Treatment of wastewater coming from culture of scallop *Argopecten purpuratus* using O_3/photo-Fenton and membrane distillation processes

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Abstract

The treatment and recovery of industrial wastewater is a necessary contribution to solve the water scarcity problems that affect an increasing part of the world's population. One of the industries that produces a larger amount of polluted wastewater is aquaculture, where water is used to wash the biofouling from the culture systems. The aim of this research is the evaluation of the use of a treatment line consisting on coagulation/flocculation-filtration, advanced oxidation by ozone/solar photo-Fenton, and membrane distillation (MD) to treat wastewater coming from the wash of a Chilean aquaculture facility of the scallop *Argopecten purpuratus*. The technologies were arranged in series, with the feed water to the MD process being the remaining wastewater from the previous sequential stages.

The pretreatment reduced the total suspended solids (TSS) from 204.7 to 15.4 mg/L, the chemical oxygen demand (COD) from 6236.2 to 2993.3 mg/L and the colour from 205.4 to 109.4 Platinum Cobalt Units (PCU), with a removal of 92%, 52% and 46.7%, respectively. The ozone/solar photo-Fenton process further reduced the COD and the colour to 448.7 mg/L and 18.7 PCU, respectively. Finally, the resulting wastewater was treated with MD to remove the pollutants still present. Permeate flux was almost constant around 18 L/h/m^2, and no permanent fouling layer was observed during the MD treatment. Total Organic Content in the permeate was reduced from 166.2 mg/L to 5.2 mg/L, which is equivalent to a COD reduction from 448.7 to 14 mg/L.

The integration of the pretreatment stages, the ozone/solar photo-Fenton process and the MD process allows to achieve a significant removal of the pollutants present in the wastewater, being thus a very useful strategy for dealing with the climate crisis and water scarcity.

Keywords: Industrial wastewater; Advanced oxidation process; membrane distillation; operational conditions; experimental

1.- Introduction

Water scarcity is a serious problem in several places around the world (Greve et al., 2018). It is worsening by the increase in the population, industrial uses and climate change, provoking a reduction of the availability of water (Gosling & Arnell, 2016). This situation of drought has affected Chile, especially the north of the country, where regions with a strong scarcity of water resources have a growing demand of water (Herrera-León et al., 2022).

Wastewater (WW) treatment is mandatory and very important for recovering this scarce resource for human activities and reducing the negative effect of the industrial activity (Saleh et al., 2022). One of the most important industries located in this region of water scarcity, the north of Chile, is the culture of the scallop ***Argopecten purpuratus*** (Bakit et al., 2022, González et al., 2021). This is a bivalve mollusc relevant to the Chilean aquaculture market (Guenard, 2021;). It grows on suspended submarine polyethylene plastics structures. In these systems, called lantern and pearl nets, biofouling occurs (Sievers et al., 2019). It is a progressive settlement of marine microorganisms and invertebrates on the surface of the structures (Kim et al., 2021), which is a complex problem for this industry. On the one hand, it causes a negative effect on the flotation of the system. On the other hand, it also affects the growth of the scallops (Bera et al., 2018), since it reduces the seawater flow rate across the lantern and pearl nets (Jeong et al., 2021), disturbing the stability of suspended culture systems (Nobakht-Kolur et al., 2021).

To remove the biofouling from the culture systems high pressure water jets are used for washing. This treatment consumes a significant amount of freshwater (Comas et al., 2021), producing a high quantity of WW that needs to be treated, especially in the actual context of drought. There are no publications in the literature about the treatment of this kind of water. However, it is known that coagulation/flocculation is a useful pretreatment which attains high levels of solid removal, and enhances the performance of further photo-induced processes, as photo-Fenton process (GilPavas et al., 2017).

Photo-Fenton is a very interesting advanced oxidation process (AOP). It is useful to achieve a high removal of organic pollutants, due the formation of powerful oxidants as hydroxyl radicals ($OH^{\bullet}$). These are based on the decomposition of hydrogen peroxide by ferrous/ferric species, which are photocatalized using UV irradiation. These oxidants allow the degradation of recalcitrant compounds (Elmobarak et al., 2021). Under the reaction, ferric aquo-complexes as $Fe(OH)^{2+}$ are formed. They have a high irradiation absorption, ranged between 290 and 410 nm (Pignatello et al., 2006). As a source of UV irradiation, it is possible to use solar energy, allowing to reduce operational costs.

