, temperature, pH, and type of electrolyte were varied. In addition, the experimental setup was slightly modified to operate in continuous mode. **Figure 3** shows the experimental setup of a continuous mode persulfate generation process. The electrolyte is continuously fed into the system while persulfate and unreacted electrolyte are extracted from the system. The continuous mode allows working in a more automated way for a possible industrial application.

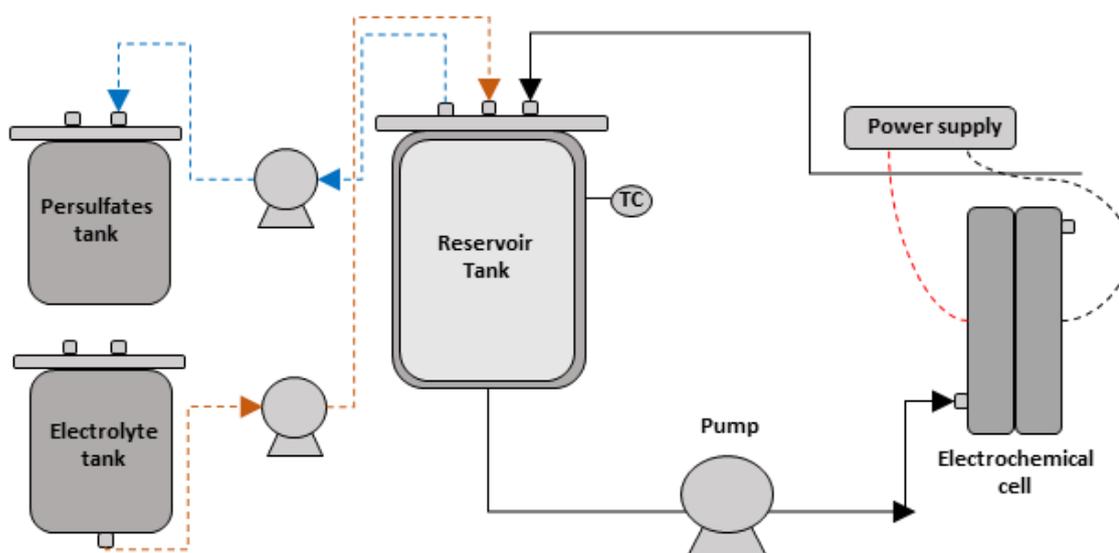


Figure 3: Bench scale experimental setup in continuous mode.

Table 1 shows the effect of the tested operating parameters. It can be concluded that persulfate generation improves at high current densities, temperatures below 25 °C and with the use of acid electrolyte. Regarding the operation mode, a higher persulfate concentration is obtained in batch mode, but the continuous mode is more favourable in terms of production, obtaining higher persulfate values, and being able to adapt the system for a possible industrial application.

Table 1: Effect of the tested operating parameters.

Reference experiment: $j/mAcm^{-2}$: 300; Q/ AhL^{-1} : 79.8; Electrolyte/M:H ₂ SO ₄ /1; T/°C:25; [Persulfate]/mM: 200		
Parameters varied/ %	Effect Persulfate concentration	Effect / positive or negative
Temperature decrease/ 40%	Increase	positive
pH alkaline medium	Decrease	negative
Current density decrease/ 50%	Equal value	positive
Current density decrease/ 75%	Decrease	negative

5.2 Chlorine Dioxide production

Chlorine dioxide production is a combination of hydrogen peroxide and chlorate both produced electrochemically as described in **Figure 4**. The left side of the figure shows the chlorate bench scale set up whose electrochemical reactor is composed of a DSA (dimensional stable anode, manufactured by mixed metal oxides) anode and a titanium plate as cathode, both 78.5 cm², in a thin film reactor. It is composed of 4 plastic pieces, two corresponding to the anodic and cathodic parts and the other two to the tightening plates. Combining anodic and cathodic parts with a gasket in between them form the cell volume with 1 mm separation between electrodes, which gives low ohmic drop and good mass transfer, thus assuring low power consumption. Near the liquid inlet, several fins are deployed to help proper liquid distribution all along the cell. Tightening

plates are used to close the cell using M8 screws, washers, and nuts. Electric contact to the electrodes is made using cold welding on the rear part of the compartments, right in the exposed electrode.

