

Deliverable Report

D2.4 Design of photoreactor prototype

Work package:	WP2 Treatment technology and prototype.
Lead beneficiary:	University Porto - FEUP
Authors:	Vítor J. P. Vilar, Ana I. Gomes, Carla S. Santos
Place, country:	Porto, Portugal
Type:	Hardware
Dissemination level:	Public
Due date (in months):	Project month 17
Date finalised:	20.11.2023 (project month 27)

Version	Date	Reason for changes
1	7.11.2023	Draft
2	20.11.2023	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.....	3
5	Results	3
	5.1 Main components	3
	5.2 Specific features: Inlet and outlet lids	5
	5.3 Specific features: Reflective surfaces	7
6	Publications and other dissemination activities	9
7	Literature	9



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 1st September 2021. The project has a duration of 36 months and will end 31st 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

A tubular photoreactor is applied for the removal of CECs from NF concentrate of secondary urban wastewater effluent. The photoreactor allows the integration of different mechanisms for generating reactive oxygen species in a single unit operated in continuous flow mode. In this report, the construction details, materials, and parts of the tubular photoreactor prototype are shown and addressed.

After having verified the effectiveness of the photoreactor on a laboratory scale through several studies carried out, a pilot-scale photoreactor was developed to be integrated into the prototype built and installed at the Universidad Castilla La-Mancha, in Ciudad Real, Spain. This system encompasses the membrane filtration unit, disinfection, advanced oxidation and electrochemical production of oxidants.

3 Deliverable description as stated in the Project Description

Resulting from T2.5, The best configuration of the membrane photoreactor (length; inlet/outlet offset from ends; inlet/outlet radius; inner/outer diameter and length of quartz tube; location and number/power of UV lamps; ceramic membrane properties and dimensions) for the treatment of concentrate from the NF system, aiming its discharge into aquatic system, will be reported along with the best operational conditions (UV and oxidant dose), being able to reduce CECs at minimum in 80 %.

4 Introduction

Wastewater reuse represents a promising solution to water scarcity problems in various fields of application, particularly in the agricultural sector, where water supply represents more than 70% of demand (FAO, 2017). However, traditional treatment technologies used in Wastewater Treatment Plants (WWTP) demonstrate limitations in removing several pollutants, known as contaminants of emerging concern, CECs (Rizzo et al., 2019). For this reason, it is imperative to apply advanced treatment methods to improve the quality of effluents after secondary treatment (activated sludge). A highly promising method for the tertiary step is membrane filtration, specifically reverse osmosis (RO) and nanofiltration (NF). However, the application of the RO or NF process generates an inevitable flow, known as concentrate, which is generally characterized by high levels of inorganic salts, refractory organic substances, and traces of micropollutants (Deng, 2020). To reduce the pollutant load of concentrate flows generated by membrane filtration methods, it is essential to apply specific methodologies, such as advanced oxidation processes, AOP. One example is the combination of UV radiation and oxidants, generating reactive oxygen species (ROS) with high oxidation potential. Over the past few years, sulfate radicals ($\text{SO}_4^{\cdot-}$) have emerged as a potential technology for removing CECs from municipal wastewater due to their high redox potential (2.5–3.1 V vs. NHE). To generate $\text{SO}_4^{\cdot-}$ radicals, a suitable oxidant such as persulfate (PS, $\text{S}_2\text{O}_8^{2-}$) needs to be activated. PS is a strong oxidant with a standard oxidation potential of 2.01 V, has high stability, high solubility (730 g L⁻¹, at 25 °C), high molar extinction coefficient (21.1 M⁻¹ cm⁻¹) and a high quantum efficiency (1.8 mol Einstein⁻¹) at 254 nm (He et al., 2014; Ike et al., 2018; Waclawek et al., 2017).

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 ozone) can achieve a considerable depletion of the CECs in wastewater plants effluents. To study the removal of CECs present in concentrates resulting from the tertiary treatment of urban wastewater (Route B of the SERPIC project), a pilot-scale tubular photoreactor was built to promote the UVC/PS photochemical oxidation process. The tubular photoreactor allows the integration of different ROS generation mechanisms within a single unit operated in continuous flow mode. In this reactor, a porous ceramic tube provides uniform distribution of the oxidant through multiple dosing points along its entire length. Initially, the process variables were optimized at a laboratory level, such as the oxidant dose, residence time and optical path of the photoreactor.

