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# Deliverable Report
# D2.7 Prototype 1st version

| | |
|---|---|
| Work package: | WP2 Treatment technology and prototype |
| Lead beneficiary: | UCLM |
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| 1 | 9.7.2024 | Draft |
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| 3 | 30.1.2025 | Dissemination level changed to public |

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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 1st September 2021. The project has a duration of 40 months and will end on 31st December 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 ozone gas 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 conditions. 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

This deliverable presents the most significant results from the construction of the initial version of the SERPIC treatment plant. The construction process involved receiving all units comprising the prototype plant at the facilities of the University of Castilla-La Mancha (UCLM) in Ciudad Real, Spain. This milestone enabled the completion of tasks 2.1 through 2.8. The previous stage, nanofiltration, is seamlessly integrated into the prototype, along with the two treatment routes. Route A includes the disinfection tank and the ozone gas electrogeneration unit, while Route B encompasses the membrane photoreactor and the persulfate electrogeneration unit. Before this stage, a preliminary prototype plant featuring a reverse osmosis membrane and a custom-designed photoreactor by UCLM was developed to study the hydrodynamics of the plant prior to the integration of all technologies.

# 3 Deliverable description as stated in the Project Description

This 1st version of the prototype set-up, developed in T2.1 – T2.8, will be reported, including plans for piping and control. A preliminary user manual with all expertise regarding mechanical design, sizing, operation, and maintenance procedures will be included.

# 4 Introduction

To complete the assembly and installation of the prototype plant, it was necessary to accomplish tasks T2.1 to T2.7, each focusing on the development of units comprising the multi-barrier technology of the SERPIC prototype plant. Task T2.1 *Developing processes* was finalised upon the development and delivery of the treatment units to the University of Castilla-La Mancha (UCLM) facilities, where the prototype plant is located. Tasks T2.2 *Design electrolyser cells* and T2.3 *Manufacture diamond electrodes* entailed designing the electrolysers for oxidant electrogeneration (ozone and persulfate) and delivering boron-doped diamond (BDD) electrodes for the persulfate cell.

In subsequent tasks (T2.4 *Build-up and test electrolyser*, T2.5 *Build-up and test photoreactor*, T2.6 *Build-up and test nanofiltration*, T2.7 *Build-up and test electrical and control*), the remaining treatment units were constructed and tested. This included the design of novel electrolysers using 3D printing for ozone and persulfate electrogeneration, the development of an innovative photoreactor to enhance the removal of CECs in Route B, and the adaptation of a nanofiltration membrane to an existing nanofiltration system to facilitate the initial separation of the two streams. Additionally, basic meters and controllers were assembled to enable automation of the plant. These tasks were essential for building and integrating all SERPIC treatment prototype plant units.

# 5 Results

## 5.1 Nanofiltration unit

The nanofiltration unit provided by UCLM is a compact domestic system using membranes approximately 1.8 inches in diameter. These nanofiltration membranes were sourced from Oltremare, a division of Mann+Hummel, which specializes in manufacturing custom elements in any desired size. The technical specifications are found in Annex 1 of Deliverable D2.5 *Nanofiltration unit*. Upon receipt, the module supplied by NIVA was integrated into the treatment train, replacing the reverse osmosis membrane tested during the initial prototype construction stage.

The secondary effluent of the Ciudad Real WWTP is stored in a tank and passes through a series of 10- and 5-µm filters as pretreatment to separate particles and avoid a rapid fouling and clogging of the NF membrane. Then, it passes through the NF membrane, separating the inlet stream and generating two treatment streams: permeate (Route A) (19 $L \cdot h^{-1}$) and concentrate (Route B) (21 $L \cdot h^{-1}$). Figure 1 shows a schematic of this treatment stage and Figure 2 illustrates the filtration unit and the applied membranes.

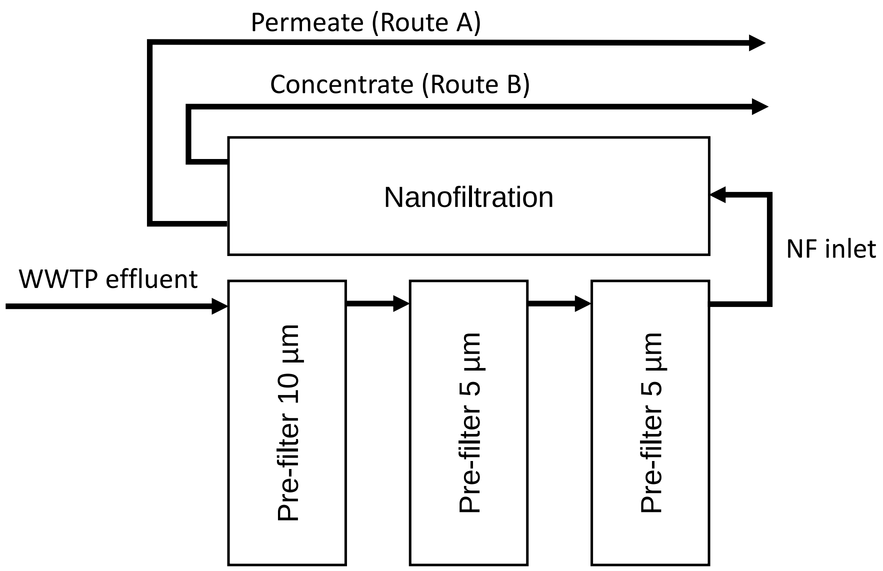



**Figure 1**: Schematic representation of the filtration unit.


**Figure 2**: a) Nanofiltration cartridge and b) Filtration unit installed in the SERPIC prototype plant.

### 5.2 Route A for irrigation of crops

Route A is designed to treat the permeate stream, which contains low concentrations of CECs. It is disinfected using electro-generated ozone gas in a cell with an innovative design and printed using 3D printing technology. Figure 3 shows the assembly diagram of Route A.

