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Deliverable Report
D1.3 Performance of bench-scale process units

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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 next 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 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

The report contains the description of the different units tested at lab scale in order to optimize the operational conditions in the prototype treatment plant, as well as the results achieved during the experimental investigations carried out so far. The tested technologies include: a nanofiltration unit, a reverse osmosis unit, a disinfection unit (ozonation) and a photoreactor unit. They were investigated in the labs at NIVA, UCLM, and UP.

3 Deliverable description as stated in the Project Description

This deliverable reports the analytical results achieved in **T1.2** by the bench-scale process modules in terms of the main regulated parameters and the target CECs.

4 Experimental setup

As reported in the Project description, the Process chain under investigation includes different steps: a nanofiltration unit, a disinfection tank and a photoreactor. They are enclosed by red dotted lines in Figure 1. The aim is to remove the six target CECs that were selected in the project, see Deliverable report D1.1.

In the first part of the project, these technologies were investigated at a bench scale in the labs of NIVA, UCLM, and FEUP. In addition, at UCLM, a reverse osmosis unit was tested as an alternative to the nanofiltration unit, see Figure 1.

A brief description of the investigated units used for the bench scale tests is reported here.

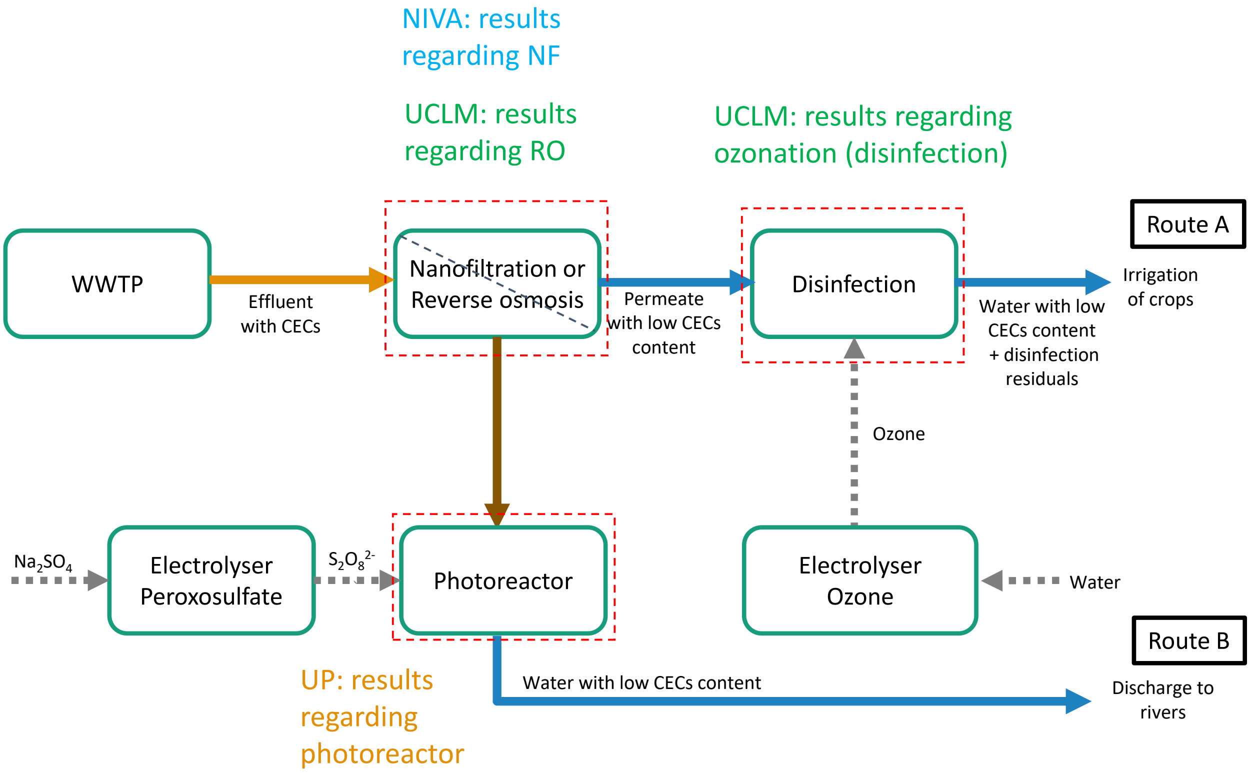

Figure 1. Process chain with the technologies tested at a bench scale in the different laboratories of the Consortium: Nanofiltration at NIVA (Norway), reverse osmosis at UCLM (Spain), Disinfection by ozone at UCLM (Spain), oxidation in a photoreactor at UP (Portugal).

4.1 Nanofiltration unit setup

A bench-scale membrane testing apparatus, operated in cross-flow mode and according to an internal standard operating procedure, was used to evaluate NF membranes (Figure 2). A detailed description of the procedure can be found in Krzeminski et al. (2020).

Figure 2. Membrane filtration unit (left) and membrane test cells used for nanofiltration investigations at NIVA at a bench scale: right top: cell for flat membranes, right bottom: cell for hollow fibre membranes (Photos: P. Krzeminski).

Based on the market assessment towards identification of the main NF membrane suppliers and the review of the recent literature on CEC and ARGs removal with NF, the suitable NF membranes for lab testing were identified. Overall, 10 commercially available NF membranes were chosen to cover a wide spectrum of nanofiltration with a broad range of molecular weight cut-off (MWCO) and membrane material. The effective membrane area used was 99.4 cm^2 for flat sheet membranes and 500 or 800 cm^2 for hollow fibre membranes. All experiments were carried out at constant feed pressure of 8 bar for flat sheet membranes and 4 bar for hollow fibre membranes. Experiments were carried out in recirculation mode, i.e. both concentrate and permeate were returned to the feed tank.

4.2 Reverse osmosis unit setup

The reverse osmosis equipment was proposed as an alternative to the nanofiltration unit present in the prototype plant (Figure 1). Figure 3 shows the commercial reverse osmosis equipment consisting of 3 filters of different pore sizes (2 of 10 μm and one of 5 μm) and Figure 4 shows a schematics and a picture of the commercial reverse osmosis membrane used.