The electrosynthesis of chlorate was carried out in an electrochemical home-designed flow cell made by 3D printing, under galvanostatic conditions, and in continuous operation mode. Delta Elektronika ES030-10 power supply (0-30 V, 0-10 A) was employed. The synthesis was conducted in continuous mode using a jacketed electrolyte tank of 1800 mL, a continuous flow rate of 95 mL·h⁻¹, and a thermostat with a heat exchanger to control the temperature at 15 °C.

On the other hand, the right side of **Figure 4** shows the bench scale set up of hydrogen peroxide, whose generation was carried out in a GDE electrochemical home-designed flow cell made by 3D printing, composed of a DSA anode and a painted carbon paper as cathode, both 10.9 cm², in a thin film reactor. The hydrogen peroxide reactor is composed of 3 plastic pieces, 1 corresponding to the anodic and cathodic parts and the other two to the tightening plates. The electrosynthesis of hydrogen peroxide was carried out under galvanostatic conditions and in continuous operation mode. Delta Elektronika ES030-10 power supply (0-30 V, 0-10 A) was employed. The synthesis was conducted in continuous mode using an electrolyte tank of 500 mL, with a continuous flow rate of 80 mL·h⁻¹.

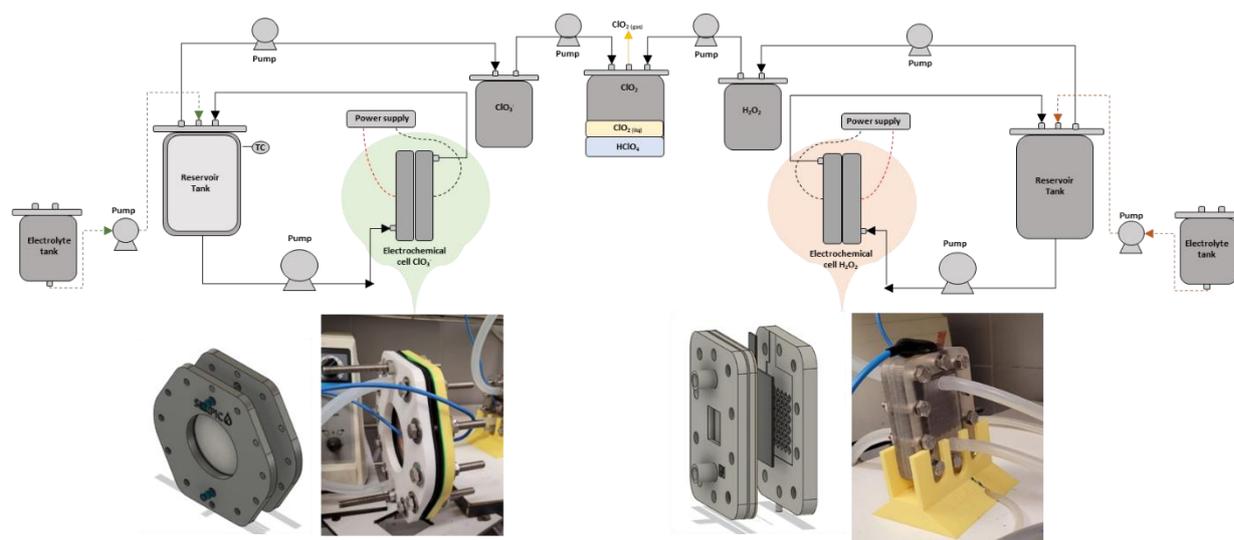


Figure 4: Bench scale experimental set up in continuous mode to produce chlorine dioxide. Electrochemical reactor used in the chlorate generation with DSA as anode and Titanium plate as cathode. CAD image of the reactor and the printed 3D reactor with the electrical connections (left). Electrochemical GDE reactor used in the hydrogen peroxide generation with DSA as anode and paper painted carbon as cathode. CAD image of the reactor and the printed 3D reactor with the electrical connections (right).

