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Deliverable Report
D2.8 Prototype final version

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 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 describes the main modifications that have been carried out during T2.10. In this case, the re-engineering stage was carried out simultaneously with tasks 2.8 and 2.9 due to delays with some treatment plant units. Therefore, this deliverable shows the final version of the treatment plant, as well as all its modifications and a user manual for its commissioning.

3 Deliverable description as stated in the Project Description

After the different reengineering modifications in T2.10, and following the further improvements during the operation during the field test period in T2.9, a modified plant will be set up, together with the engineering expertise about its construction, maintenance, and operation (included in a user manual). Scale up rules will also be faced in this deliverable.

4 Introduction

Once all the units that make up the prototype plant of SERPIC task T2.8 were introduced, testing was carried out during task T2.9. In this stage and the following T2.10, key operating problems were resolved, such as the change of process units, as well as treatment improvements to optimize the plant and increase its efficiency in the degradation and disinfection of effluents, until reaching the final version of the SERPIC prototype treatment plant. The reengineering and optimization tasks are key in the preparation of the final version as well as an easily understandable operating manual for any plant user.

5 Results

5.1 Modifications to the SERPIC treatment plant – Re-engineering

As explained in section 2 of this deliverable, due to delays in the arrival of certain processing units of the treatment plant, the reengineering was carried out at the same time as the construction of the plant and its testing. The following points show the improvements and/or changes in the units that were made in the initial plant to obtain the final version of the SERPIC prototype treatment plant. All the changes were made gradually and that means that the re-engineering of the plant was made during the first prototype of the plant. Because of that, most of the results of this report are defined in the previous Deliverable D2.7 *Prototype 1st version*.

5.1.1 Nanofiltration system

In the prototype version of the SERPIC treatment plant, a reverse osmosis (RO) system was installed as shown in Figure 1. Subsequently, as indicated in the project specifications, a nanofiltration membrane was installed, as shown in Figure 2.

Figure 1: a) Reverse Osmosis cartridge and b) Filtration unit installed in the SERPIC prototype plant.

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

Table 1 shows some key parameters of both units. In the case of nanofiltration, there should also be no *E.coli* in the permeate stream as the size of *E.coli* is larger than the nominal pore size of the NF membrane. The presence of *E.coli* indicates that the performance of the membrane may be compromised and not optimal. A lot of troubleshooting was implemented including additional analyses, visual inspection of the membrane, testing new membrane, reaching out to supplier, and testing by the supplier. Later, the company informed that there was a problem with the assembly of the membrane and possible leaks might have occurred. The problem of elevated *E.coli* level in the permeate/irrigation water was subsequently solved with disinfection of stream A using electrogenerated ozone.

Table 1: Some parameters of reverse osmosis and nanofiltration units.

Filtration Units	**Flow rate Permeate $L \cdot h^{-1}$**	**Flow rate Concentrate $L \cdot h^{-1}$**	**Permeate Conductivity $\mu S \cdot cm^{-1}$**	**Concentrate Conductivity $\mu S \cdot cm^{-1}$**	***E. coli* CFU $100 ml^{-1}$ (Permeate)**
Reverse Osmosis	13.4	21.2	53	1841	0
Nanofiltration	19	21	840	1633	28

Due to the initial problem of algae produced in the wastewater stored for treatment, a filter was installed at the outlet of the tank that feeds the treatment plant as well as another outlet for use in irrigating the crop automatically, as shown in Figure 3.

Figure 3: Filter installed at the outlet of the feed tank to the SERPIC treatment plant.

5.1.2 Cooling units

Oxidant electrogeneration units generate heat during operation, which causes the process to lose efficiency. For this reason, the use of continuous flow immersion chillers was initially proposed to maintain the temperature of the systems. However, these devices had a high energy consumption. Therefore, two alternative cooling systems were designed during the operation of the plant for each oxidant electrogeneration unit (ozone and persulfate). These systems were based on operating a cooling tower, which functions as large heat exchangers through evaporative cooling. Figure 4 shows the cooling towers used in the SERPIC treatment plant and a diagram of their location in the plant.

