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Deliverable Report
D2.1 Design of electrolyser unit

Work package:	WP2 Treatment technology and prototype.
Lead beneficiary:	UCLM
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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

SERPIC project demands the sustainable production of persulfate and chlorine dioxide (ClO_2) to fully disinfect water streams coming from nanofiltration step. New build-in reactors will be designed and made to reach the requirements optimizing energy consumption and use of reagents. The proposed persulfate and ClO_2 reactors are made by 3D printing and will be further tested to evaluate not only the product formed but also hydrodynamic conditions and energy consumption. In this report, the construction details, materials, and parts of each reactor are shown and carefully addressed.

3 Deliverable description as stated in the Project Description

With the experimental feedback provided from T2.1 and CFD modelling of T2.2, details about the mechanical design of the two selected cells (one for the production of ClO2 and one for persulfates) will be included into a report, where the construction materials, flow-dynamic conditions, current distribution issues, electric contacts, placement of electrodes, etc., will be described. Also, drawings that will help to manufacture prototypes with 3-D printers or in mechanical workshops.

4 Introduction

Many technologies have already been implemented for the treatment of municipal WWTP effluents for their direct reuse. The most basic approach is a natural solution as sewage farms, in which sewage is used for both irrigation and fertilizing crops, although this solution does not always fulfil the minimum security and environmental requirements for water reuse defined on national or European scale. Rapid sand filtration followed by UV irradiation represents a widely applied treatment sequence, able to reduce suspended solids, bacteria and viruses, but with limited efficiency to some CECs and without a persistent disinfection effect. Adsorption on activated carbon, implemented for the treatment of drinking water, has recently been used at full scale for municipal wastewater reclamation. The process bottleneck is the limited efficiency in the reduction of CECs. The application of chlorination is developed at full-scale to produce drinking water, but has limited efficiency for the abatement of CECs in wastewater. Furthermore, the formation of chlorinated by-products as the hazardous trihalomethanes and haloacetic acids is known. Ozonation has been shown at full scale in Germany and Switzerland to reduce a wide spectrum of CECs; however, by-products formation, cost-intensive installations and high-power consumption are major impediments.

Membrane processes, commonly applied as a barrier for pathogens, have the potential to reduce CECs. Especially nanofiltration (NF) and reverse osmosis (RO) have been reported to reduce ARGs below levels of detection. NF, being less energy intensive than RO, seems to be more promising for the reduction of CECs [1,2]. However, the accumulation of the rejected constituents in the membrane concentrate is not sufficiently solved yet and remains a problem. Other technologies are currently being researched, such as photo-Fenton, photocatalytic ozonation or electrochemical oxidation. The results of these investigations have shown limited reduction efficiencies, limited scalability, and large energy consumption, respectively. The efficiency of these technologies is also challenged by the variance in CEC reduction within a specific CEC class. On the other hand, electrochemical generation of powerful oxidants like Persulfate of Chlorine Dioxide, are low cost and have promising scalability prospect due to the possibility of stacking electrochemical reactors [3,4]. These devices can be easily powered by renewable energy sources without requiring large power inputs.

In this sense, SERPIC aims to perform a multi-barrier approach in which a combination of membrane filtration process and electrochemical generation of powerful oxidants (persulfate and chlorine dioxide) can achieve a considerable depletion of the CEC in wastewater plants effluents. To produce the oxidants, new electrochemical reactors are designed to fit the low energy requirements of the project and also to adapt to the electrochemical process to be developed. In this report the main features and parts of developed electrolysers for the production of persulfate and chlorine dioxide are presented. This report describes the first task developed in Work Package 2 of the SERPIC project, which is devoted to the electrochemical generation of the oxidants and its further use in the wastewater treatment.

5 Results

5.1 Persulfate electrolyser unit

The necessary material to electrochemically produce persulfate in the adequate concentration is made of boron-doped diamond (BDD) anodes and they are provided by IST Fraunhofer. Moreover, these electrodes have a 50 mm x 50 mm dimensions according to the optimal fabrication process, from both technological and economical point of view. In the other hand, the cathode is mainly producing H_2, so any corrosion resistant material is suitable, in this case stainless steel is selected as a proper option. In consequence, the electrolyser unit is designed to fit BDD electrodes, using a filter-press structure with the adequate modifications to allow: i) good fluid-dynamic conditions with no death-zones, ii) enough gas evacuation to avoid gas bags inside the electrolyser and iii) easy connection and versatility o operate in one or two compartments. Figure 1 depicts the designed electrolyser showing the internal part including the

BDD electrode in black (left image) and the complete cell ready to be used (right image). A gasket is placed between the two parts of the reactor to assure a correct sealing. Near the liquid inlet several fins are made to help liquid distribution all along the cell. Finally, the electrolyser is closed with M8 screws, washers, and nuts. The construction materials and the number of pieces is fully described in table 1.