The concentration of chlorate was measured by ion chromatography (IC) using a Metrohm Compact Ion Chromatograph Flex (Madrid, Spain) coupled to a conductivity detector. A Metrosep A Supp 7 column was used as the stationary phase and 85:15 v/v 3.6 mM sodium carbonate/acetone as the mobile phase. The flow rate was 0.8 mL min⁻¹ and the volume injection of each sample was 20.0 μm. Hydrogen peroxide concentration was monitored by spectrophotometry, due to the yellow colour formed between hydrogen peroxide and Ti²⁺ at a wavelength of 410 nm.

For the generation of hydrogen peroxide, the best operation conditions are the application of current densities in the nearness of 5.0 mA cm^{-2} to an electrolyte containing 100 mM of NaClO_4 . To produce chlorate, the optimum operation conditions involve the application of current densities close to 150 mA cm^{-2} to solutions containing close to 100 mM of NaCl . The ratio between both reagents to produce chlorine dioxide is $1:30 \text{ mol ClO}_3^- : \text{mol H}_2\text{O}_2$, and they should be added to a tank with a concentration of 70 % HClO_4 . The product is generated in the liquid phase, but after that, the chlorine dioxide was released into the gaseous phase, reaching amounts higher than 20 mmol after 4 hours.

6 Publications and other dissemination activities

Castro, M. Pilar.; Montiel, Miguel. A.; Fernández Mena, I.; Lobato, J.; Sáez, C.; Rodrigo, Manuel. A. Persulfates electro-generation using BDD anodes and 3D-printed reactors. In: XVI Young Science Symposium, Ciudad Real June (2022). Oral contribution.

Castro, M. Pilar.; Montiel, Miguel. A.; Fernández Mena, I.; Schäfer, L.; King, H.; Gäbler, J.; Sáez, C.; Rodrigo, Manuel. A. Generación electroquímica de persulfato utilizando ánodos de BDD en un reactor electroquímico adaptado mediante impresión 3D. In: XLII Reunión del Grupo Especializado de Electroquímica de la Real Sociedad Española de Química, Santander July (2022). Poster presentation.

Castro, M. Pilar.; Montiel, Miguel. A.; Fernández Mena, I.; Rodrigo, Manuel. A.; Gäbler, J.; Höfer, M.; Armgardt, M.; Schäfer, L. Electrochemical production of persulfate with boron-doped diamond electrodes. In: IOA Conference & Exhibition, Toulouse November (2022), poster. - Submitted

7 Literature

Serrano, K.; Michaud, P. A.; Comninellis, C.; Savall, A.: Electrochemical preparation of peroxodisulfuric acid using boron-doped diamond thin film electrodes. In: *Electrochimica Acta* 48 (2002), p. 431-436.

Fryda, M.; Mattheé, T.; Mulcahy, S.; Hampel, A.; Schäfer, L.; Tröster, I.: Fabrication and application of Diachem electrode. In: *Diamond and Related Materials* 12 (2003) p. 1950-1956.

Ganiyu, O. S.; Martínez-Huitle, C.A.: Nature, mechanism and reactivity of electrogenerated reactive species at thin- film boron-doped Diamond (BDD) electrodes during electrochemical wastewater treatment. In: *ChemElectrochem* 6 (2019) p. 2379-2392.

Monteiro K. S. Mayra; Moratalla, A; Sáez, C.; Dos Santos, Elisama. V.; Rodrigo, Manuel. A.: Production of Chlorine Dioxide using hydrogen peroxide and chlorates. In: *Catalysts* 11 12 (2021) 1478.

Monteiro K. S. Mayra; Moratalla, A; Sáez, C.; Dos Santos, Elisama. V.; Rodrigo, Manuel. A.: Towards the production of chlorine dioxide from electrochemically in situ produced solutions of chlorate. In: *Journal of Chemical Technology & Biotechnology* 97 8 (2022) p. 2024-2031.

Moratalla, A.; Monteiro, K. S. Mayra.; Sáez, C.; Dos Santos, Elisama. V.; Rodrigo, Manuel. A.: Full and sustainable Electrochemical Production of Chlorine Dioxide. In: *Catalysts* 12 3 (2022) 315.