Figure 3. Commercial reverse osmosis equipment investigated at UCLM (Spain) as an alternative to nanofiltration unit.

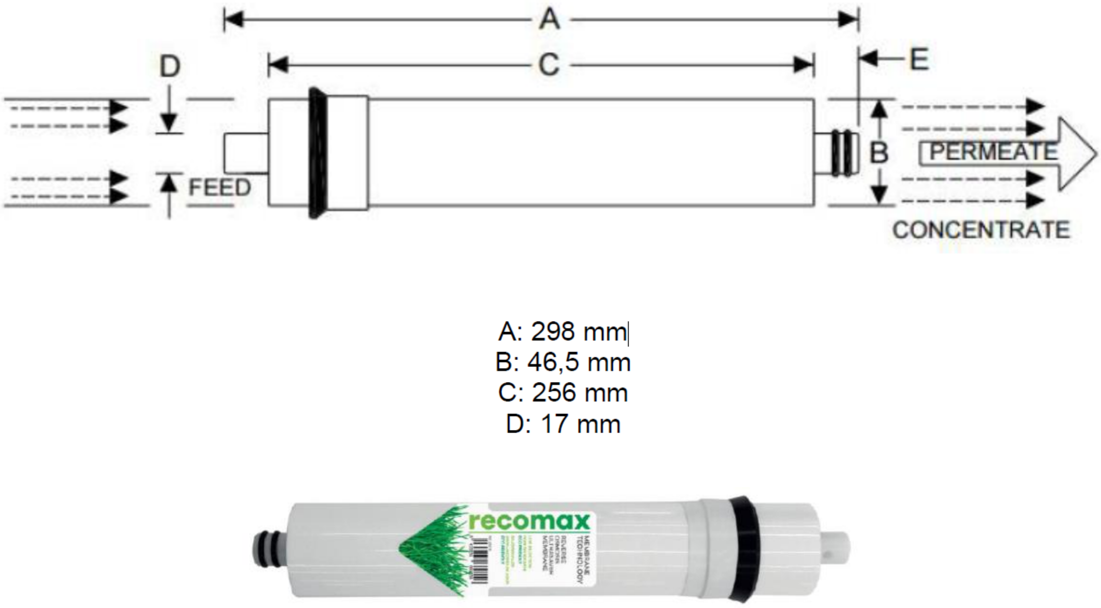

Figure 4. Commercial reverse osmosis membrane investigated at a bench scale and installed in the prototype plant.

4.3 Disinfection unit (ozonation) setup

The disinfection (ozonation) unit consists of a tailored cell in which a membrane electrode assembly (MEA) (from CONDIAS GmbH, Germany) was inserted into a casing mechanically designed and manufactured using 3D printing.

The MEA consists of two DIACHEM® lattice boron-doped diamond (BDD) electrodes, used as cathode and anode, which are assembled with a NAFION® proton exchange membrane (PEM), with a total surface area of 73 cm^2 and a cell dimension of 132 × 77 × 27 mm. The electrolyte and the current density used were 1 mM $HClO_4$ and 100 $mAcm^{-2}$ respectively. A scheme and photos of the cell is shown in Figure 5.

Figure 5. Ozone electrochemical cell investigated at UCLM at a bench scale.

Figure 6 shows a schematic of the disinfection unit where the reverse osmosis permeate stream was fed to the disinfection tank. The electrochemically generated ozone gas was added into the disinfection tank and the ozonated effluent will be used for irrigation of the crops. As we use clean water to produce ozone in gaseous phase, we thus avoid the presence of compounds that can be scavengers of the ozone or can reduce the ozone production.

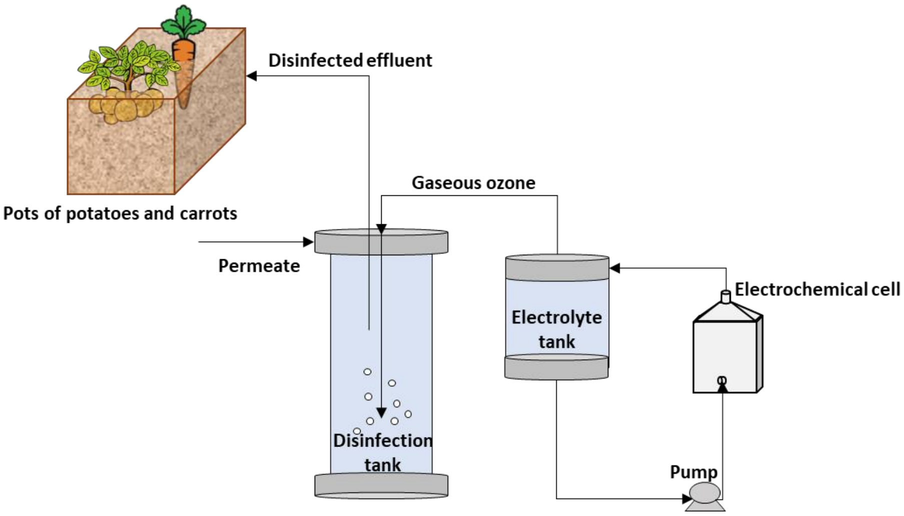

Figure 6. Schematics of the disinfection unit tested at UCLM at a bench scale.

4.4 Photoreactor setup

All photo-oxidation tests were carried out in a bench-scale membrane photoreactor (Figure 7) comprising an inner tubular ceramic membrane (γ-Al_2O_3 membrane from Inopor®, pore size = 10 nm; porosity = 30-55%; $Ø_{external}$ = 20.3 mm; $Ø_{internal}$ = 15.5 mm; total length = 200 mm; illuminated length = 174 mm) and an outer quartz tube ($Ø_{external}$ = 42 mm; $Ø_{internal}$ = 38 mm; total length = 200 mm; illuminated length = 174 mm).

In this system, the oxidant – in this case, persulfate (PS) - is continuously permeated through the membrane pores as a smart-dosing strategy that allows a more homogeneous axial and radial distribution of the oxidant molecules in the annular reaction zone (ARZ) and a constant oxidant gradient along the entire reactor length.