Other useful AOP is ozonation, which produces hydroxyl radical and other radicals, such as $O_2^{-\bullet}$ and $HO_2^{\bullet}$, that react with organic compounds (Kim et al., 2020). These reactions can happen via two main mechanisms, directly with dissolved ozone or indirectly due the generation of $OH^{\bullet}$ (von Sonntag & von Gunten, 2015). The direct reaction, at acid pH, oxidizes selectively the electron-rich moieties, such as activated aromatics, non-protonated amines, phenols, and olefins. In the indirect way, ozone produces the non-selective $OH^{\bullet}$, at basic pH, that interacts with organic molecules (Asghar et al., 2022; Staehelin & Hoigne, 2002). A way to improve the removal of pollutant contaminants under ozonation is the use of UV radiation or photo-Fenton, allowing to intensify the efficiency of the treatment (Prada-Vásquez et al., 2021; Fernandes et al., 2020).

The recovery of freshwater from saline sources is being made for decades by means of desalination techniques, especially reverse osmosis (RO). However, membranes developed for this technology are not tolerant to waste waters prone to fouling, and the whole process would require an excessive amount of pretreatments. Membrane distillation (MD) is a thermal desalination technique using hydrophobic microporous membranes made of different materials, such as polytetrafluoroethylene (PTFE), polypropylene (PP), polyethylene (PE) and polyvinylidene fluoride (PVDF), which are inert to most inorganic and organic compounds. The driving force of the process is the vapour pressure gradient generated by the temperature difference between the hot and the cold side of the membrane (Alkhudhiri et al., 2012). MD has important advantages over RO, such as its higher tolerance to salinity, organic matter and suspended solids in the feed, its comparable salt rejection factor, and the use of low temperatures and atmospheric pressure (Drioli et al., 2015). In addition, modularity and scalability of MD makes possible its use at a small scale to complement new processes such as that proposed in this work.

The application of MD in the treatment of WW has gained growing interest in the last 15 years (Julian et al., 2022). The removal of key contaminants was extensively studied. For example, due to its harmful action in agriculture, the removal of boron from saline residual waters in Asia, North America and Australia was evaluated, resulting in rejection factors of up to 99.8%, much higher than those obtained with RO (Eryildiz et al., 2021; Tomaszewska et al., 2020; Criscuoli et al., 2010). Separation of arsenic was also assessed considering several groundwater sources in different regions of Latin America. Estimations concluded that MD powered by geothermal energy has the potential to reduce the concentration of arsenic below 10 µg/L (the maximum allowed in potable and irrigation water by the World Health Organization) without the chemical pretreatments required to achieve that level with RO modules (Tomaszewska et al., 2020).

MD treatments were also assessed for a wide variety of WWs, such as those coming from metallurgical, textile and petrochemical industries. Furthermore, promising results were reported from the treatment of WWs with a high amount of organic compounds, such as those from municipal sewage and from food industry (Julian et al., 2022; Chin et al., 2020). The comparative assessment carried out by Davey et al., (2021) demonstrated that MD is a suitable technology to treat real black WW with very high concentrations of organic compounds, although the operational mode must be taken into account to maximize the performance. Results showed that air gap MD (AGMD) performed better than vacuum MD (VMD) for the removal of those contaminants. The strong vacuum suction applied in the latter operational mode promoted pore wetting and sped up the formation of fouling on the membrane, despite improving the permeate flux by around 30%. A maximum COD removal of up to 98% was achieved in AGMD mode.

Regarding food industry, the treatment of WW from aquaculture is nowadays of special interest because of the increasing number of fish farms around the world (Chin et al., 2021). Compounds containing nitrogen and phosphorus from the animal metabolism also cause severe negative effects in water ecosystems, such as eutrophication and unhealthy conditions (Dauda et al., 2019). Recovery of at least 86% of those elements by MD was demonstrated by Teoh et al. (2022) using real water from a Malaysian fish farm.

The ability of MD to treat aquaculture WW and its advantage over other membrane operations was thus previously demonstrated. However, as far as authors are aware, there is a lack of studies about the complete treatment of the WW resulting from the washing system of the culture of scallops. Therefore, this is the first research focused on the evaluation of the feasibility of a novel WW treatment line, which consists of coagulation/flocculation, filtration, ozone/solar photo-Fenton and MD, aiming at finally recovering a reduced volume of concentrated saline residue, and freshwater with minimum organic carbon, thus with enough quality to be used in irrigation.

The removal of organic matter achieved in this research was higher than that published by Borba et al. (2022), who obtained a removal of COD of 48% using ozone in the treatment of wastewater coming from biodiesel production. Also, Blanco et al. (2014) reported a removal of a 79% of COD using photo-Fenton process in the decontamination of real textile wastewater. Asaithambi (2017) achieved an almost complete removal of colour of wastewater from an industrial distillery, using ozone and photo-Fenton.

To the best known of the authors, there are no papers published about the treatment of WW coming from the washing operations of industrial cultures of scallops, which is of great importance in the current context of water scarcity. Therefore, the aim of this research is to evaluate the use of a treatment line consisting of coagulation/flocculation, filtration, advanced oxidation by ozone/solar photo-Fenton, and MD, to process WW coming from the washing operations of a Chilean aquaculture facility of the scallop *Argopecten purpuratus*.