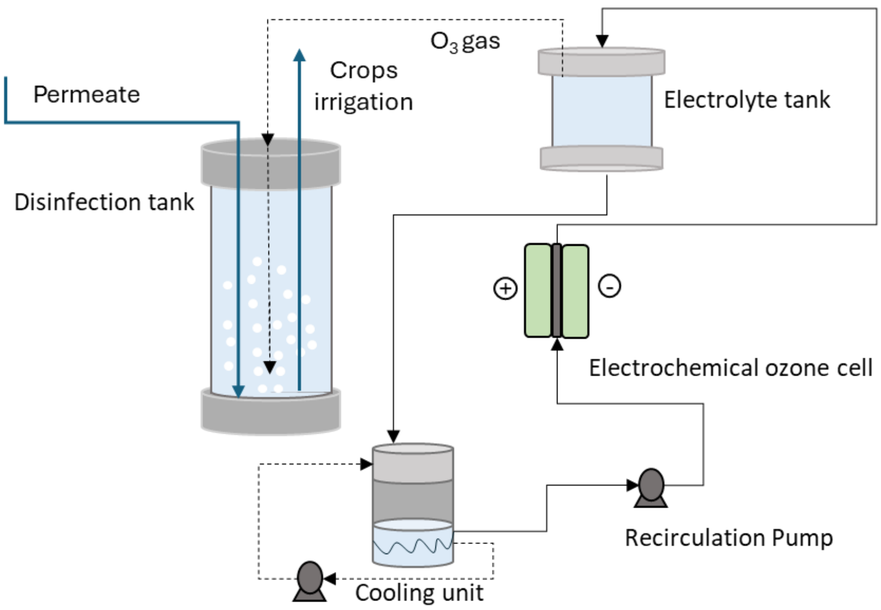



**Figure 3**: Route A treatment scheme.

It consists of a disinfection tank (Figure 4), supplied by UCLM, where bubble diffusers located in the bottom of the tank are used to inject the electrogenerated ozone gas stream (Figure 5), to allow the treatment of the permeate stream. The most important unit of Route A is the ozone electrogeneration unit, which comprises a customized proton-exchange membrane (PEM) cell incorporating a commercial membrane electrode assembly (MEA) within a 3D-printed reactor. The MEA consists of two DIACHEM® lattice BDD electrodes (CONDIAS GmbH, Germany), used as cathode and anode, assembled with a NAFION® proton exchange membrane. The cell has a total surface area of 73 cm² and dimensions of 132 mm × 77 mm × 27 mm. The cell design facilitates the evacuation of gases generated during electrolysis, preventing ozone decomposition reactions and ensuring optimal fluid dynamics. The liquid electrolyte used is 1 mM $HClO_4$. A cooling unit is essential to maintain ambient temperatures and to prevent system damage. Detailed information on this unit was included in section 4.3 of Deliverable D1.3 *Performance of bench-scale process units* of the project.


**Figure 4**: Disinfection tank with electrogenerated ozone gas fed into NF permeate.

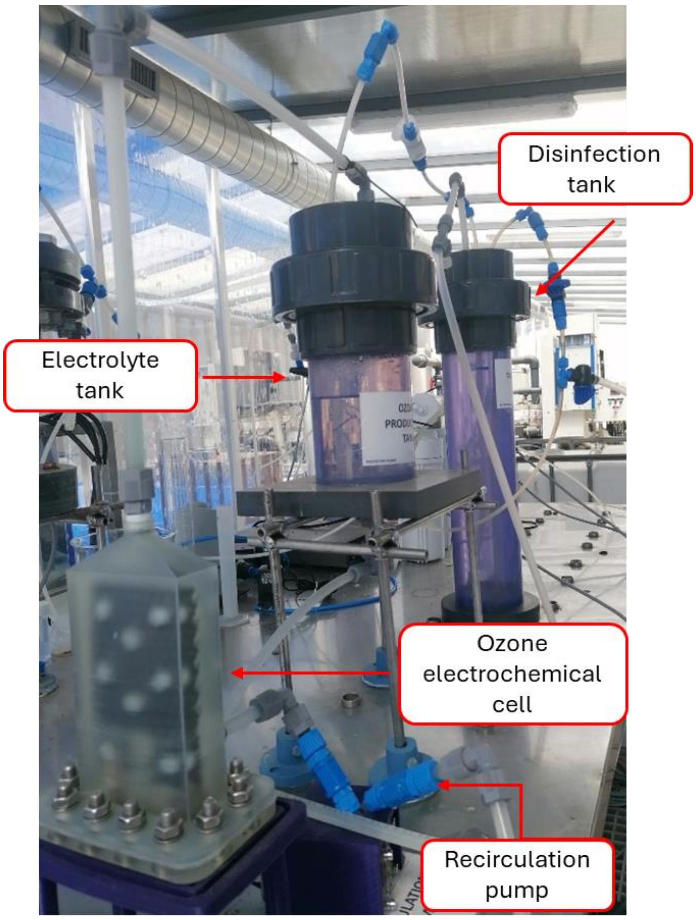



**Figure 5**: Ozone gas electrogeneration system.

Finally, the output stream of this treatment route is used to irrigate 8 $m^3$ of crops in experimental planting beds.