Its operation consists of continuously repeating a cooling cycle. To do this, the tank in Figure 4 a) is filled with a certain volume of water; within this water, the pipe through which the electrolyte to be cooled circulates, is placed in contact. The cooling system consists of the heated water being recirculated using a low-consumption pump through nozzles that spray small drops, increasing the surface of the water and allowing heat loss through greater evaporation. The purpose of the fan at the top of the tank is to draw air in from the bottom of the tower and move it up and out in the opposite direction to the hot water. The air will carry heat by evaporating water from the cooling tower into the atmosphere.

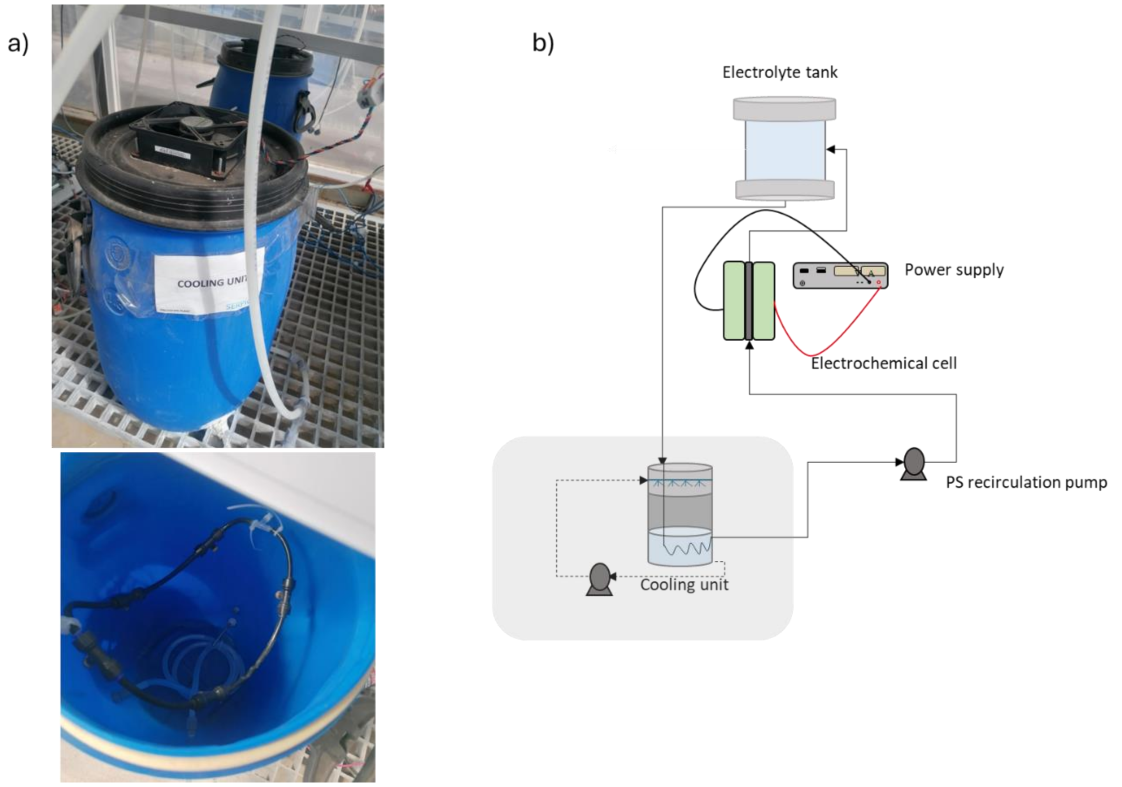


Figure 4: a) Cooling unit installed at the SERPIC prototype plant. b) Location diagram of the cooling unit.

5.1.3 Route A. Disinfection and Irrigation of Crops

Treatment route A consists of nanofiltration plus disinfecting the permeate stream that contains low concentrations of CECs and pathogens. The disinfection of this stream consists of injecting ozone gas, electrogenerated in an electrochemical reactor printed with 3D technology, into the disinfection tank and subsequent use for irrigation of agricultural crops.