2.- Materials and methods

WW used in this study came from the washing operations carried out in an industrial culture facility of the scallop *Argopecten purpuratus*, placed in Tongoy, Coquimbo (Chile). Lanterns used as suspended systems for growing this scallop (Figure 1a) were rinsed with water to remove the residual biofouling attached on them. The main species conforming the fouling are *Ciona intestinalis* and *Polydora sp*., that provoke important economic damage to the industry (Bakit el al., 2022).

The liquid phase was then separated from the organic debris by means of a rotary drum filter (Figure 1b), which generated WW with very dark colour, aggressive odour, and high presence of total suspended solids (TSS), organic matter as chemical oxygen demand (COD) and total organic carbon (TOC). Figure 1c shows this residual WW, and Table 1 summarises its main analytical parameters.

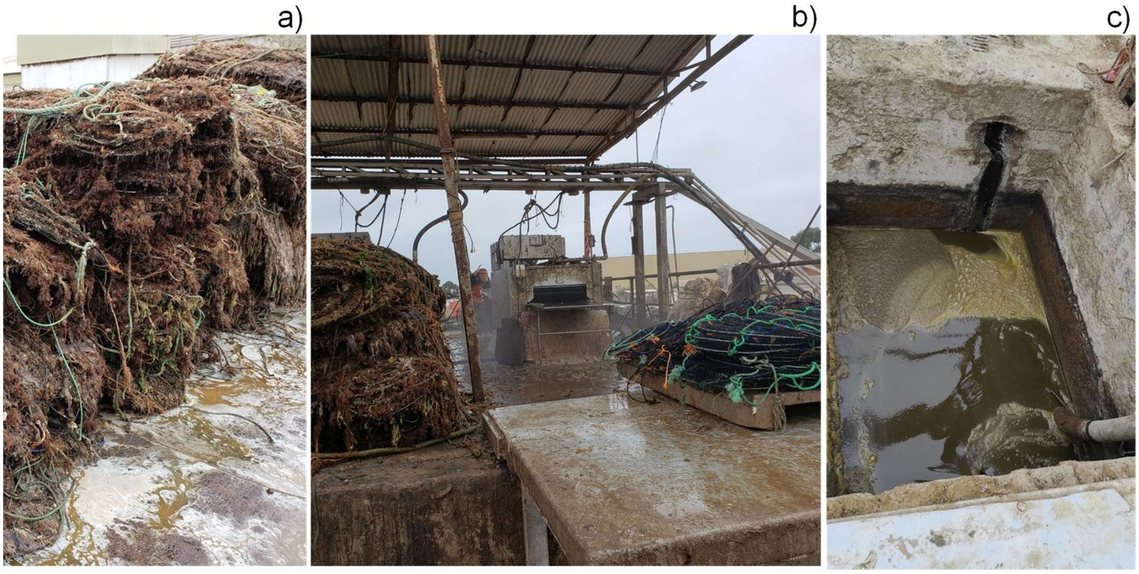

Fig. 1. a) lanterns before washing, b) wash machine and lanterns before and after the wash, c) WW generated.

This work was focused on studying the complete treatment to depurate the resulting WW. To do that, a volume of 200 L was sampled from the rotary drum filter, and operations described below were applied in sequence to the remaining aqueous solution.

Table 1. Main characteristics of the WW from the wash of systems used in the culture of ***A. purpuratus***

Parameter	Value
pH	8.4
COD, mg/L	6236.2
TOC, mg/L	2309.7
Colour, PCU	205.4
Conductivity, mS/cm	38.4
TSS, mg/L	204.7

2.1. Wastewater treatments

WW samples were transferred to the Central Laboratory for Marine Aquaculture of the Marine Sciences Department of the Universidad Católica del Norte, Coquimbo, Chile. They were stored in the dark and refrigerated at 3 °C, before characterization and evaluation of a train of treatments. Due the complexity of the samples, which include a wide scope of organic compounds and salts in the WW, several processes are required to attain an acceptable quality of water. A sequence of coagulation/flocculation, advanced oxidation and thermal desalination processes was studied to remove the pollutants present in the WW. Fig. 2 shows a schematic diagram of the processes carried out.

2.1.1. Pretreatments

The first technology evaluated was coagulation/flocculation to remove the TSS, COD and colour of the WW, using 1 and 2 g/L of $FeCl_3$ (Merck) and alternatively using 0.1 g/L of a cationic polyelectrolyte (Polyacrylamide, C1250, Tianfloc). A cationic polyelectrolyte was selected, taking into consideration the initial alkaline pH of the WW (around 8.4) and its affinity with the pollutants to be removed (López-Maldonado, 2014). Both coagulation/flocculation processes were carried out stirring the reagent for 5 minutes at 150 rpm. After that, the supernatant of the coagulated/flocculated WW was taken out and submitted to a filtration at 5 µm.