Four UVC lamps (HNS 11W G5) are placed equidistantly outside the quartz tube and a square aluminum foil reflector has been applied to surround the lamps (photonic flux of 2.3 ± 0.5 W, determined by ferrioxalate actinometry).

The influent to be treated – in this case, reverse osmosis (RO) or nanofiltration (NF) concentrate - is continuously pumped through a gear pump (Ismatec BVP-Z) from a cylindrical glass vessel to the reactor and is partially recirculated back using another gear pump (Ismatec BVP-Z). A peristaltic pump (Shenchen LabK1) is used for the dosage of the oxidant solution to the ARZ of the photoreactor.

The inlet and outlet of the fluid are located tangentially to the internal wall of the quartz tube and perpendicular to the fluid movement, which promotes a helical movement of the fluid around the membrane.

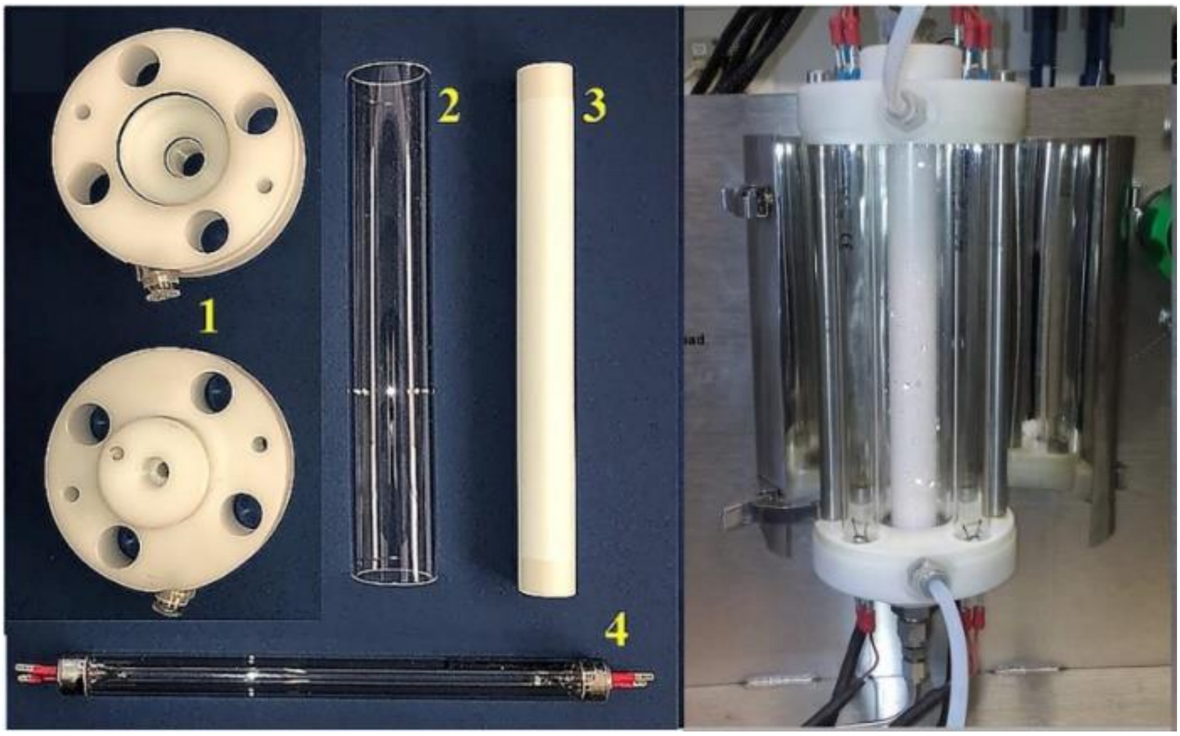

Figure 7: Photographs of the bench-scale membrane photoreactor: components (left) and assembled (right).

5 Results

5.1 Nanofiltration unit (NIVA)

The nanofiltration tests were done using the effluent of the secondary wastewater treatment plant in Oslo, Norway. Each time, a 30L sample was collected and immediately transported to the laboratory where experiments and analyses started as soon as possible to keep the characteristics of the samples relatively unchanged. The effluent samples were used as the influent in the membrane filtration experiments. From each membrane test, samples of influent, permeate and concentrate were collected for further water quality (nutrients, chemical and bacterial) analyses.

10 commercially available NF membranes were investigated covering a wide spectrum of nanofiltration with a broad range of MWCO and membrane material. The specifications of the individual membranes are listed in Table 1.

Table 1. Description of evaluated membranes.

Producer and brand name	**MWCO [Da]**	**Membrane ID**	**Membrane type**	**Membrane material**
SUEZ/GE, PW	10 000	NF#9	FS	Polyethersulfone
Alfa Laval, UFX-10pHt	10 000	NF#8	FS	Polysulphone
SUEZ/GE, GE	1 000	NF#7	FS	Polyamide
Pentair, HFW	1 000	NF#6	HF	Polyethersulfone
NX Filtration, dNF80	800	NF#5	HF	Polyethersulfone
DuPont NF270	200-400	NF#1	FS	Polyamide
SUEZ/GE, DL	250	NF#2	FS	Polyamide
SUEZ/GE, DK	150-300	NF#4	FS	Polyamide
Toray, TM600	150	NF#3	FS	Polyamide
Toray, TMH	100-150	NF#10	FS	Polyamide
MWCO – molecular weight cut off [Da]; FS - Flat sheet; HF – hollow fibre;				

The experimental assessment of nanofiltration membranes was carried out in a stepwise approach. Initially, the effectiveness of all 10 selected NF membranes was experimentally verified for the removal of a genetic marker, kanamycin and ampicillin ARG, representing a microbial CEC. A different marker (from sul 1) has been used for better comparability with historical data. Nevertheless, the removal effectiveness is expected to be similar or worse. This is because, the ARG (or to be precise a purified ARG plasmid) is kind of a worst-case scenario as the target is sitting on a small genetic element, a small plasmid. In addition, the sul family is associated with transposon class 1 (Poey et al., 2019) which are frequently carried by conjugative plasmids. Hence, the sul genes would react quite similarly to kanamycin and ampicillin ARG marker when it comes to membrane removal/rejection. At least 98.9% and up to 99.9% ARG marker removal by membranes with MWCO below 10 kDa was observed. The log reduction value (LRV) varied between 2.0 and 6.2 (Figure 8). The highest LRV was achieved by the NF#1 and NF#4 membranes.