During the re-engineering of this part of the treatment, the following improvements have been developed and implemented.

a) Ozone gas diffuser

For the correct distribution of ozone gas into the disinfection tank, various diffusers were tested. Figure 5 shows the diffusers tested, as well as the one chosen.

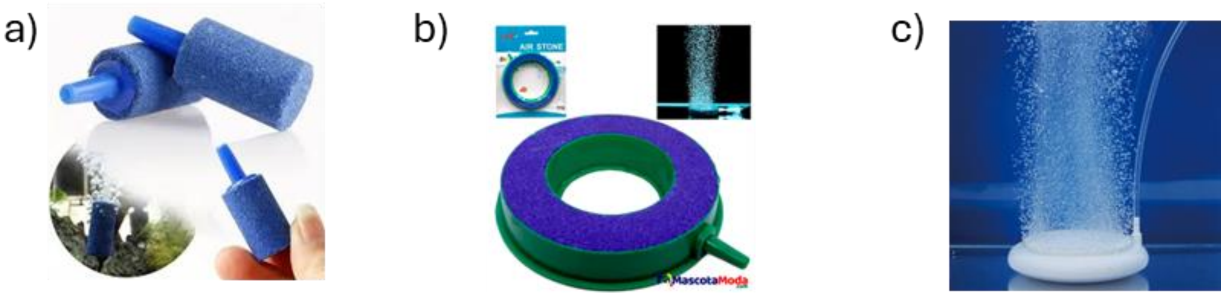


Figure 5: Types of ozone gas diffusers tested.

The ozone gas diffuser finally installed is shown in the schematic in Figure 6, where its location in the SERPIC treatment plant can be observed. This diffuser allows for a homogeneous distribution of bubbles across the entire surface of the disinfection tank, helping to maximize the transfer between the gas and the liquid to be treated.

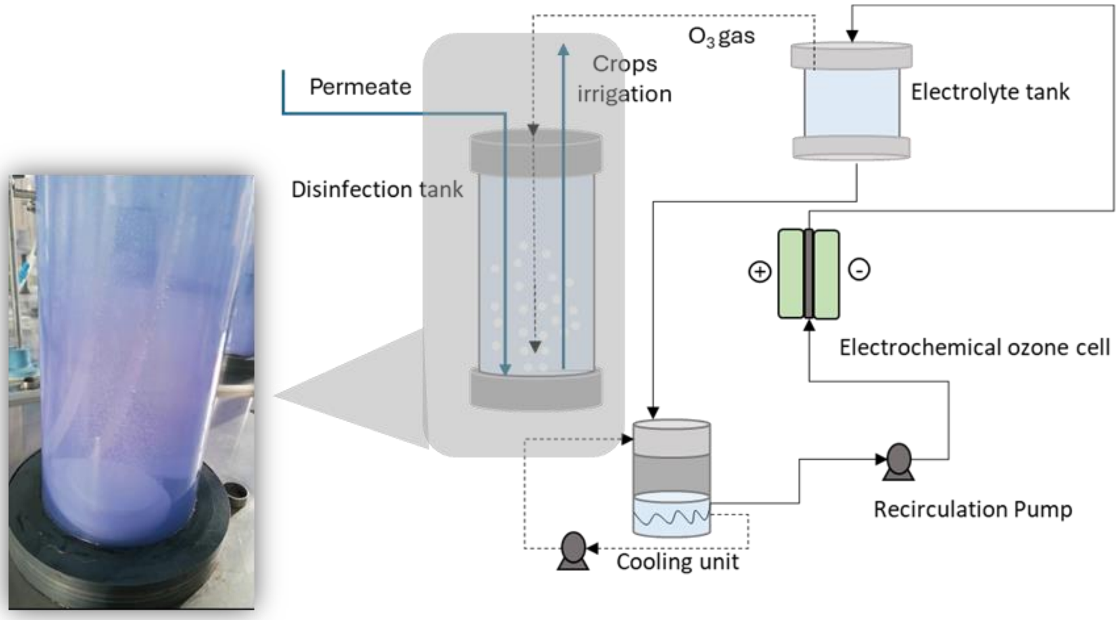


Figure 6: Schematic diagram of treatment route A and disinfection tank diffusor installed.