2.1.2. Advanced oxidation processes

Subsequently, an ozone/solar photo-Fenton process (O_3/s-pF) was applied to remove the remaining organic matter and microorganisms in the WW. The O_3/s-pF run was carried out using the solar photoreactor and methodology applied in Poblete et al. (2019a). Briefly, the pH of the coagulated/flocculated and filtrated WW was adjusted to 3, using H_2SO_4, due to the iron radicals that act as a catalyst in the photo*-Fenton process are very dependent on the pH of the solution and react if maximums lever al pH near to 3 It was then placed in a solar photo-reactor, which is a cylindrical borosilicate glass tube (110 mm external diameter and 1100 mm length), collated in the focus of a compound parabolic collector (CPC), that has a solar irradiated area of 0.36 m^2. The run was done in batch mode during 24 h of sunlight. The glass tube and the parabolic mirrors were placed at 30° of slope, which corresponds to the latitude of Coquimbo. The photo-Fenton reaction was applied under $FeSO_4$ and H_2O_2 concentrations of 0.3 g/L and 0.67 g/L, respectively, and in each sample, the amount of H_2O_2 consumed was replaced. The concentrations of the reagent used were chosen taking into account the previous results obtained by our research group (Poblete et al., 2019b). The addition of ozone gas into the solar reactor was made using an ozone generator (3 gO_3/h, Netech CH-KTB 3 G, 100 W).

2.1.3. Membrane distillation

After performing the coagulation/flocculation, filtration, and O_3/s-pF processes, the remaining WW was treated using a lab-scale MD unit placed in the solar MD facilities at CIEMAT-Plataforma Solar de Almería (Spain). As explained before, for the proper functioning of the photo-Fenton process the pH of the WW was set to 3. However, after that and to protect the piping and instrumentation of the MD unit against the hot acid feed solution, the pH was adjusted to 8.3 using NaOH prior to processing it.

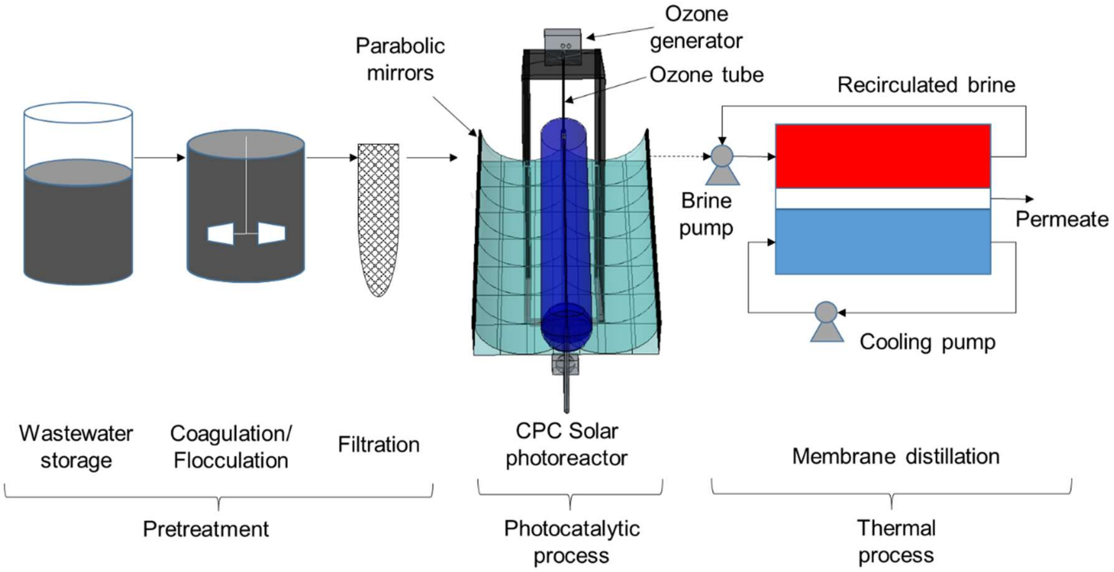

Fig. 2. Schematic diagram of the treatments applied to WW samples.