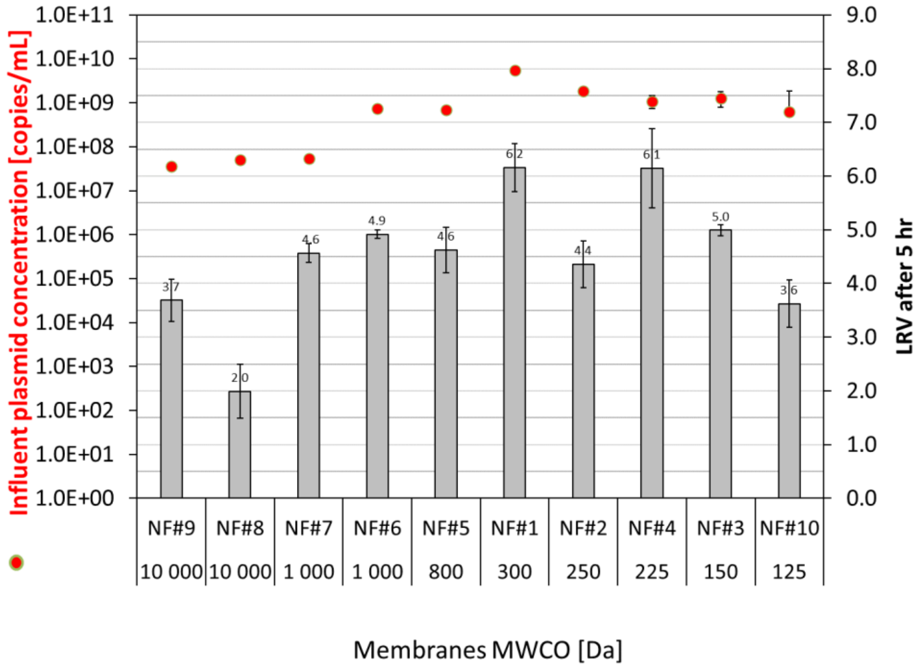

Figure 8. Influent plasmid concentration and LRV after 5 h operation for NF membranes with MWCO between 10 kDa and 0.1 kDa.

Although all membranes reached the SERPIC objective for Route A set at 90 % reduction of target CECs (including ARGs), the NF#9 and NF#10 membranes were excluded from further investigations due to their lower effectiveness, below 4 LRV. The NF#8 has not been excluded, even though it provided LRV of 2, due to uncertainty related to somewhat lower than previously reported data (Krzeminski et al., 2020).

During the next stage, eight different NF membranes were assessed for effectiveness in separating basic nutrients measured by total phosphorous content (TP), total nitrogen content (TN), NH_4, and NO_3, from WWTP effluent. Nutrients retention in the membrane permeate (expressed by a low percentage of rejection achieved) is desirable due to the planned use of the permeate for agricultural irrigation purposes. Nitrogen was generally more easily retained in the permeate than phosphorous as all membranes retained at least 70 % of TN and only up to 25 % of TP. While the results were comparable, the membrane with MWCO < 150 Da (NF#3) was deemed less suitable due only app. 4% retention of TP. The analysis of NF#2 permeate samples was not possible due to insufficient sample volume and thus was excluded from further assessment.

To assess chemical CECs removal potential, historical data on the removal of 11 CECs has been used when available: N,N-diethyl-m-toluamide (DEET), benzophenone-3 (BP3), octocrylene (OC), ethylhexylmethoxycinnamate (EHMC), 2-(2H-Benzotriazol-2-yl)-4-(2,4,4-trimethyl-2-pentanyl)phenol (UV-329), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyran or Galaxolide® (HHCB), 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphtalene or Tonalide® (AHTN), tris(2-chloro-isopropyl)phosphate (TCPP), tris(2-chloroethyl)phosphate (TCEP), dibutyldiphenylphosphate (DBPP), tributylphosphat (TBP). The NF#1, NF#3, NF#7, and NF#8 membranes have provided an average rejection effectiveness of 79 %, 71 %, 50 % and 54 %, respectively. For the most effective membrane, NF#1, with the average removal of 79 %, and a median of 89 %, the removal for individual compounds were: 79-97 % for DEET, 65-99 % for BP3, 63-94 % for OC, 13-72 % for EHMC, 87 % for UV-329, 96-98 % for HHCB, 93-97 % for AHTN, 54-99 % for TCPP, 74-94 % for TCEP, 81 % for DBPP, and 39-

91 % for TBP. The NF#7 and NF#8 have been excluded from further assessment due to insufficient rejection of the chemical CECs.

The best-performing membranes (NF#1, NF#3) and remaining membranes (NF#4, NF#5 and NF#6) were further experimentally evaluated for the removal of selected SERPIC target chemical CECs [Diclofenac (DCF), Sulfamethoxazole (SMX), Venlafaxine (VLX)], antibiotic resistant bacteria (ARB) [*Escherichia coli* (*E. coli*)], ARG marker (sul1), and additionally for retention of nutrients (TN, TP, K, Ca, Mg). Iopromide, final SERPIC target indicator for chemical CECs, was not analyzed for since it is not used in Norway and thus was not expected to be detected in wastewaters in Norway. Due to technical problems, the NF#1 results are unavailable. All membranes provided complete removal of the ARB *E. coli*, between 2.0 and 3.0 LRV for sul1 ARG, and varying effectiveness of retaining nutrients and rejecting selected chemical CECs (Table 2). None of the NF membranes managed to provide 90 % removal of selected CECs, but NF#3 and NF#5 were closest to the 90 % target of the SERPIC project for the permeate stream for irrigation (Route A). The NF#4 and NF#6 provided below 50 % removal of the selected CECs.