5 Results

5.1 Main components

According to bench-scale tests, the photoreactor prototype (Figure 1) was projected comprising the following main components/materials: (i) quartz tube; (ii) porous ceramic tube inside mono channel substrate (from Fraunhofer IKTS); (iii) low-pressure UVC lamps (Philips) and ballasts (OSRAM); and (iv) reflective aluminium sheets (from Alanod GmbH & Co. KG). All details of the different components of the photoreactor are summarized in Table 1.

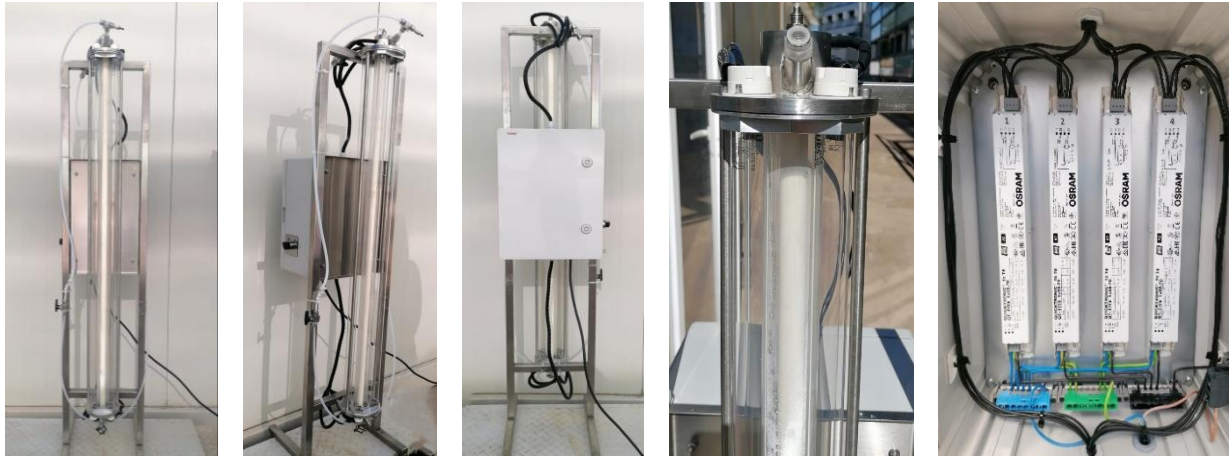


Figure 1 - Photoreactor for the SERPIC prototype treatment plant.

Table 1 - Components and respective characteristics of the prototype photoreactor.

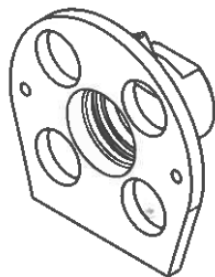
Component	Characteristics	
Quartz tube	Transmissibility for λ_{254} nm (%)	>90
	$\varnothing_{\text{External}}$ (cm)	4.20
	$\varnothing_{\text{Internal}}$ (cm)	3.80
	Total length (cm)	120.00
	Illuminated length (cm)	117.4
	Area (cm ²)	11.34
	Illuminated volume (cm ³)	1331.45
Ceramic tube	Material	$\gamma\text{-Al}_2\text{O}_3$
	$\varnothing_{\text{External}}$ (cm)	2.05
	$\varnothing_{\text{Internal}}$ (cm)	1.55
	Total length (cm)	120.00
	Illuminated length (cm)	117.40
	Area (cm ²)	3.30
	Illuminated volume (cm ³)	387.49
UVC lamps	Model	TUV 75W HO 1SL/6
	Number of lamps	4
	UVC radiation (W)	25.5
	Power (Rated) (Nom) (W)	75
	Lamp Current (Nom) (A)	0.835
	Voltage (Nom) (V)	110
	Electrical ballast	Model
Maximum output power (W)		70
Input voltage AC (V)		198 - 264
Nominal voltage (V)		220 - 240
Mains frequency (Hz)		50 - 60
Reflective Aluminium sheets	Model	MIRO [®] 4 UV-C
	Total reflectance for λ_{250} nm (%)	90 \pm 2
	Thickness (mm)	0.5