The MD unit showed in Fig. 3a was supplied by the company SolarSpring GmbH and bears a plate-and-frame module with effective membrane area of 25 x 15 cm^2. Experiments were performed using a commercial MD membrane coupon with area of 375 cm^2, the main features of which are summarised in Table 2. Fig. 3b illustrates the system flow diagram, indicating the main currents and operational variables. Heating and cooling flows circulate counter-current in separate circuits, which include the corresponding tanks for feed and cooling water, respectively. Electrical supply was used for a heater and a separate chiller unit. Feed water was the remaining WW from the previous stages, with electrical conductivity EC = 19.5 mS/cm (Jumo CTI-500), equivalent to a concentration of 12.5 g/L of marine salt (according to correlation in Ruiz-Aguirre et al. (2019)). It enters the MD module with hot inlet temperature (TEI) of 80 °C (which is the maximum allowed to preserve the integrity of the membrane material) and feed flow rate (FFR) of 50 and 150 L/h (Krohne Optiflux 4300). Setpoint of cooling flow rate (CFR) was in all cases the same as FFR. Inlet temperature of cooling water (TCI) was fixed to 25 °C, which is a typical value used in MD literature.

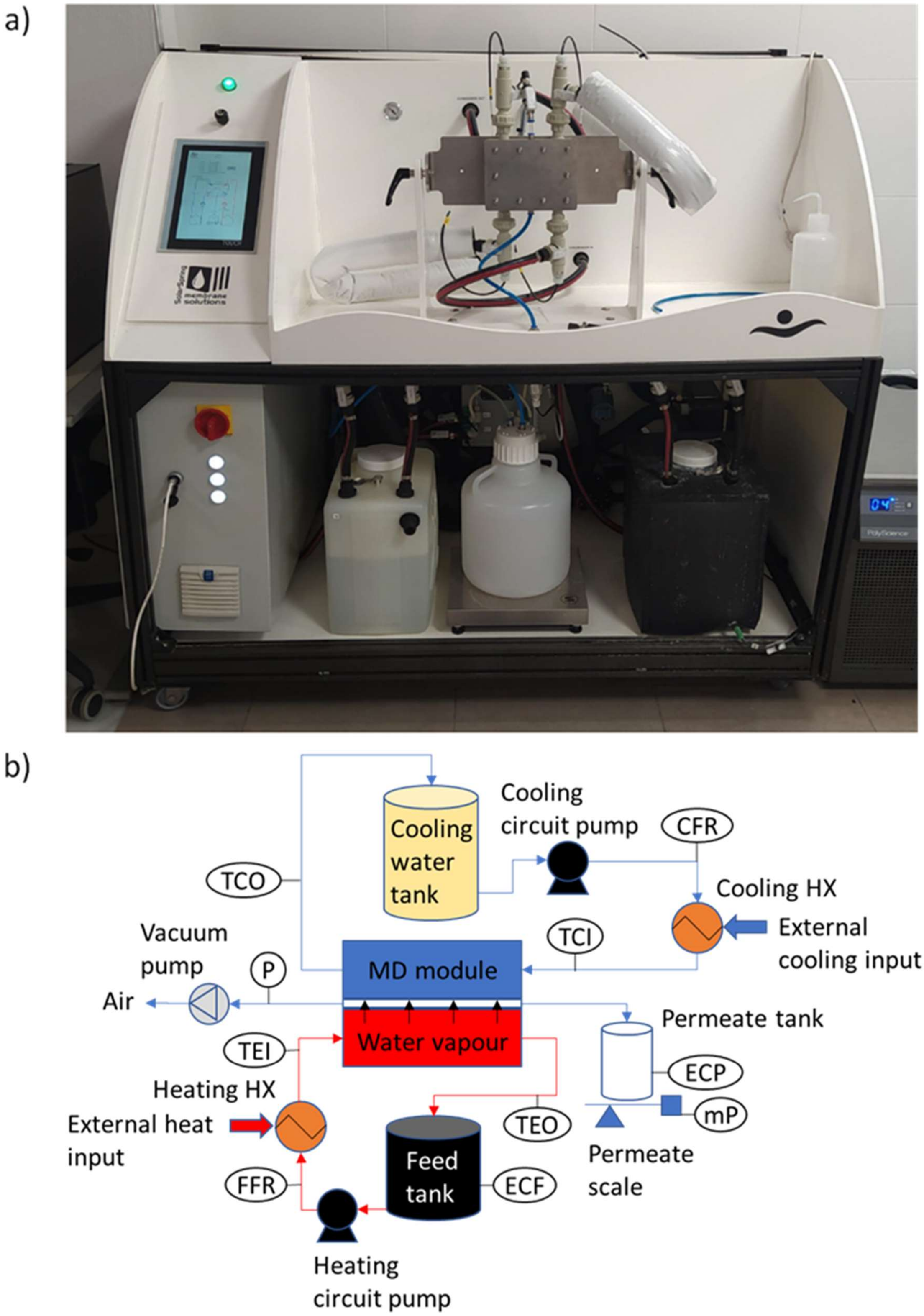
a)
b)
Cooling water tank
Cooling circuit pump
CFR
TCO
Cooling HX
External cooling input
TCI
Vacuum pump
P
MD module
Air
Permeate tank
Water vapour
TEI
ECP
Heating HX
mP
External heat input
TEO
Feed tank
Permeate scale
FFR
ECF
Heating circuit pump

Fig. 3. MD unit of SolarSpring used in this study (a), and system flow diagram (b).