Table 2. Results for the different parameters for the selected NF membranes

Membrane supplier and product type	**Membrane ID**	**ARB** *E. coli* % of rejection	**ARG** *sul*1 LRV	**Nutrients** TN, TP, K, Ca, Mg % of rejection	**Chemical CECs** DCF, SMX, VLX % of rejection
DuPont, NF270	NF#1	100	6.2	17, 91, NM, NM, NM	NM, NM, NM, 79*
Toray, TM600	NF#3	100	2.0	12, 96, 32, 68, 76	88, 85, 89
SUEZ/GE, DK	NF#4	100	2.2	11, 76, 25, 34, 29	44, 43, 41
NX Filtration, dNF80	NF#5	100	3.0	10, 90, 19, 37, 32	61, 65, 72
Pentair, HFW	NF#6	100	2.1	9, 74, 9, 37, 32	28, 33, 37
* - average removal of the 11 CECs (DEET, BP3, OC, EHMC, UV-329, HHCB, AHTN, TCPP, TCEP, DBPP, TBP)					

Based on the carried-out assessment, 5 NF membranes were identified as promising for pilot testing. However, NF#5 and NF#6 were of a hollow fiber configuration not suitable for the pilot unit, NF#4 and NF#6 had lower expected efficiency for CECs removal, and NF#3 turned out to be less available from a supplier. Therefore, considering both the lab-scale evaluation results and the technical compatibility with the RO system at UCLM, the NF#1 (DuPont NF270) membrane has been selected for the pilot-scale evaluation. The NF#1 membrane had provided > 6 LRV for ARG, >70 % retention of TN, and app. 80 % rejection of chemical CECs, was compatible with the pilot unit and readily available. The 1812 module size nanofiltration membranes were delivered to UCLM where they will be integrated into the treatment train, replacing the current reverse osmosis unit tested in the last months.

5.2 Reverse osmosis (alternative option to nanofiltration) (UCLM)

The tests were done with the effluent of the secondary wastewater treatment plant of Ciudad Real (Spain). It was stored at UCLM in a 10 m^3 tank and pumped into the reverse osmosis unit. Then, this stream passed to a three-filter system in order to remove particles still present in the feed (the secondary effluent) that could foul and damage the membrane.

The reverse osmosis system operated with an inlet flowrate equal to 34.6 Lh^{-1} and the generated effluents (permeate and concentrate) flowrates are those reported in Table 3.

Both inlet and outlet streams have been characterized. Table 4 shows the target parameters.

Table 3. Flow rates of reverse osmosis equipment.

Parameters	**Influent**	**Permeate**	**Concentrate**
Flow rates / Lh^{-1}	34.6	13.4	21.2

Table 4. Selected CECs and physico-chemical parameters measured in the streams of the osmosis equipment.

Selected CECs	**Physico-chemical parameters**
E.coli	pH
*sul*1	Conductivity
Diclofenac	Turbidity
Iopromide	Chloride, Bromide Sulphate Phosphate
Sulfamethoxazole	Nitrite, Nitrate, Chlorate, Ammonium
Diclofenac	Sodium, Potassium, Calcium, Magnesium

Samples of all the streams were taken daily and stored to be analysed according to the defined protocol. Samples not included in the protocol were stored for further analysis. In particular:

- analyses of the **influent** (=secondary effluent of the WWTP) were carried out every week and at each water renewal in the tank.
- analyses of the daily samples of **permeate** and **concentrate** were done weekly.

Preliminary results are shown below (Table 5) for some of the selected parameters. The range of values corresponds to 10 different samples taken on different days. Analysis will be done according to the analytical methods developed within UCLM and described in the deliverable D1.2.

Table 5. Preliminary results for the different parameters selected for the influent and effluents of the reverse osmosis unit.

Parameters	**Influent**	**Permeate**	**Concentrate**
pH	7.10-8.75	5.80-8.18	7.15-9.08
Conductivity / µS cm^{-1}	934-1500	35-53	1001-1841
Chloride / mg dm^{-3}	155.6-186.7	3.8-7.4	259.1-263.5
Nitrate / mg dm^{-3}	9.13-10.8	1.10-2.75	11.1-15.9
Sulphate / mg dm^{-3}	180.8-195.1	1.9-2.3	215.3-283.1
Sodium / mg dm^{-3}	105.7-108.3	3.1-6.64	125.3-166.07
Ammonium / mg dm^{-3}	3.6-5.71	0.31-0.39	4.1-7.0
Potassium / mg dm^{-3}	27.3-29.5	0.8-1.3	32.3-46.23
Calcium / mg dm^{-3}	62.3-99.7	1.5-2.65	99.45-144.55
Magnesium / mg dm^{-3}	34.9-49.4	0.59-0.98	50.3-72.2
E. coli / CFU 100ml^{-1}	$1\cdot10^{3}$- $4.0\cdot10^{6}$	0	$1\cdot10^{3}$- $4.1\cdot10^{6}$
*sul*1 / nº copies mL^{-1}	$5\cdot10^{1}$- $8.5\cdot10^{3}$	$1\cdot10^{1}$- $3\cdot10^{3}$	$4.5\cdot10^{1}$- $8.3\cdot10^{3}$
Diclofenac / µg dm^{-3}	0.303-0.606	N.d	0.412-0.830
Iopromide / µg dm^{-3}	0.403-0.806	N.d	0.564-1.281
Sulfamethoxazole / µg dm^{-3}	0.041-0.128	N.d	0.052-0.167
Venlafaxine / µg dm^{-3}	0.196-0.513	N.d	0.304-0.862

5.3 Disinfection unit (ozonation) (UCLM)

Table 6 reports the influent and effluent flow rates as well as the mass flow rate of ozone added in the unit during the bench scale tests. The influent corresponds to the reverse osmosis unit permeate.

Table 6. (Volume and mass) Flow rates in the disinfection unit test.