b) Crop irrigation

As mentioned above, the destination of route A is to irrigate crops, in our case potatoes and carrots during the field test. For this purpose, during tasks T2.8, T2.9, and T2.10, several long-term cultivation tests were carried out, as well as improvements in the irrigation methods.

First, a long-term test of the cultivation of potatoes and carrots in small pots of 50 cm x 50 cm x 70 cm dimensions was carried out. The characteristics of the cultivation soil described in the project were considered: a layer of gravel at the bottom, followed by a layer of sand and a silty loam and vegetable soil coverage.

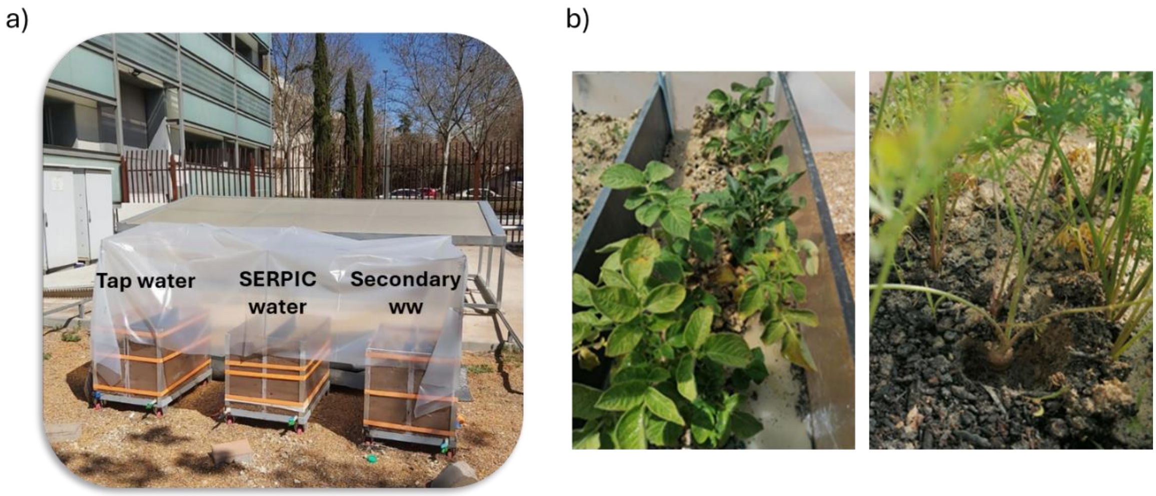


Figure 7: a) Small pots for potato and carrot cultivation, and b) Crop growth.

During the experimentation of this first long-term field test, three types of water were supplied manually: (i) tap water, (ii) secondary effluent from Ciudad Real WWTP, and (iii) secondary effluent from Ciudad Real WWTP treated by SERPIC. This agricultural cultivation field test can be observed in Figure 7.

A second long-term cultivation test was carried out afterwards. In this case, the potatoes and carrots were planted in 48 m^3 of soil in their corresponding layers, separated into 6 pots of 8 m^3 each, to be watered in the same way as the previous test with the three types of water, as shown Figure 8.

Figure 8: Long-term crop field test in a 48 m^3 pot.

In this case, improvements were introduced in terms of irrigation. Irrigation dispersers were installed so that irrigation would be more homogeneous across the entire planted surface and thus minimize the evaporation phenomenon, as can be seen in Figure 8 a). This irrigation went from being manual to automatic by installing solar automatic irrigation pumps such as those shown in Figure 9.

Figure 9: Solar pump for irrigation of crops.