The MD unit was initially operated in air gap MD (AGMD) mode. Vapour coming from the hot feed circulating through the evaporation channel of the module passed through the hydrophobic pores of the membrane and through the gap. The pressure gradient generated by the temperature difference between both sides of the membrane is the driving force of the process. That vapour was then condensed onto a condensing plate inside the module and collected in the permeate vessel. The latent heat of condensation was delivered to the water in the cooling channel. Hot and cold currents leave the module at outlet temperatures TEO and TCO, respectively. The feed was recirculated through the module to concentrate it further until the minimum water level required in the feed tank to operate the unit was reached. Temperatures were measured with probes with maximum measurement error of 0.05 K. Pure permeate was produced simultaneously, and its electrical conductivity (EC) was measured online to control its quality (Jumo Midas S-05). The mass of permeate produced was measured by means of a precision balance (Soehnle LN 15265). In addition, TOC was quantified externally in permeate samples of each experiment.

In addition, the MD system integrated the necessary improvements to extract air from the gap, that is, modifications in the gap of the module, a vacuum circuit with a manual regulation valve, a pressure transmitter (Jumo N816.3KN18), and a vacuum pump (KNF N836.3AP.40E). Therefore, vacuum-assisted AGMD (V-AGMD) mode was also tested by reducing the absolute pressure inside the gap down to 400 – 500 mbar in all cases, high enough not to influence the condensation process inside the MD module, unlike in vacuum MD.

Table 2. Features of the commercial MD membrane used in this study.

Supplier	Aquastill BV
Material	PE without backing
Mean pore diameter, μm	0.32
Thickness, μm	95
Porosity, %	85

2.2. Analytical methods and measurements

To assess the removal of pollutants present in the WW along the applied treatments, the following parameters were measured: COD, colour, total solids, TOC, pH and solar irradiance and conductivity.

The colour of initial and treated WW samples was determined according to the colorimetric platinum cobalt method in Platinum Cobalt Units (PCU), in a Hanna HI83099 spectrophotometer

COD was measured according to the EPA 410.4 procedure and Colorimetric Method, using the same spectrophotometer. pH was measured using a pH meter (WTW 3150i). TOC was determined by measuring the dissolved organic carbon by direct injection of the filtered samples into a Shimadzu 5050A TOC analyser. All the samples were measured in triplicate.

The UV solar irradiance was measured using a UV pyrometer Kipp&Zonen, (Model CUV 5) tilted at 30°, equipment that provides data regarding solar irradiance, expressed in W/m^2 and allows to determine the accumulated solar UV irradiance (kJ/L) using Equation 1 (Malato et al., 2003):

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n UV_{g,n,} \frac{A_i}{V_R}, \quad \Delta t_n = t_n - t_{n-1} \tag{1}$$

where Q_{UV} is the amount of UV_A irradiation energy received by the CPC during the experiment per unit of volume of WW; t_n is the time of exposure (s) and $UV_{G,n}$ is the global UV irradiance average during treatment time (W/m^2).

Regarding MD, measurements of the main operational variables and the corresponding instrumentation have been previously mentioned. Permeate production rate was calculated dividing the permeate mass (mP) by the corresponding time interval. More common in the context of MD is the use of permeate flux (PFlux), which is the permeate production divided by the membrane area. Methods used to quantify the amount of pollutants in the permeate were the same that have been described before. Thermal efficiency of MD is usually quantified by the specific thermal energy consumption (STEC), defined as the thermal energy input required to produce 1 m^3 of permeate (Equation 2)

$$STEC = \frac{FFR \cdot Cp_{feed} \cdot \rho_{feed} \cdot (TEI - TCO)}{PFlux \cdot A} \tag{2}$$

where FFR is the feed flow rate, TEI in the inlet temperature of the hot feed, TCO is the outlet temperature of the cooling water, PFlux is the permeate flux, A is the membrane area, Cp_{feed} is the specific heat capacity of the feed, and ρ_{feed} is the density of the feed. These two physical properties have been estimated as a function of temperature and salinity by applying correlations given by Sharqawy et al. (Sharqawy et al. 2010)

3.- Results and discussion

3.1. Pretreatments

In the evaluation of the coagulation/flocculation process, $FeCl_3$ was applied. However, the treatment produced no changes in the water in terms of removal of TSS and colour. Therefore, the addition of 0.1 g/L of Tianflod cationic polyelectrolyte was tried instead of using $FeCl_3$. The cationic polyelectrolyte allowed obtaining a significant improvement on the parameters measured, with a change in the concentration from 204.7 to 28.1 mg/L of TSS, 6236.2 to 4985.7 mg/L of COD, and 205.4 to 126.7 PCU of colour, before and after the treatment, respectively. This represents a relative decrease of 85.9%, 20.0% and 38.3% of TSS, COD and colour, respectively.