Parameter	**Influent**	**Gaseous ozone**	**Disinfected effluent**
Flow rate	13.4 L h^{-1}	≈36 mg h^{-1}	13.4 L h^{-1}

A Sampling plan was drawn up:

- Regarding the influent (= reverse osmosis permeate), every day from Monday to Friday a sample was taken from the permeate stream, to be stored and processed once a week,
- Regarding the disinfected effluent, analyses were done on daily samples (from Monday to Friday).

The investigated parameters for both streams were the selected CECs and the physico-chemical parameters reported in Table 2.

Analysis will be done according to the analytical methods developed within UCLM and described in the deliverable D1.2.

Table 7 shows the results, for the selected parameters in the influent and ozonated effluent, based on ten samples taken. The values regarding the influent in Table 5 are the same reported for the reverse osmosis permeate of Table 3.

Table 7. Preliminary results for the different parameters selected.

Parameters	**Influent**	**Ozonated effluent**
pH	5.80-8.18	5.60-8.15
Conductivity / µS cm^{-1}	35-53	36-52.7
Chloride / mg dm^{-3}	3.8-7.4	3.7-7.9
Nitrate / mg dm^{-3}	1.10-2.75	0.41-1.1
Sulfate / mg dm^{-3}	1.9-2.3	2.1-3.4
Sodium / mg dm^{-3}	3.1-6.64	4.1-5.6
Ammonium / mg dm^{-3}	0.31-0.39	0.35-0.40
Potassium / mg dm^{-3}	0.8-1.3	0.9-1.1
Calcium / mg dm^{-3}	1.5-2.65	1.4-2.57
Magnesium / mg dm^{-3}	0.59-0.98	0.46-1.06
E. coli / CFU 100 ml^{-1}	0	0
*sul*1 / nº copies mL^{-1}	$1 \cdot 10^{1}$- $3 \cdot 10^{3}$	0 - $2.8 \cdot 10^{3}$
Diclofenac / µg dm^{-3}	N.d	N.d
Iopromide / µg dm^{-3}	N.d	N.d
Sulfamethoxazole / µg dm^{-3}	N.d	N.d
Venlafaxine / µg dm^{-3}	N.d	N.d

It emerges that *E. coli* was not present in the influent to the unit due to the upstream treatment by reverse osmosis, able to retain all the microorganisms. The same occurred for the selected organic CECs. The ozonation step mainly react with the conventional pollutants, resulting in a reduction of the corresponding variability range for most of them.

5.4 Photoreactor unit (UP)

The production of the CEC concentrates was carried out in a membrane filtration pilot, integrating a RO or NF membrane (RE 4040-BE or NE 4040-70, respectively) and installed in a municipal wastewater treatment plant located in Northern Portugal. The influent to the (RO or NF) unit was collected downstream of the second clarifier, stored in a 1 m^3 capacity feed tank and pumped to the RO/NF unit via an EFAFLU pump. The produced concentrate was reintroduced into the feed tank (concentration factor ≈ 2.7) and afterwards filtered through a sand filtration system in order to minimize the amount of solids.

Photo-oxidation tests were performed in the bench-scale membrane photoreactor (described above) with RO or NF concentrate, under natural pH and without CECs fortification, applying a feed flow (Q_F) of 2.5 L h^{-1} and recirculation flow (Q_R) of 27.5 L h^{-1} (equivalent to a residence time (RT) of 3.4 min and a flow in the reaction zone (Q_{ARZ}) of 30 L h^{-1}), under UVC radiation (3.3 kJ L^{-1}). The stock oxidant solution, in this case persulfate (PS), was either prepared from sodium peroxydisulfate (Merck, ≥99 % w/w, CAS# 775-27-1) or generated electrochemically. The electrochemical production of PS was carried out using diamond anodes (from IST) and the electrochemical cell was integrated with the membrane photoreactor. Table 8 summarizes the experimental conditions applied in the photo-oxidation tests.

Table 8. Experimental conditions applied in the photo-oxidation tests.

Test #	**Concentrate**	**PS production**	**$[PS]_{stock}$ (mM)**	**$[PS]_{ARZ}$ (mM)**
1	RO	Commercial	267.5	1.2
2		Electrochemical		1.2
3	NF	Commercial	241.3	1.2
4		Electrochemical		1.2
5		Electrochemical		2.4

In a regular operation, the tubular membrane is initially filled with the PS stock solution which, during the photo-treatment and at a pre-defined rate, is forced to permeate through the membrane pores (radial permeation) to be delivered to the ARZ. The photo-oxidation tests start with the simultaneous activation of the pumps for feeding and recirculating the concentrate to the reactor, the UVC lamps and the peristaltic pump that doses the oxidant. Under steady-state conditions, at least three samples were collected for analysis and characterization. To avoid oxidation after sampling, a solution of sodium sulfite (Na_2SO_3) was immediately added to the samples in a 5:1 molar ratio considering the PS dose.

Analytical determinations

The influent to the filtration unit (RO or NF), corresponding to the secondary effluent of the wastewater treatment plant, and the respective permeates (P) and concentrates (C) were characterized regarding the main physicochemical parameters and a selection of CECs, including those defined for the SERPIC technology tests (Table 9).

The pH and temperature were measured using a Hanna Instruments HI8424 portable pH meter and the conductivity was determined using a Hanna Instruments Edge HI2003-02. Chemical oxygen demand (COD) and total suspended solids (TSS) were measured according to the Standard Methods for the Examination of Water and Wastewater. All the UV-Vis measurements were carried out using a Spectroquant® Prove 600 spectrophotometer. Dissolved Organic Carbon (DOC) and Dissolved Inorganic Carbon (DIC) were determined in a Shimadzu TOC-VCSN analyser. Inorganic ions concentration was analyzed by ion chromatography (Dionex ICS-2100 LC equipped with an IonPac® AS11-HC 250 mm x 4 mm column and an anion self-regenerating suppressor ASRS® 300, 4 mm; and Dionex DX-120 LC equipped with an IonPac® CS12A 250 mm x 4 mm column at ambient temperature and a cation self-regenerating CSRS® Ultra II, 4 mm). The PS concentration (total or residual) in the photo-oxidation tests was determined by iodometric titration.