5.2 Specific features: Inlet and outlet lids

The effluent to be treated, in this case nanofiltration concentrate, is fed tangentially (Figure 2a and 2b) to the wall of the quartz tube, allowing a helical movement around the outer surface of the ceramic tube. The stainless-steel inlet and outlet lid design incorporate this feature while enclosing the ceramic membrane and quartz tube (in central position) and supporting the UV lamps (equidistantly surrounding the photoreactor). The oxidant, PS produced electrochemically through sulfuric acid using an electrochemical cell with a diamond-doped boron anode, is fed into the interior of the porous ceramic tube and dosed through the pores, which allows its uniform distribution along the outer surface of the membrane. The photoreactor is now being integrated with the other components at UCLM facilities in Ciudad Real, Spain, to form the SERPIC prototype treatment plant.



B-B (1 : 2)



A-A (1 : 2)

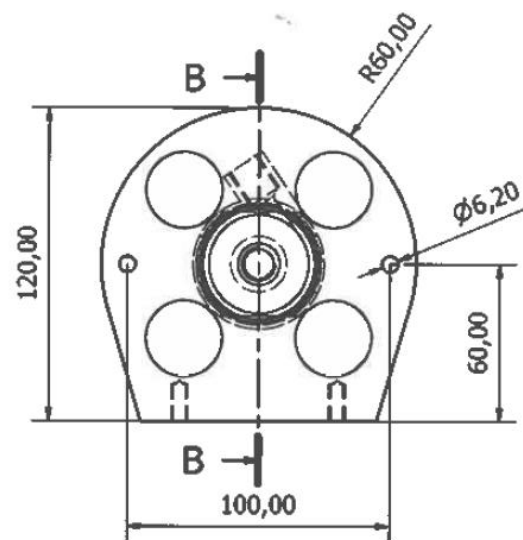
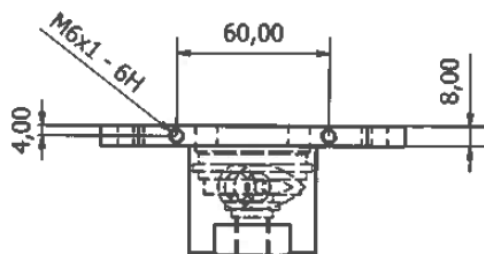
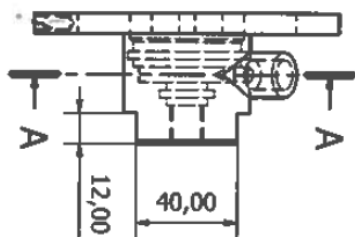
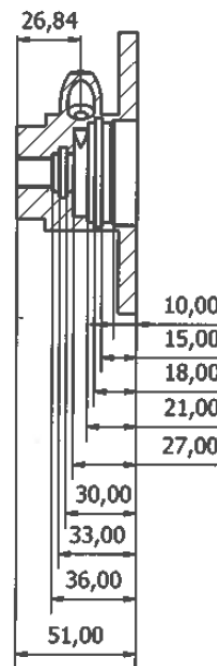
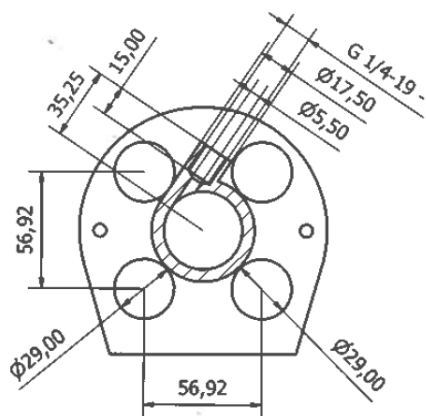


Figure 2 – Details for the **(left)** tangential inlet and outlet of the effluent (photographs) and **(right)** technical drawings of the stainless-steel lid that integrate the effluent inlet and outlet.

The data obtained in the Residence Time Distribution (RTD) tests made it possible to carry out Computational Fluid Dynamics (CFD) simulation and determine the flow rate of 130 L h⁻¹ as necessary to guarantee the helical movement of the fluid along the entire length of the photoreactor (Figure 3).