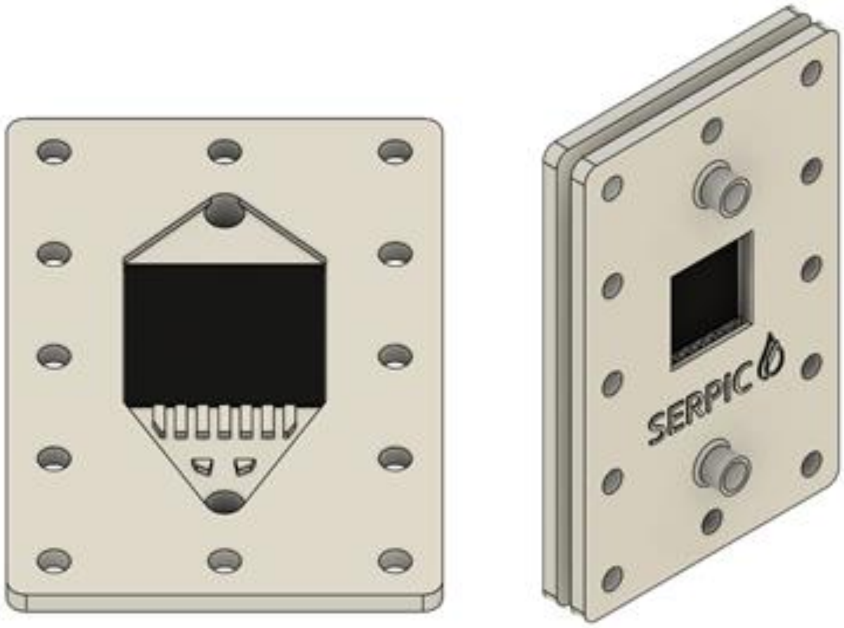

Figure 1: Persulfate electrolyser. Left anodic compartment with BDD electrode and right the complete electrolyser.

Table 1: List of components of persulfate electrolyser, number of units, and materials.

Component	No. of units	Material
Reactor compartment	2	Polyacrylate/Polyurethane
BDD anode	1	Niobium, BDD
Cathode	1	Stainless steel
Gasket	2	Silicone
M8 Screws	12	Stainless steel
M8 Washers	24	Stainless steel
M8 Nuts	12	Stainless steel

BDD anode and stainless steel cathode are placed one in front the other and separated by ca. 5 mm. This narrow distance between electrodes warranties low ohmic drop across the electrolyser and thus driving to a lower power consumption. The low cell volume helps to sustain high lineal velocity in the fluid with low pumping power, which helps to have good mass transfer and gas evacuation in the reactor. Electric contact to the electrodes is made by cold welding on the rear part of the compartments.

5.2 Chlorine dioxide electrolyser unit

Chlorine dioxide is produced combining perchlorate and hydrogen peroxide, both electrochemically produced in different reactors. Perchlorate electrochemical reactor is composed by a Cl_2 DSA (mixed metal oxide electrode) anode and stainless steel cathode, both 100 mm diameter cercles, in a thin film reactor. Figure 2 depicts the chlorate reactor with (right) and without (left) tightening plates. The reactor is composed by 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 up using M8 screws, washers, and nuts. The construction materials and the number of pieces is fully described in table 2. Electric contact to the electrodes is made using cold welding on the rear part of the compartments, right in the exposed electrode.