### 5.3 Route B for discharging into the aquatic system

The concentrate stream, which presents high concentrations of CECs and pathogens, is treated in Route B. This route is equipped with a novel photoreactor supplied by the University of Porto, where electrogenerated persulfate is introduced and activated by ultraviolet light to enhance CECs degradation. The persulfate is electrogenerated in an innovative electrochemical cell designed and supplied by UCLM and equipped with a BDD anode supplied by Fraunhofer IST. Stainless steel is used as the cathode. Further details are included in Deliverables 2.1 and 2.3. Figure 6 shows the assembly diagram of Route B.

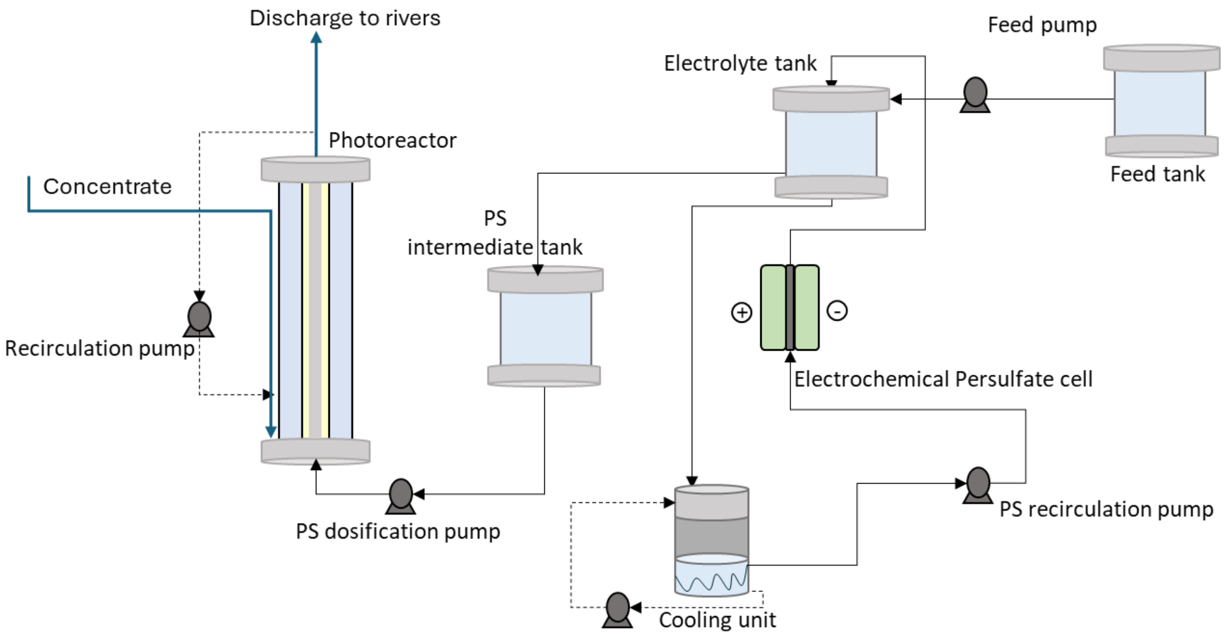



**Figure 6**: Route B treatment scheme.

In this treatment route, one of the most important units is the photoreactor. It is formed by the following components: (i) an external quartz tube; (ii) an internal porous ceramic tube to distribute the persulfate evenly (from Fraunhofer IKTS); (iii) low-pressure UVC lamps (Philips) located externally to the quartz tube; and (iv) reflective aluminium sheets (from Alanod GmbH & Co. KG) around the UVC lamps. Figure 7 shows a picture of the membrane photoreactor installed in SERPIC prototype and widely described in Deliverable 2.4 *Photoreactor unit*.

**Figure 7**: Membrane photoreactor.

Regarding the persulfate electrogeneration unit, it consists of several reservoir tanks, the novel electrochemical cell, and a cooling unit to maintain the temperature at the desired set point to minimize the thermal decomposition of electrogenerated oxidant. Figure 8 shows the persulfate electrogeneration unit installed in the prototype plant. More information in section 5.1 of Deliverable D2.3 *Electrolyser unit*.