5.1.4 Route B. Degradation

In treatment route B, the nanofiltration concentrate stream with high concentrations of CECs and pathogens is oxidized by electrogenerated persulfate and activated in a photoreactor. In the prototype version of the SERPIC treatment plant, a photoreactor homemade by UCLM was installed as shown in Figure 10. Subsequently, a photoreactor from UP with the appropriate flux and oxidant distribution characteristics was then installed, redesigned, and tested, as shown in Figure 11.

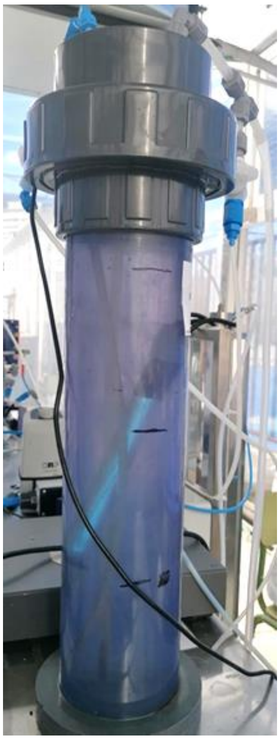


Figure 10: Homemade photoreactor of UCLM.

Figure 11: Final photoreactor of UP.

During the installation of the photoreactor and various tests, it was observed that the inlet pressure increased, when the oxidant was introduced into the porous ceramic tube of the photoreactor, and the dosing was not correct. Therefore, after several stages of re-engineering, an intermediate persulphate storage tank and a dosing pump were added. Moreover, the fluid inside the photoreactor must have a helical trajectory to ensure a good distribution of the oxidant and the concentrate to be treated. Therefore, a recirculation pump was installed to increase the turbulence inside the photoreactor. All these improvements are shown in the diagram in Figure 12.