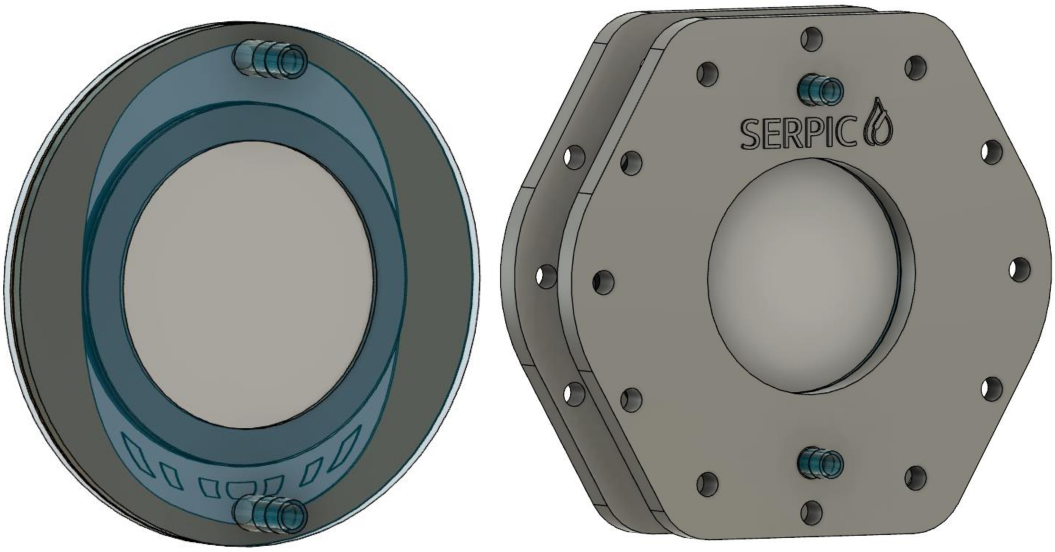

Figure 2: Chlorate electrolyser. Left the electrochemical reactor with DSA anode and stainless steel cathode. Right the reactor with the tightening plates.

Table 2: List of components of chlorate electrolyser, number of units, and materials.

Component	**No. of units**	**Material**
Reactor compartment	2	Polyacrylate/Polyurethane
DSA anode	1	Ti, RuO_2, PtO_2
Cathode	1	Stainless steel
Gasket	1	EPDM
Tightening plate	2	Polylactic acid
Tightening gasket	2	EPDM
M8 Screws	12	stainless steel
M8 Washers	24	stainless steel
M8 Nuts	12	stainless steel

On the other hand, as the peroxide production requirements are quite feasible and already reached at UCLM, an already tested reactor will be used (figure 3). Briefly, it is a flow-through reactor made of PVC in which a Vulcan-Teflon ink is used over a Ti mesh (25 mm x 25 mm) to produce hydrogen peroxide, while a Ti/Pt mesh is used as anode material. Anodic and cathodic mesh are separated by 3 EPDM gaskets which gives an inter-electrode distance of CA 3 mm. Electric contact is made using Pt wires to connect the mesh with an Al tape outside the wet zone (see figure 3). The reactor is closed using M8 screws, washers, and nuts. The construction materials and the number of pieces is fully described in table 3.

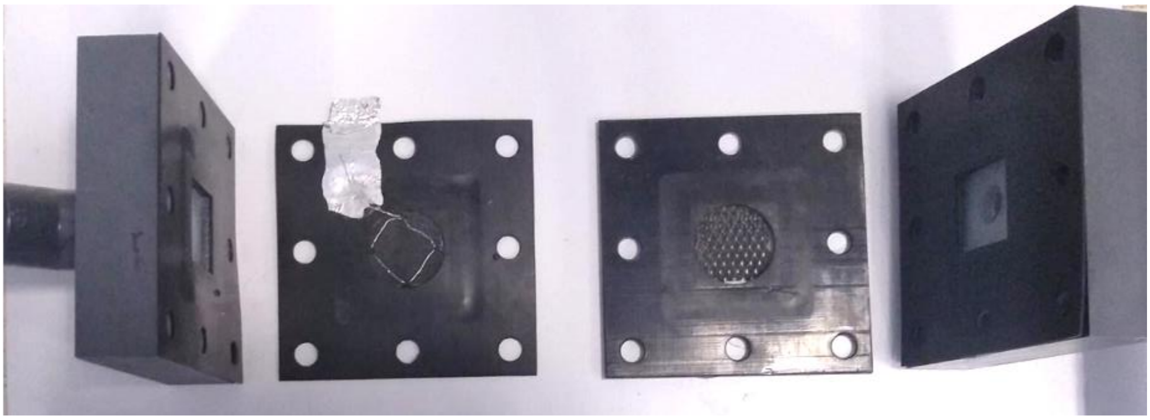

Figure 3: Hydrogen peroxide flow-through electrolyser with anodic and cathodic mesh in the central part.

Table 3: List of components of hydrogen peroxide electrolyser, number of units, and materials.

Component	No. of units	Material
Reactor compartment	2	PVC
Anode	1	Ti/Pt
Cathode	1	Ti/C
Gasket	5	EPDM
M8 Screws	8	Stainless steel
M8 Washers	16	Stainless steel
M8 Nuts	8	Stainless steel

6 Publications and other dissemination activities

Montiel, Miguel. A.; Castro, M. Pilar; Granados-Fernández, R; Fernández Mena, I; Lobato, J; Sáez, C; Rodrigo, Manuel. A. Diseño y construcción de reactores para procesos de oxidación mediante impresión 3D. In: XLII Reunión del Grupo de Especializado de Electroquímica de la Real Sociedad Española de Química, Santander July (2022). Oral contribution.

7 Literature

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2 Krzeminsky et al., Journal of Membranne Science, 2020, 598, 117676.
3 Monteiro et al., Journal of Chemical Technology and Biotechnology, 2022, 97, 2024-2031.
4 Montiel et al., Current Opinion in Electrochemistry, 2022, 33, 100928.

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