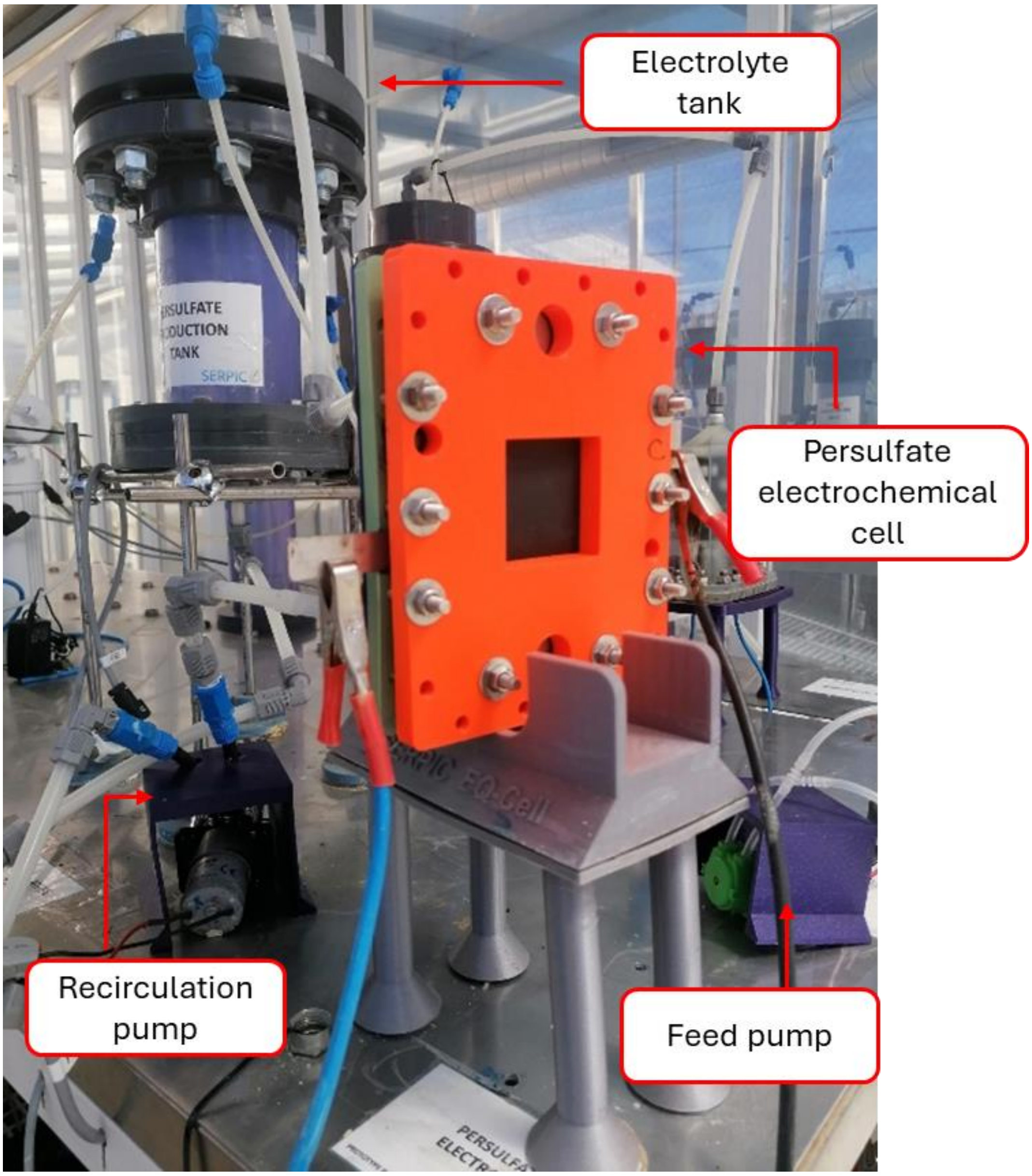



**Figure 8**: Persulfate electrogeneration unit.

In the prototype plant, the output stream of this treatment route was discharged into the sewer system. In real application, it would be discharged to the aquatic environment.

### 5.4 SERPIC Prototype plant

Once all the units described above were integrated, the SERPIC prototype plant was put to operation. The overall treatment sequence consists of a feeding tank, placed outdoor, filled with the Ciudad Real WWTP (secondary) effluent. This real water is sent to the nanofiltration unit which generates a permeate (Route A: disinfection) and a concentrate (Route B for the degradation of CECs and pathogens). These two treatment routes have been described previously. Figure 9 schematically shows the hydraulic connection.