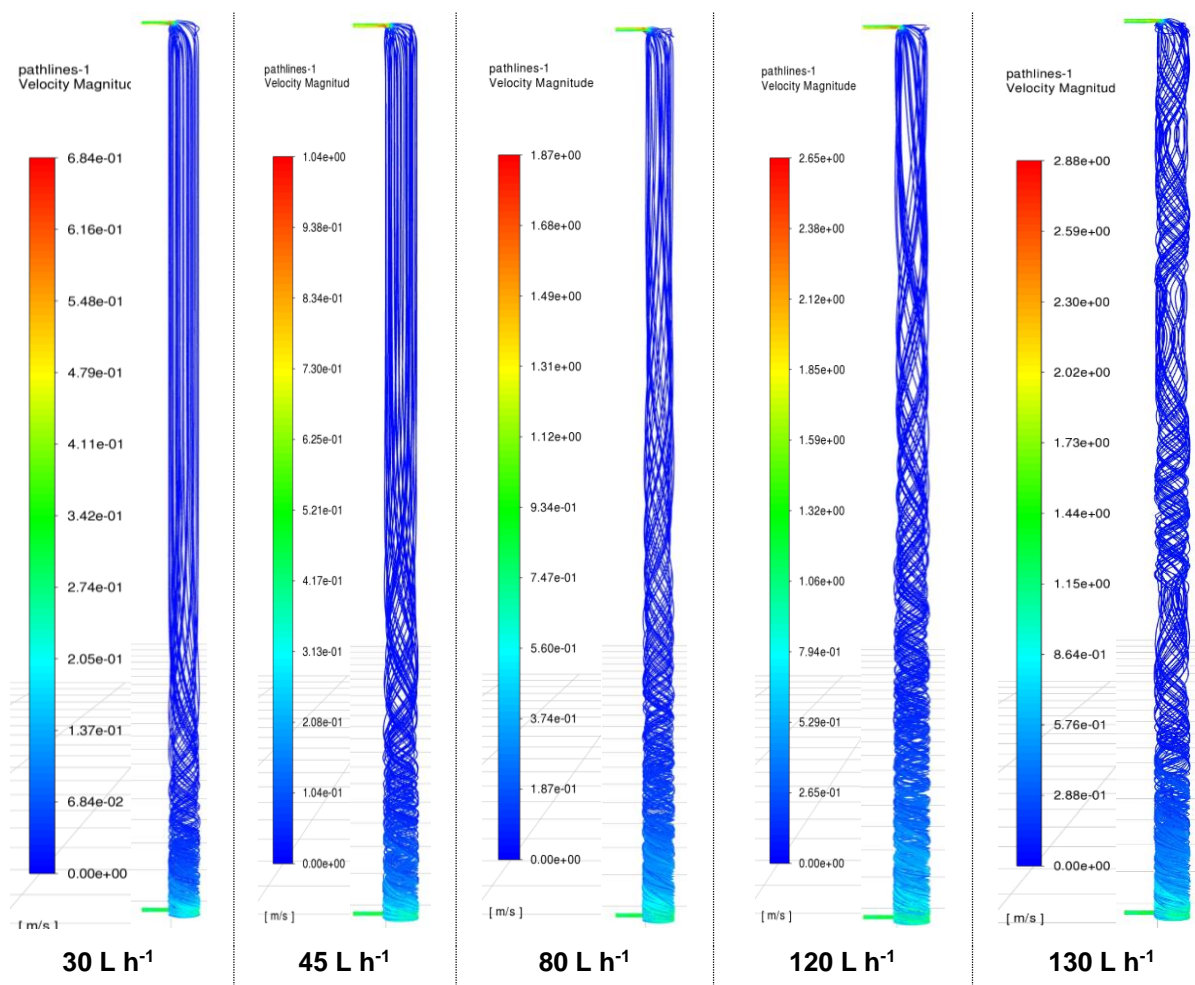


Figure 3 - CFD simulation based on data obtained in RTD tests.

5.3 Specific features: Reflective surfaces

The photoreactor is integrally enclosed by a 3-sided geometry reflector, which surround the lamps (Figure 4a and 4b). The aluminium structure avoids direct contact with the radiation source and, simultaneously, increases the photonic flux that reaches the reaction zone, due to its reflective capacity (Figure 4c). Actinometric measurements indicate that the application of this reflector allows a 2.8-fold increase in photonic flux than when absent.