The removal of TSS after the addition of cationic polyelectrolyte was due to these substances reducing the electrostatic repulsion between the particles in the wastewater. This is explained by the compressed double layer (Ajao et al., 2018) or DLVO theory, so called because of its developers (Derjaguin, Landau, Verwey, and Overbeek), that describes charged particles with a double layer of counterions surrounding the particle. The concentration of ions in the diffuse layer decreases with distance from the particle surface until the concentration of ions equals that of the bulk solution. The polyelectrolyte decreases the repulsion between particles, permitting the aggregation of organic matter and particles (Sobeck & Higgins, 2002).

After the filtration process the WW changed from 28.1 to 15.4 mg/L of TSS, from 4985.7 to 2995.3 mg/L of COD, and from 126.7 to 109.4 PCU of colour, achieving a relative decrease of 45.2%, 39.9% and 13.6%, respectively.

3.2. Advanced oxidation process

Due to the application of the O_3/s-pF process, the TSS in WW did not suffer any change. However, the COD changed from 2995.3 to 448.7 mg/L, and from 109.4 to 18.7 PCU of colour, with a relative decrease of 85.0% and 82.9%, respectively.

The removal of COD and colour from the WW after the application of O_3/s-pF process can be explained by the formation of hydroxyl radicals in the advanced oxidation process carried out, in which the reagents Fe^{2+} and H_2O_2 produce $OH^{\bullet}$, which oxidizes the recalcitrant organic compounds (eqs. 3 and 4) (Wang et al., 2021):

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$ (3)
$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + H^+ + OH^\bullet$ (4)

UV irradiation (*hv*) in the case of this research was obtained from a solar source. Under the presence of ozone in the same photoreactor, it is possible to enhance the production of $OH^\bullet$ in the WW because of the following reaction (Kim et al., 2022):

$$3O_3 + OH^- + H^+ \rightarrow 2\ OH^\bullet + 4O_2 \quad (5)$$

Also, the interaction between ozone and H_2O_2 produces the hydroxyperoxyl and the hydroxyl radicals, as can be seen in equation (6), increasing the oxidation potential in the reactor:

$$O_3 + H_2O_2 \rightarrow HO_2^\bullet + OH^\bullet + O_2 \quad (6)$$

3.3. Membrane distillation process

Finally, the remaining WW coming from the AOP was treated in the MD unit. Setpoints of TEI, TCI, and CFR were those aforementioned in section 2.1.

Steady-state experiments were initially carried out to determine how the removal of TOC from the feed WW was influenced by the FFR and the operational mode. Feed concentration of all compounds was maintained constant because the permeate was returned back to the feed tank after analysing it. Regarding permeate productivity, on one hand, increasing the FFR resulted in higher PFlux in both AGMD and V-AGMD operational modes. This is because a raise in feed velocity (from 8.3 to 24.8 cm/s in this module) improves the temperature gradient between both sides of the membrane. This leads to a larger transmembrane vapour pressure difference, which is the driving force of the MD process. However, to upscale the operation using full-scale spiral-wound modules (which are the most thermally efficient so far), the trade-off between permeate productivity and heat recovery must be considered. An increase in the thermal energy input into the module (for example, by increasing the FFR) leads to a reduction in the thermal efficiency of the MD process because less amount of heat is recovered in the cooling side of the module than when working at reduced FFR (Winter et al., 2017). On the other hand, the application of light vacuum inside the gap of the module (400 – 500 mbar abs) increased 29% the PFlux in comparison with that of conventional AGMD operation (Fig. 4). Operation in V-AGMD is thus beneficial for desalination because permeate productivity improves without a relevant increase of electrical conductivity in the permeate (Andrés-Mañas et al., 2020). In all the experiments performed, this was lower than 50 µS/cm, which means that salt rejection factors were higher than 99.8%.