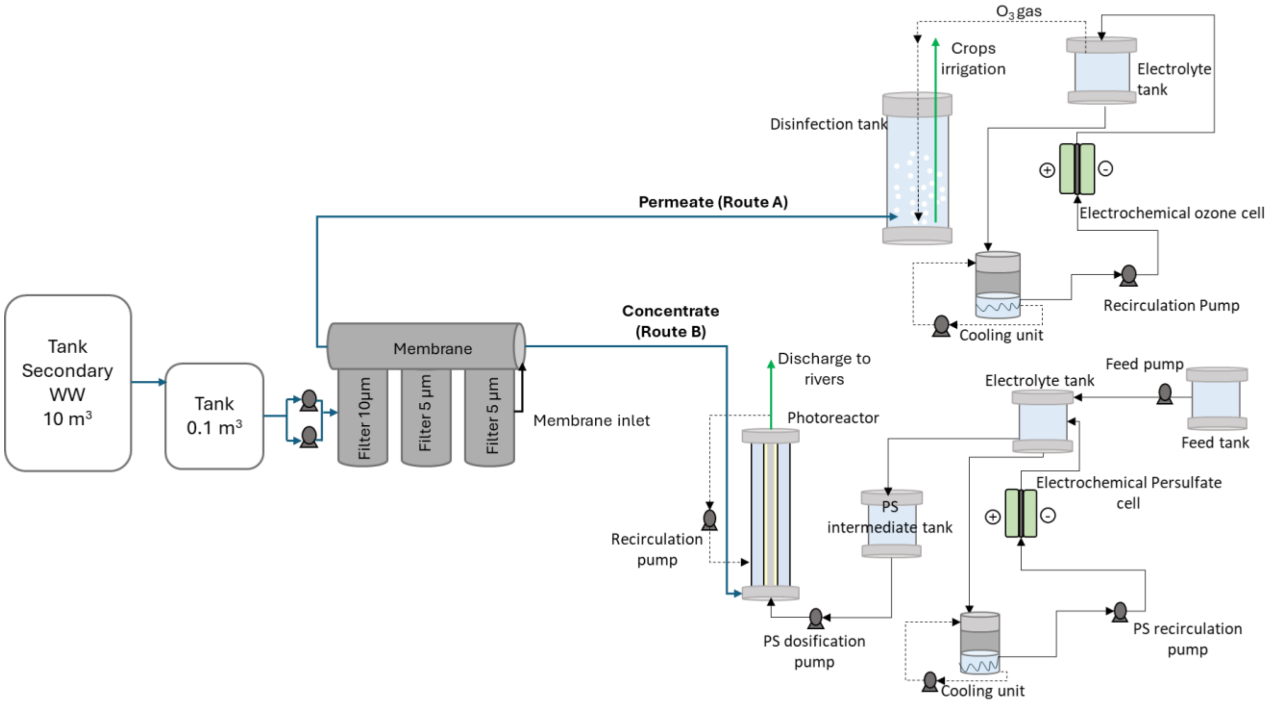



**Figure 9**: Hydraulic connection of the SERPIC prototype plant

The layout of the SERPIC prototype treatment plant is shown in Figure 10, where the arrangement of the individual units can be seen.

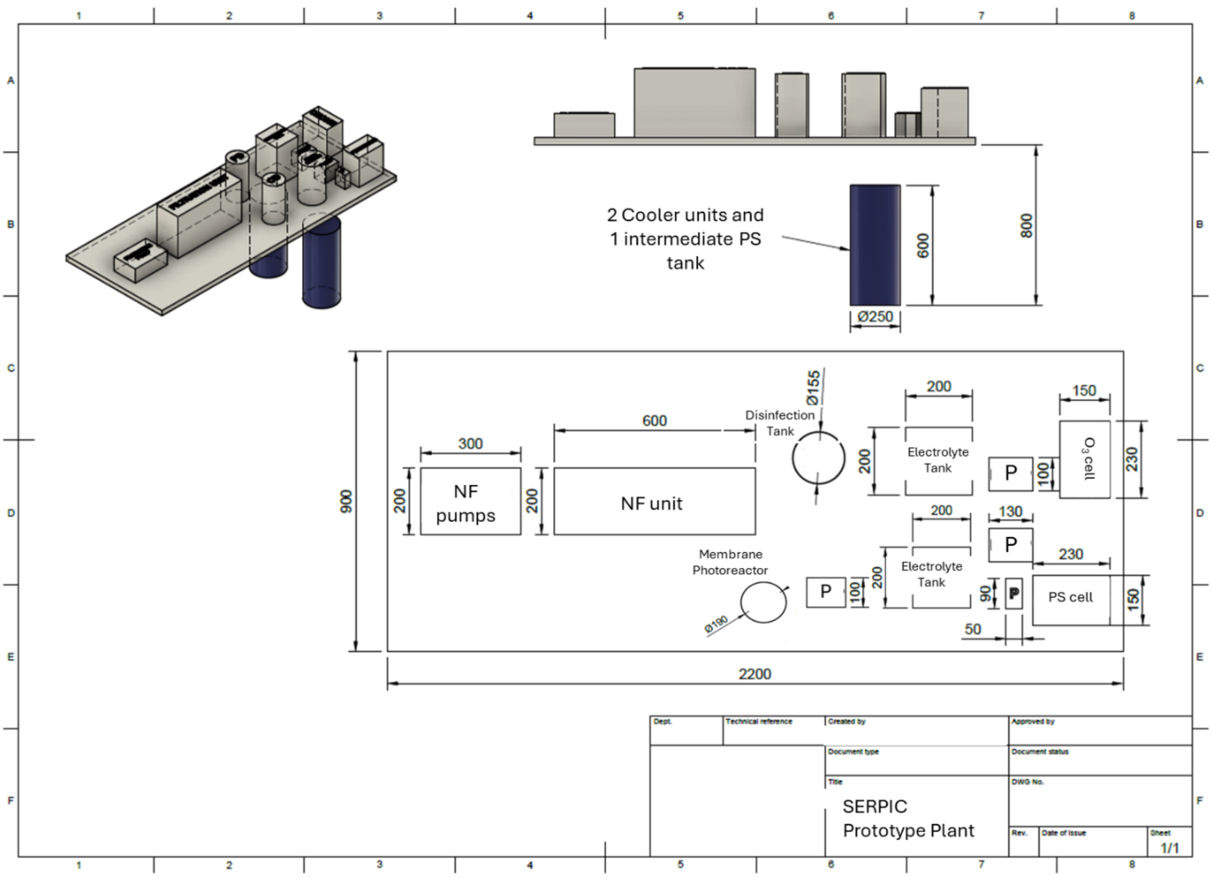
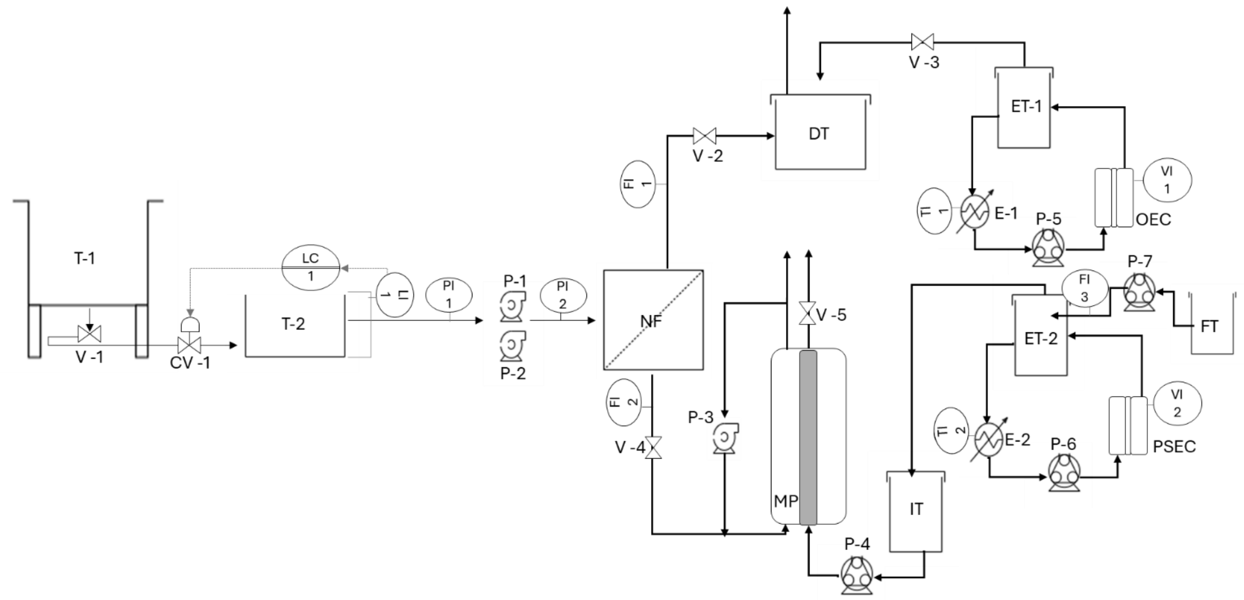