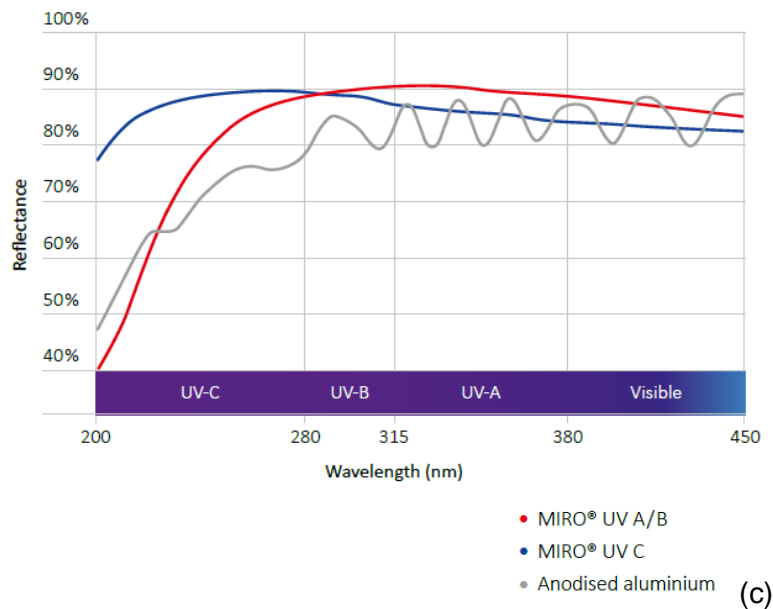
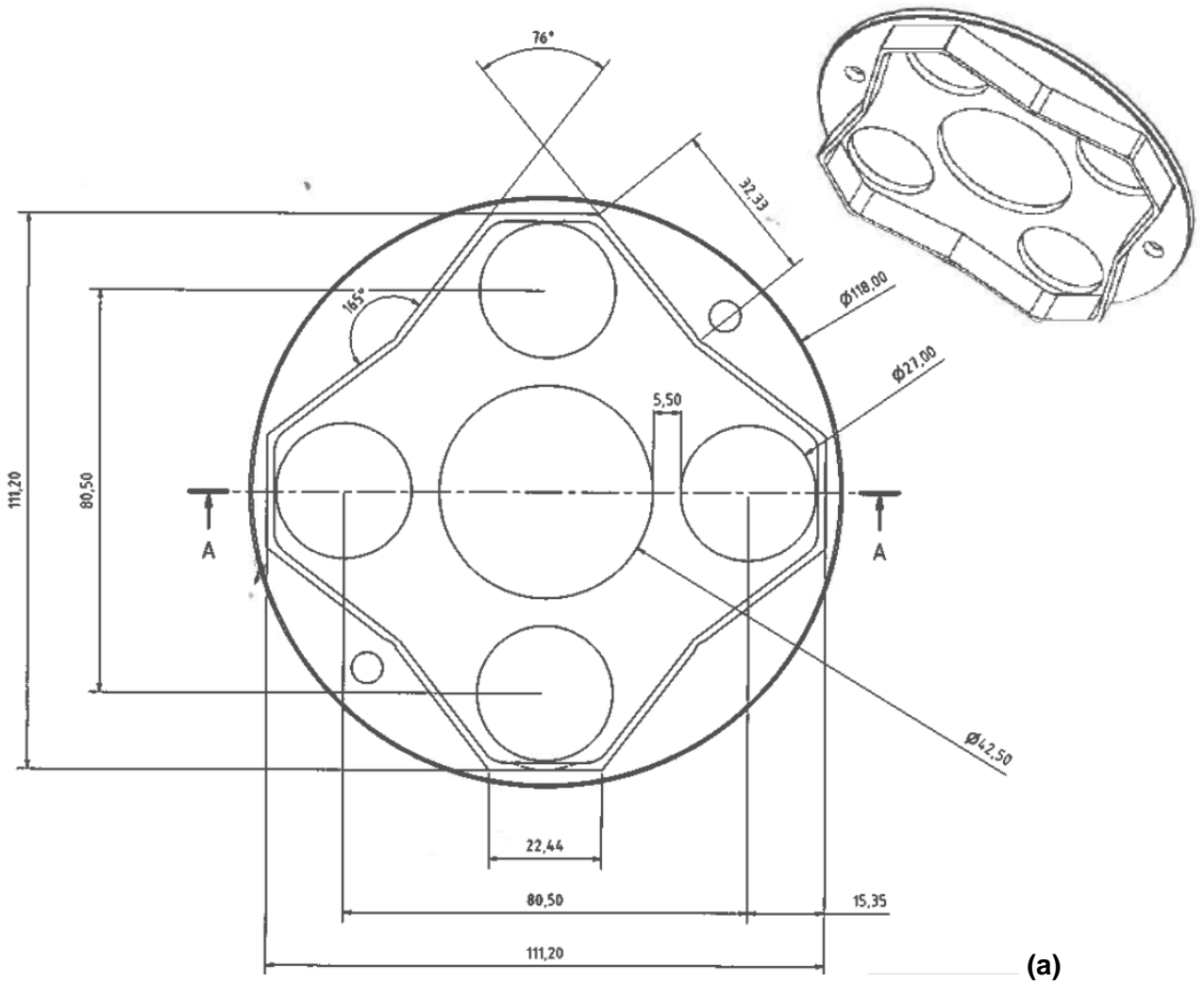