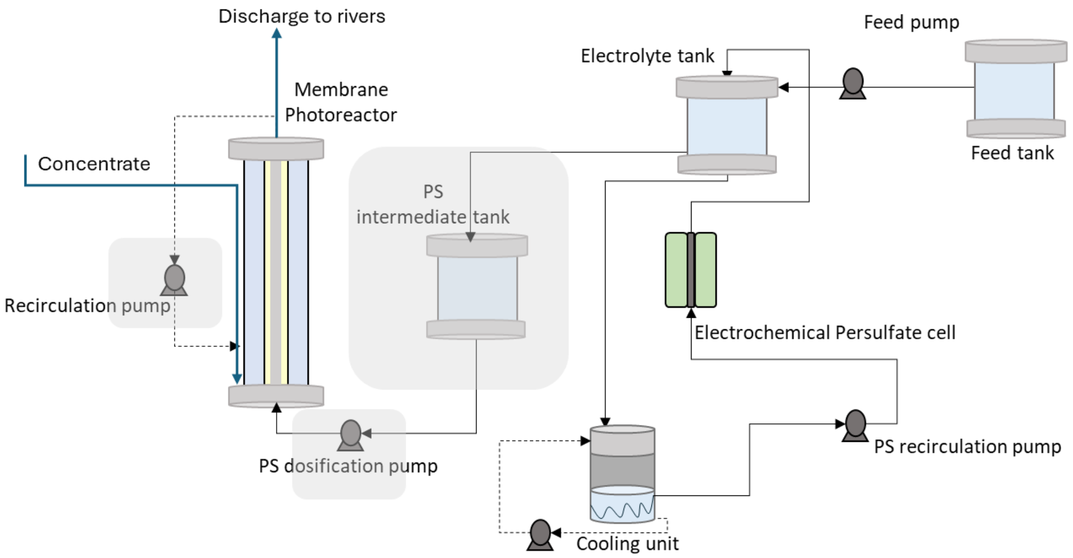
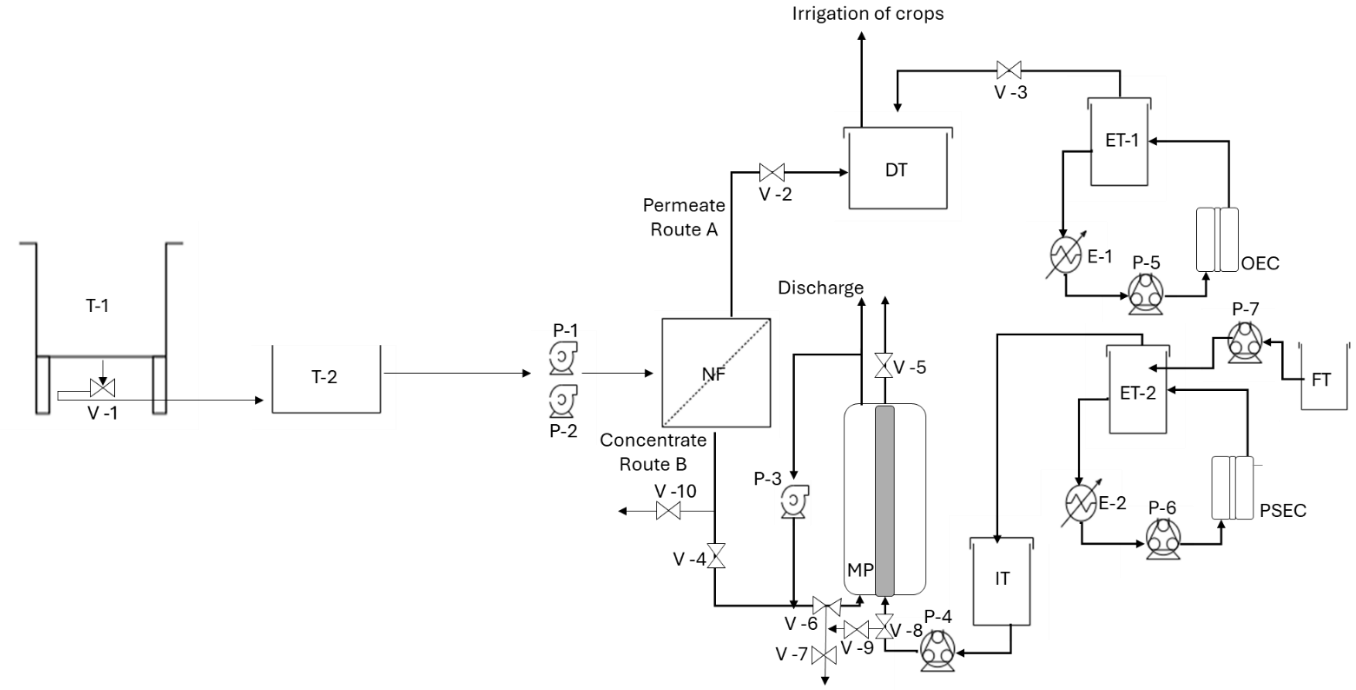


Figure 12: Proposed improvements to Route B

5.2 SERPIC prototype final version

The first version of the prototype plant has been tested and all the re-engineering improvements described above have been incorporated. The schematic of the final version of the SERPIC prototype plant is shown in Figure 13.



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

Valves	DESCRIPTION
V-1	Gate valve. Secondary WW Tank
V-2	Gate valve. Permeate
V-3	Gate valve. Ozone gas
V-4	Gate valve. Concentrate
V-5	Gate valve. Membrane outlet
V-6	Gate valve. Concentrate cleaning
V-7	Gate valve. Discharge
V-8	Gate valve. Membrane inlet
V-9	Gate valve. Discharge
V-10	Gate valve. Discharge

Figure 13: Piping and Instrumentation Diagram (P&ID) of the SERPIC prototype plant final version.

Considering the diagram in Figure 13, the user manual for starting up and operating the SERPIC prototype plant in its latest version is as follows.

5.2.1 User Manual

1. Preliminary stage before plant start-up

Before the plant operates correctly, it is necessary to carry out some preliminary steps: activation of the nanofiltration membrane as well as the continuous production of the two oxidants ozone and persulfate and the preparation of the photoreactor.