**Figure 10**: Location of the units integrated in the SERPIC prototype plant.

For the control and automation of the plant, various flow, pressure, temperature, level and other meters were installed. Figure 11 shows a Piping and Instrumentation Diagram (P&ID) of the SERPIC prototype plant with all valves and sensors installed. SolarSpring designed a program to control the SERPIC prototype plant. For the actual control, three *Siemens Logo PLCs! 8* were connected to each other in network mode. For remote monitoring, an *INSYS LTE* router was used, which is specially adapted to Logo! 8 and, after defining limit values, can report events and warnings in different ways. This prototype control system is very basic for the size of the plant, relying only on stopping the plant if any set point does not meet the determined value. The ruggedness of the treatment plant means that preliminary automation is carried out manually.




| P&ID Equipments | DESCRIPTION |
|---|---|
| T-1 | Secondary wastewater 10 $m^3$ tank |
| T-2 | Secondary wastewater 0.1 $m^3$ tank |
| P-1 | Nanofiltration pump |
| P-2 | Nanofiltration pump |
| P-3 | Recirculation pump |
| P-4 | Persulfate feed pump |
| P-5 | Recirculation pump |
| P-6 | Recirculation pump |
| P-7 | $H_2SO_4$ feed pump |
| NF | Nanofiltration unit |
| DT | Disinfection tank |
| ET-1 | Ozone Electrolyte tank |
| ET-2 | Persulfate Electrolyte tank |
| E-1 | Ozone cooler unit |
| E-2 | Persulfate cooler unit |
| OEC | Ozone electrochemical cell |
| PSEC | Persulfate electrochemical cell |
| IT | Persulfate Intermediate tank |
| MP | Membrane Photoreactor |

| P&ID elements | DESCRIPTION |
|---|---|
| CV-1 | Control Valve |
| V-1 | **Gate valve** |
| V-2 | Gate valve |
| V-3 | Gate valve |
| V-4 | Gate valve |
| V-5 | Gate valve |
| LI-1 | Level indicator |
| LC-1 | Level controller |
| PI-1 | Pressure Indicator |
| PI-2 | Pressure Indicator |
| FI-1 | Flow Indicator |
| FI-2 | Flow Indicator |
| FI-3 | Flow Indicator |
| TI-1 | Temperature Indicator |
| TI-2 | Temperature Indicator |
| VI-1 | Voltage Indicator |
| VI-2 | Voltage Indicator |

**Figure 11**: P&ID of the SERPIC prototype plant.

Figure 12 shows the plant fully built and commissioned for operation in a long-term cultivation stage, where the required analyses can be carried out (see deliverable report D1.4 *CECs in* *product water of v1 prototype*, D1.5 *CECs in soil* and D1.6 *CECs in plants*) as well as all necessary optimization and reengineering (see D1.7 *Performance of final prototype version* and D2.8 *Prototype final version*.