Analytical methods for the detection of the target CECs in different water matrices (influent to the filtration unit, permeate and concentrate from RO or NF) were tested and validated in an Acquity UPLC® liquid chromatograph interfaced to a XEVO TQD® triple quadrupole mass spectrometer (LC-MS/MS) equipped with an electrospray interface (ESI) from Waters (Milford, MA, USA). In addition to the four target chemical compounds selected for the SERPIC project - diclofenac (anti-inflammatory), iopromide (X-ray contrast media), sulfamethoxazole (antibiotic), and venlafaxine (psychiatric drug) - 10 more CECs were also analyzed, namely melamine (flame retardant), DEET (insect repellent), diuron (herbicide), carbamazepine and carbamazepine 10,11-epoxide (metabolite), the beta-blockers atenolol and bisoprolol, and the angiotensin II receptor blockers losartan, valsartan and irbesartan.

Table 9. Characterization of the influent, concentrate (C) and permeate (P) of the two filtration units (RO and NF).

Parameters	**Units**	**Influent**	**RO**		**Influent**	**NF**	
			C	P		C	P
pH	-	7.2	7.6	7.6	7.3	7.9	7.0
Conductivity	µS cm^{-1}	1387	5700	430	1079	2315	874
Chemical Oxygen Demand (COD)	mg L^{-1}	130	195	12.5	70	206	1.2
Dissolved Organic Carbon (DOC)	mg L^{-1}	16.2	48	7.1	13.1	51	0.9
Dissolved Inorganic Carbon (DIC)	mg L^{-1}	61.5	178	34.9	50	65	41.5
Total Suspended Solids (TSS)	mg L^{-1}	64.5	52	2.7	31.5	1.2	1.5
Chloride (Cl^-)	mg L^{-1}	132	689	26.9	159	232	152
Nitrite (NO_2^-)	mg L^{-1}	13.8	25.2	4.2	8.1	18.8	2.0
Sulfate (SO_4^{2-})	mg L^{-1}	58	315	0.3	57	298	1.1
Nitrate (NO_3^-)	mg L^{-1}	19.2	9.9	0.4	5.8	19.1	0.1
Phosphate (PO_4^{3-})	mg L^{-1}	14.4	14	<0.03	10.6	43.1	0.7
Sodium (Na^+)	mg L^{-1}	109	855	64.4	124	422	99
Ammonium (NH_4^+)	mg L^{-1}	43.6	223	30.6	27.4	53.8	23.6
Potassium (K^+)	mg L^{-1}	24.1	196	15.6	25.4	84.3	20.4
Magnesium (Mg^{2+})	mg L^{-1}	7.0	36.0	0.1	5.2	99.0	1.9
Calcium (Ca^{2+})	mg L^{-1}	32.7	128	1.2	28.5	111.6	13.2
Melamine (MLN)	µg L^{-1}	1.8	20.5	0.7	3.0	10.5	<0.58
DEET (DEET)	µg L^{-1}	0.6	2.2	0.4	<0.4	<0.4	<0.4
Diuron (DRN)	µg L^{-1}	<0.06	0.2	<0.06	0.2	0.3	0.2
Carbamazepine (CBZ)	µg L^{-1}	0.5	2.4	<0.06	0.9	3.4	0.3
CBZ 10,11-epoxide (CBZ-EPX)	µg L^{-1}	<0.12	0.5	<0.12	0.5	0.9	0.4
Atenolol (ATNL)	µg L^{-1}	<0.12	0.2	<0.12	<0.12	<0.12	<0.12
Bisoprolol (BSPL)	µg L^{-1}	0.3	1.3	<0.05	0.6	1.7	0.3
Losartan (LSTN)	µg L^{-1}	0.4	3.6	<0.37	0.6	2.8	<0.37
Irbesartan (ISTN)	µg L^{-1}	1.0	4.2	<0.14	2.0	8.6	<0.14
Valsartan (VSTN)	µg L^{-1}	1.1	5.5	<0.17	<0.17	<0.17	<0.17
Diclofenac (DCF)	µg L^{-1}	0.7	6.5	<0.51	1.8	8.5	<0.51
Iopromide (IOP)	µg L^{-1}	4.6	18.6	<1.06	3.8	16.0	<1.06
Sulfamethoxazole (SMX)	µg L^{-1}	0.4	0.8	<0.08	0.3	1.3	<0.08
Venlafaxine (VLX)	µg L^{-1}	0.3	2.4	<0.07	0.8	2.3	0.4

Main results

The main results obtained for the photo-treatments with RO and NF concentrates are summarized in Table 10. Overall, for the same dose of PS (1.2 mM for tests #1 to #4), the efficiency of CECs removal between the concentrate streams from RO and NF was quite similar, as well as the use of electrochemically generated PS and commercial PS.

The CECs that showed greater degradation were DCF, IOP and SMX. These compounds are known to exhibit high photodegradability, as evidenced by their high molar absorptivity ($\varepsilon_{\lambda 254} > 10^3$) and quantum yields ($\Phi_{\lambda 254}$). In turn, CBZ, ISTN and MLN were the contaminants with the lowest levels of removal, followed by BSPL and VLX. For the NF concentrate, increasing the PS dose for 2.4 mM (test #5) allowed to obtain removals >80 % for 3 out of the 4 target CECs selected for the SERPIC (DCF, IOP, and SMX), while VLX was removed ca. 65 %.

Furthermore, it should be mentioned that only when a PS dose of 2.4 mM is applied (test #5), all physicochemical parameters comply with the legally required COD, TSS and BOD_5 values (maximum allowable of 125 mg L^{-1}, 35 mg L^{-1} and 25 mg L^{-1}, respectively, according with the Council Directive 91/271/EEC) for direct discharge into the environment.

Table 10: Results for the removal (%) of the CECs in the photo-treated RO and NF concentrates.