Figure 4 - Details for the (a) 3-sided geometry reflector bracket and dimensions; (b) photograph of the 3-sided geometric reflector enclosing the photoreactor prototype, and (c) reflectance values for MIRO®UVC aluminium reflector (source: technical brochure from Alanod).

6 Publications and other dissemination activities

Martín-Sómer, M.; Moreira, J.; Santos, Carla; Gomes, Ana I.; Moreno-SanSegundo, J.; Vilar, Vítor J.P.; Marugán, J. (2023): Reflector design for the optimization of photoactivated processes in tubular reactors for water treatment. In: *Journal of Environmental Chemical Engineering* 11 (5), S. 110609. DOI: 10.1016/j.jece.2023.110609.

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, DCE23 – 5th Doctoral Congress in Engineering, Porto, Portugal, 15th - 16th June 2023.

Santos, Carla; Montes, Rosa; Rodil, Rosario; Quintana, José Benito; Gomes, Ana; Vilar, Vítor. Tratamento terciário de águas residuais urbanas para produção de água para irrigação de culturas combinando nanofiltração e oxidação avançada. In: Encontro Nacional de Entidades Gestoras de Água e Saneamento, Porto, Portugal, 27th November 2023.

7 Literature

Deng, H.: A review on the application of ozonation to NF/RO concentrate for municipal wastewater reclamation. In: *Journal of Hazardous Materials*, 391 (2020), 122071

Food and Agriculture Organization of the United Nations: Water for Sustainable Food and Agriculture. In: A report produced for the G20 Presidency of Germany (2017) Roma

He, X.; Mezyk, S. P.; Michael, I.; Fatta-Kassinos, D.; Dionysiou, D.D. Degradation kinetics and mechanism of β -lactam antibiotics by the activation of H_2O_2 and $Na_2S_2O_8$ under UV-254nm irradiation. In: *Journal of Hazardous Materials* 279 (2024), pp. 375-383.

Ike, I. A.; Linden, K. G.; Orbell, J. D.; Duke, M.: Critical review of the science and sustainability of persulphate advanced oxidation processes. In: *Chemical Engineering Journal* 338 (2018), pp. 651-669

Rizzo, L.; Malato, S.; Antakyali, D.; Beretsou, V. G.; Đolić, M. B.; Gernjak, W.; Heath, E.; Ivancev-Tumbas, I.; Karaolia, P.; Ribeiro, A. R. L.; Mascolo, G.; Mcardell, C. S.; Schaar, H.; Silva, A. M. T.; Fatta-Kassinos, D.: Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater. In: *Science of The Total Environment*, 655 (2019), 986-1008.

Wacławek, S.; Lutze, H. V.; Grübel, K.; Padil, V. V. T.; Černík, M.; Dionysiou, D. D.: Chemistry of persulfates in water and wastewater treatment: A review. In: *Chemical Engineering Journal* 330 (2017), pp. 44-62.