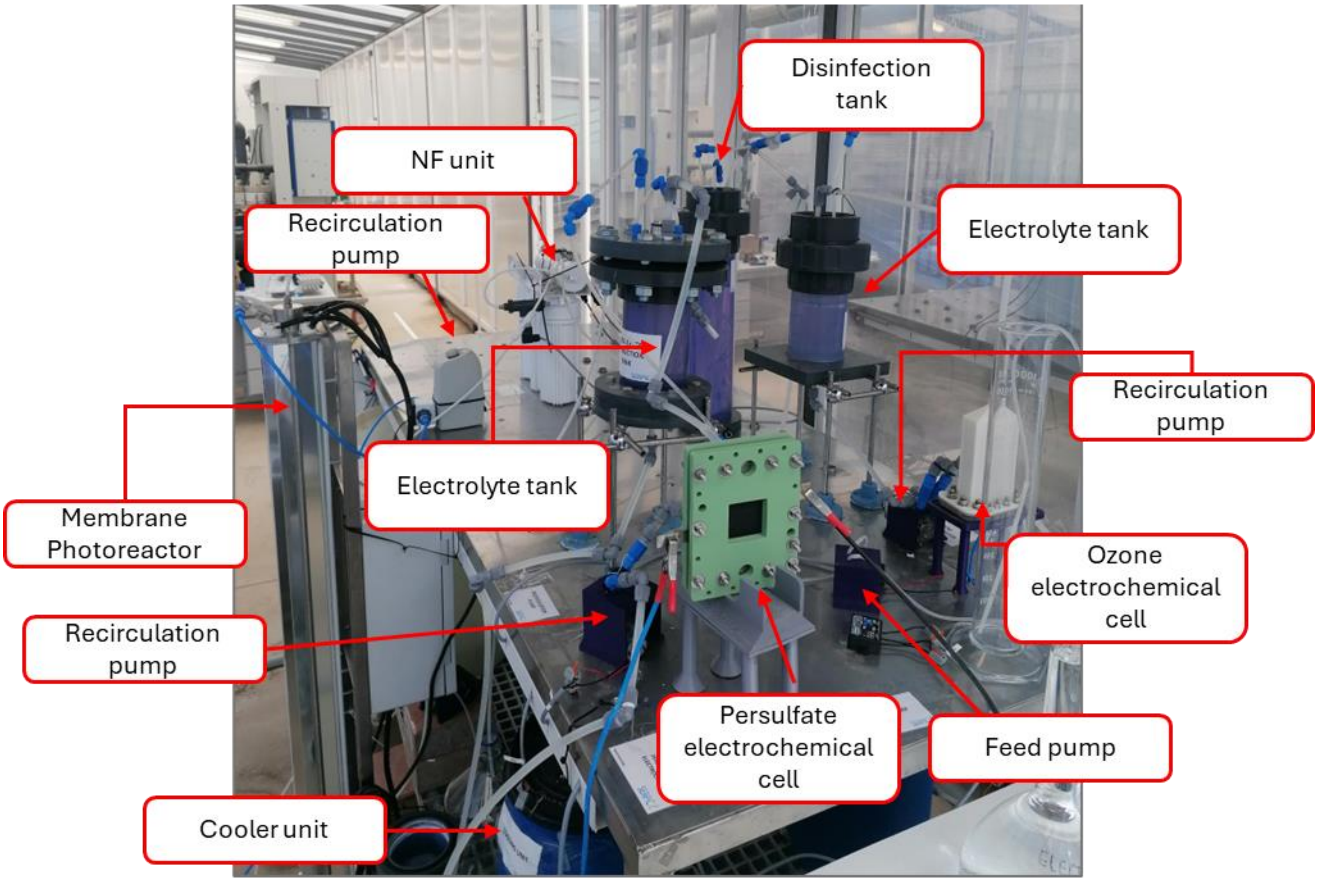



**Figure 11**: Prototype SERPIC plant assembled and commissioned for testing.

## 6 Publications and other dissemination activities

Mena, Ismael F.; Montiel, Miguel A.; Sáez, Cristina; Rodrigo, Manuel A. (**2023**): Improving performance of proton-exchange membrane (PEM) electro-ozonizers using 3D printing. In: *Chemical Engineering Journal* 464, S. 142688. DOI: 10.1016/j.cej.2023.142688.

Castro, M. Pilar; Montiel, Miguel A.; Mena, Ismael F.; Gäbler, Jan; King, Hunter; Sáez, Cristina; Rodrigo, Manuel A. (**2023**): Outstanding productions of peroxymonosulfuric acid combining tailored electrode coating and 3D printing. In: *Journal of Water Process Engineering* 53, S. 103902. DOI: 10.1016/j.jwpe.2023.103902.

Castro, M. P.; Mena, I. F.; Montiel, M. A.; Gäbler, J.; Schäfer, L.; Sáez, C.; Rodrigo, M. A. (**2023**): Optimization of the electrolytic production of Caro's acid. Towards industrial production using diamond electrodes. In: *Separation and Purification Technology* 320, S. 124118. DOI: 10.1016/j.seppur.2023.124118.