	Photo-treatment tests				
	#1	**#2**	**#3**	**#4**	**#5**
pH	8.1	7.4	7.6	7.5	6.8
COD (mg L^{-1})	174	196	143	181	116
DOC (mg L^{-1})	46	46	54	55	51
BOD_5 (mg L^{-1})	<5	<5	<5	20	15
TSS (mg L^{-1})	34	45	20	19	11
CECs removal %					
Melamine	22.9 ± 0.9	22.2 ± 0.4	<10	<10	<10
DEET	10.4 ± 0.3	11 ± 2	n.a.	n.a.	n.a.
Diuron	62 ± 1	52 ± 2	65 ± 4	67.3 ± 0.1	73 ± 3
Carbamazepine	17 ± 3	12 ± 1	10 ± 1	21 ± 3	26 ± 2
CBZ 10,11-epoxide	72.1 ± 0.1	53.8 ± 0.4	52 ± 4	51 ± 1	80 ± 1
Atenolol	50.7 ± 0.1	54.5 ± 0.1	n.a.	n.a.	n.a.
Bisoprolol	38 ± 1	16 ± 7	32.2 ± 0.2	23.7 ± 0.5	43 ± 3
Losartan	61 ± 3	49 ± 3	45 ± 3	52.1 ± 0.9	62 ± 2
Valsartan	20 ± 6	13 ± 4	n.a.	n.a.	n.a.
Irbesartan	19 ± 2	<10	24 ± 2	<10	23.8 ± 0.8
Diclofenac	≥92	≥92	91 ± 2	90 ± 2	≥92
Iopromide	81.1 ± 0.5	79 ± 10	81 ± 2	84 ± 2	86 ± 3
Sulfamethoxazole	70.4 ± 0.1	66 ± 3	81 ± 1	69 ± 4	91.2 ± 0.6
Venlafaxine	26.8 ± 0.4	<10	42 ± 2	36 ± 1	64 ± 1

n.a. not applicable.

It should be highlighted that simulations based on ray-trace analysis were carried out to optimize the reflective surface of the system and increase its photonic efficiency (i.e., greater number of photons effectively reaching the reaction zone). Simulations were carried out using different lamps/reactor arrangements with 1, 2 and 3-sided flat reflectors and with circular and parabolic geometries. Results showed that direct radiation is maximized when the distance reactor-lamps is minimized, increasing optical efficiency. On the other hand, it was observed that for the flat reflectors, the closer the furthest point of the reflector to the center of the reactor, the higher optical efficiency is achieved due to the reduction in the number of bouncing rays in the reflector. In the case of parabolic geometries, some additional considerations are necessary, since not only the distance at which the reflector is placed matters but also its geometrical focus. The best performance is achieved for those in which the distance from the furthest point of the reflector to the center of the reactor was lower and the lamps placed near the focus of the parabola. For the studied reflector geometries, the calculated optical efficiencies when using anodized aluminum were 46.1%, 56.5%, 60.0%, 41.8%, and 65.9% for reflectors of 1, 2, and 3 sides, cylinder, and parabola, respectively. Model predictions were successfully validated using experimental ferrioxalate actinometry data, confirming the huge potential of this simple simulation methodology for photoreactor design purposes.

Considering these results, an increase in photolysis reactions is expected directly on the CECs or on the PS, with consequent higher production of reactive species. An improved overall performance of the photo-treatment can be anticipated to fully meet the SERPIC project reduction goals for the concentrate stream - destined for discharge into the environment (Route B). The CEC classes, including the SERPIC-specific targets in brackets, include:

- ARB, ARGs (*E. coli*, Fecal coliform; 16S rRNA, *sul*1, *sul*2): > 99 %
- Analgesic drugs (Diclofenac, Ibuprofen, Tramadol): > 99 %
- Pharmaceuticals (Amoxicillin, Azithromycin, Bezafibrate, Bisoprolol, Ciprofloxacin, Erythromycin, Furosemide, Gemfibrozil, Iopromide, Ibersartan, Sulphamethoxazole, Tetracycline, Trimethroprim, Valsartan): > 90 %
- Antiretrovirals (ARV's): > 80 %
- Psychiatric drugs (Carbamazepine, Carbamazepine 10,11 epoxide, Oxazepam, Venlafaxine): > 80 %
- Preservatives in personal care products: > 99 %
- Illicit drugs: > 90 %
- Industrial micropollutants (Bisphenol A, Nonylphenol, PFOS): > 80 %

6 Publications and other dissemination activities

Santos, C.S., Montes, R., Rodil, R., Quintana, J.B., Gomes, A.I., Vilar, V.J.P., Urban Wastewater Resources Recovery – Integration of Nanofiltration and Advanced Oxidation Processes, Conference Proceedings, DCE23 – Doctoral Congress in Engineering, June 2023, Porto, Portugal

Martín-Sómer M., Moreira J., Santos C., Gomes A.I., Moreno-San Segundo J., Vilar V.J.P., Marugán J., Reflector design for the optimization of photoactivated processes in tubular reactors for water treatment, Journal of Environmental Chemical Engineering, 11(5) (2023) 110609. https://doi.org/10.1016/j.jece.2023.110609

Krzeminski P., Eggen E., Schwermer C.U., Wennberg A.C., Umar M., Anglès d'Auriac M. (2023) Effectiveness of membrane filtration for removal of cell free antibiotic resistance genes from water and wastewater, 10th IWA Membrane Technology Conference, 23-26 July 2023, St. Louis, USA

F. Mena, I.; Montiel, M.A.; Sáez, C.; Rodrigo, M.A.: Improving performance of proton exchange membrane (PEM) electro-ozonizers using 3D printing. In: Chemical Engineering Journal 464, (2023), 142688.

7 Literature

Krzeminski, P., Feys, E., d'Auriac, M.A., Wennberg, A.C., Umar, M., Schwermer, C.U., Uhl, W. (2020) Combined membrane filtration and 265 nm UV irradiation for effective removal of cell free antibiotic resistance genes from feed water and concentrate, Journal of Membrane Science 598C, 117676

Poey, M.A., Azpiroz, M.F., Laviña M, (2019) On sulfonamide resistance, sul genes, class 1 integrons and their horizontal transfer in Escherichia coli, Microbial Pathogenesis 135, 103611