Nanofiltration system

First, the pre-filters of the nanofiltration system must be installed. Afterwards, the membrane used in the nanofiltration system must be soaked and pre-conditioned for 24 hours with tap water and 24 hours with the wastewater to be treated before use. During the pre-conditioning, the water is filtered through the nanofiltration membrane for 24 hours.

Valve V-1 is opened, and tank T-2 is filled. Once full, valve V-1 is closed again, pumps P-1 and P-2 are started, and valves V-2 and V-10 are opened and V-4 closed. The permeate stream will fill the disinfection tank DT and the concentrate stream is discarded by V-10 until the photoreactor is started.

Electrolysers

According to the operating conditions studied at the laboratory scale, the electrolysers are started up.

Treatment route B: first, the FT and ET-2 tanks are filled with 0.1 M sulfuric acid. The E-2 exchanger and the P-6 recirculation pump are started up. Then, the power supply of the persulfate electrolyser PSEC and the P-7 feed pump are started simultaneously. Depending on the electrolyte concentration conditions and the feed flow rate, a steady state of persulfate production will be reached after 2 hours of operation. From here, the persulfate is stored in the IT tank, ready to be activated in the photoreactor.

On the other hand, to start the disinfection of the permeate of route A, it is necessary to first fill the ET-1 with 1 mM of perchloric acid, leaving an air chamber inside. Subsequently, the recirculation pump P-5 and the heat exchanger E-1 are started up. Then, the power supply of the OEC ozone electrolyser is switched on. After a few minutes, the valve V-3 is opened, which will take the electrogenerated ozone gas to the disinfection tank DT. It will be possible to observe if ozone gas is coming out through the diffuser. The stabilization time of the ozone gas is approximately 45 minutes.

Photoreactor

Once the persulfate is stored in a stable concentration in the IT tank, the porous ceramic tube of the photoreactor MP is filled. To do this, it is necessary to calculate the flow rate of P-4 based on the concentration of persulfate that we want to introduce in our treatment.

To fill the porous ceramic tube, P-4 must be working, V-5 and V-8 are opened, and V-9 is closed. When persulfate starts to come out through the stream where the V-5 valve is located, it is closed. Leaving everything running for a few seconds so that the persulfate permeates the pores of the ceramic tube. After these seconds, pump P-4 is stopped and V-8 is closed. Then, the surface of the porous ceramic tube must be cleaned. At this point, V-10 is closed, and V-4 and V-6 are opened so that the concentrated stream fills the photoreactor, dragging along the remains of persulfate. Once the surface has been cleaned, V-10 is opened again, and V-4 is closed. And to empty and clean it, V-7 and V-6 are opened. Once the porous ceramic tube is filled and the photoreactor is clean, the plant begins to operate.

2. Operation stage

Once all the preliminary stages of plant preparation have been completed, stable oxidant production and photoreactor are ready for use, the operations begin. To do this, it is necessary that the oxidants have reached a steady state and do not stop being produced. For this purpose, V-3 must be open, E-1, P-5, and OEC in operation, as well as FT, always be full of electrolyte, P-7, P-6, E-2, and PSEC in operation, and IT with a sufficient volume of stable persulfate for operation.

If all the above is fulfilled, the plant can operate considering that tank T-2 (through valve V-1) must always be full, P1 and P2 working as well as V-2, V-4, and V-6 open so that the photoreactor is filled. Once the photoreactor is full, P-3 is put into operation and V-8 is opened simultaneously with pump P-4. The rest of the valves that are not mentioned must remain closed during operation.

As an example, Figure 14 shows a real image of the final version of the SERPIC prototype plant, where some of the most important units and equipment can be observed.