Castro, M. Pilar; Olivera, Agustina R. de; Mena, Ismael F.; Montiel, Miguel A.; Saez, Cristina; Rodrigo, Manuel A. (**2023**): Eliminación de CECs en aguas depuradas mediante persulfatos electrogenerados. XLIII RSEQ Electrochemistry Specialist Group Meeting. Ciudad Real, Spain, July 2023.

Castro, M. Pilar; Mena, Ismael F.; Montiel, Miguel A.; Saez, Cristina; Rodrigo, Manuel A. (**2023**): Disinfection and reduction of pharmaceutical CECs in real treated wastewater using electrogenerated persulfates. 74th Annual Meeting of the International Society of Electrochemistry. Lyon, France, Sept. 2023.

Castro, M. Pilar; Moratalla, Angela; Mena, Ismael F.; Montiel, Miguel A.; Saez, Cristina; Rodrigo, Manuel A. (**2023**): Design and implementation of an electrochemical regeneration plant of treated wastewater to use in irrigation of crops. Poster. Toledo, Spain (XI Jornadas Doctorales de la UCLM), Nov. 2023.

Santos, Carla S.; Ribeirhinho, S.; Montes, R.; Rodil, R.; Quintana, J. B.; Pastor, O. et al. (**2024**): Multi-Barrier Approach for the Treatment of Secondary Urban Wastewater Targeting CECs Removal and Disinfection: Integration of Membrane Nanofiltration with UVC/Persulfate Oxidation. Winter School on Contaminants of Emerging Concern (CECs) and Disinfection By-Products (DBPs): Occurrence, Impact and Elimination. Porto, Portugal, 25.-26.11.2024.

# 7 Annex 1: Zero prototype

Before integrating all the technologies currently part of the SERPIC prototype plant, a preliminary construction phase was carried out. This construction stage was based on previous knowledge acquired in other types of installations. The significant changes concerning the current prototype plant were to incorporate a reverse osmosis system instead of nanofiltration, as well as a homemade photoreactor, as can be seen in Figures 12 and 13, respectively. The other units, (ozone and persulfate electrolysers, as well as the various required tanks installed remained unchanged).

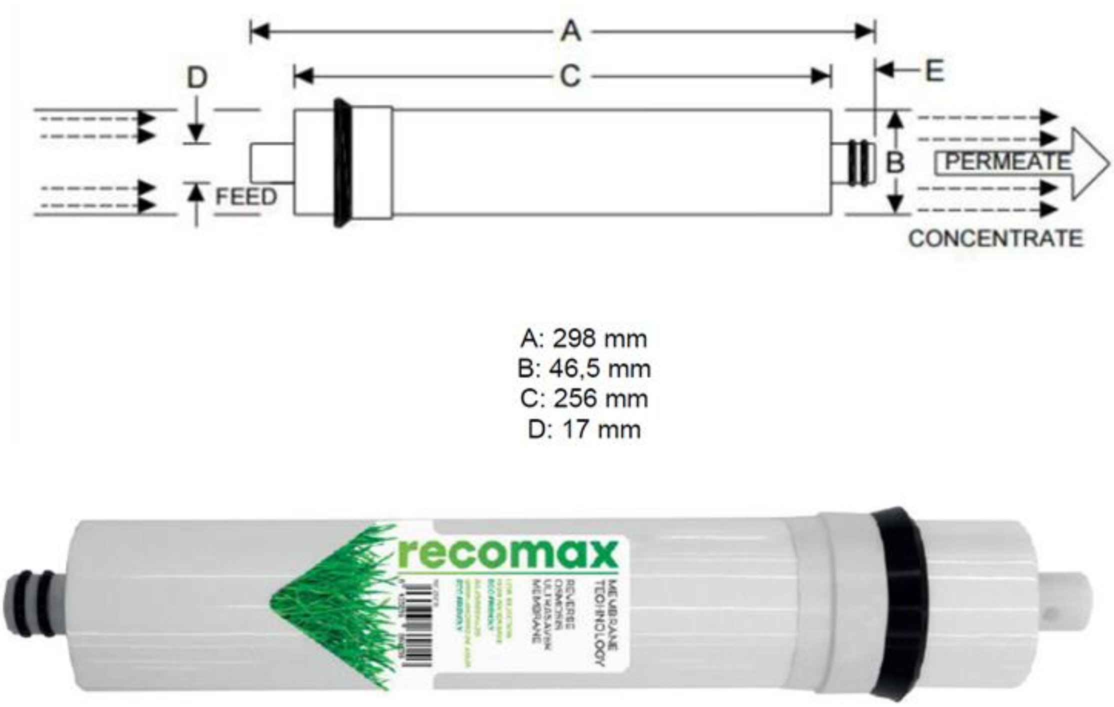



**Figure 12**: Reverse Osmosis membrane unit.

**Figure 13**: Photoreactor, designed by UCLM.

The knowledge gained from this previous stage of construction made it possible to avoid subsequent hydraulic problems as well as pressure problems in possible flows in the system. Figure 14 shows a picture of the pre-plant construction.

**Figure 13**: Prototype plant in the preliminary (Zero) stage of construction