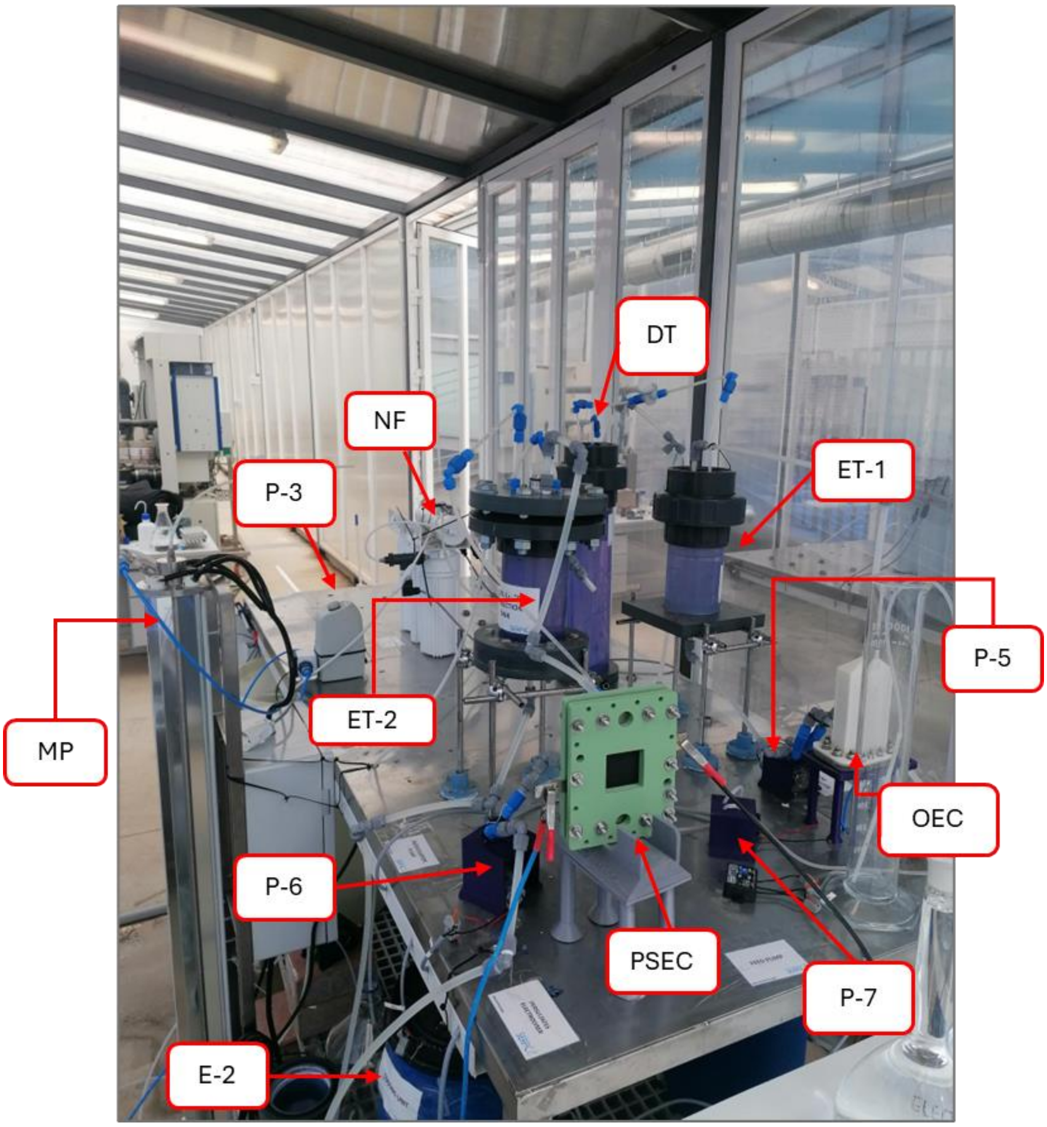


Figure 14: Final prototype of the SERPIC treatment plant assembled and put into operation.

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, p. 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, p. 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, p. 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, 11/25/2024.

Castro, M. Pilar; Mena, Ismael F.; Montiel, Miguel A.; Sáez, Cristina; Rodrigo, Manuel A. (2024): Scale-up of the electrochemical persulfate synthesis process. Oral presentation at 75th Annual Meeting of the International Society of Electrochemistry, Montréal, Canada, August 2024.