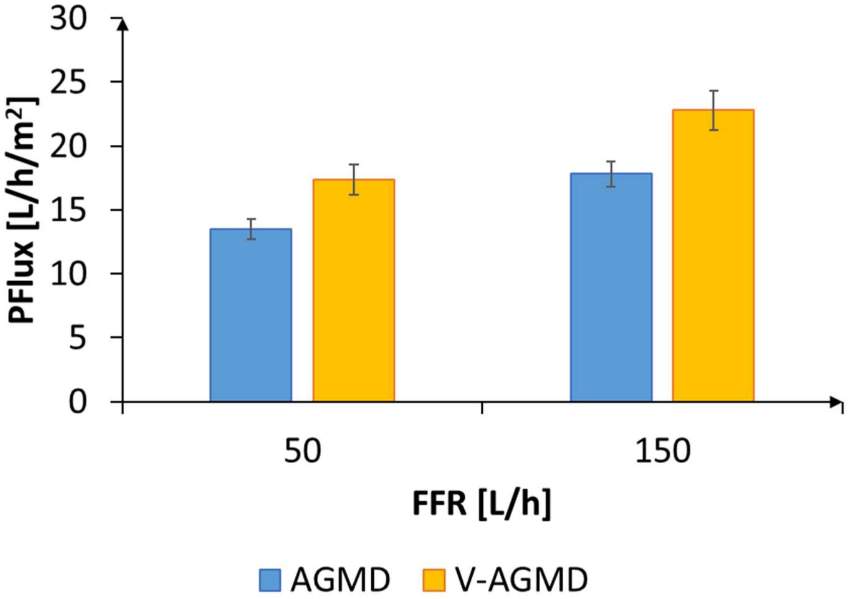

Fig. 4. Permeate productivity as a function of FFR and operational mode (TEI = 80 °C, TCI = 25 °C).

Given that V-AGMD improves PFlux, the STEC, i.e., the external heat needed to produce one cubic meter of permeate, was reduced, compared to that of AGMD mode. Considering FFR = 150 L/h, the estimated STEC of AGMD was 13800 kWh_{th}/m^3, whereas that of V-AGMD was 9600 kWh_{th}/m^3. However, the additional suction force of the vacuum pump to remove non-condensable gases seems to promote the pass of some volatile organic compounds through the membrane pores. Because of that, the values of permeate TOC were up to 38% higher in V-AGMD than in conventional AGMD, as shown in Fig. 5.

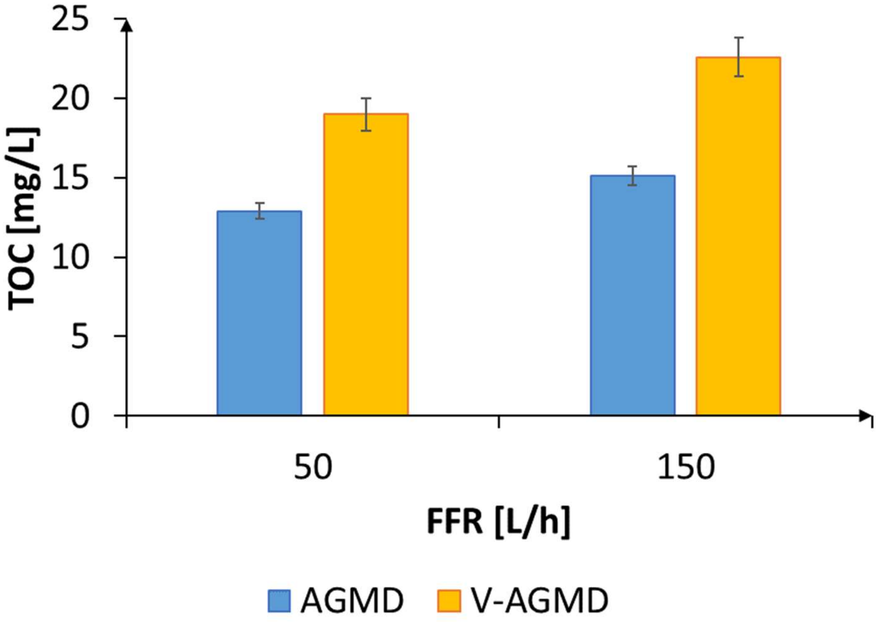

Fig. 5. Results of permeate TOC as a function of FFR and operational mode (TEI = 80 °C, TCI = 25 °C).

Taking into account the results obtained in steady-state experiments, conventional AGMD was the operational mode that minimized the TOC of the permeate, which is the main aim of this work. The use of FFR = 150 L/h was a more appropriate choice because the benefit of increasing PFlux surpassed the drawbacks of worsening 15% the permeate TOC. However, the advantages of V-AGMD for conventional seawater desalination at pilot-scale have been demonstrated, especially in terms of thermal efficiency. The aforementioned values of STEC correspond to the operation at a laboratory scale to proof the concept proposed in this study, and are not representative of those of a hypothetical upscaled plant, which can be as low as 40 kWh_{th}/m^3 (Andrés-Mañas et al., 2022). This way, the trade-off between the TOC level of the permeate and the thermal efficiency must be considered in the design and operation of a large plant, depending on the required objective.

Finally, operating conditions TEI = 80 °C, FFR = 150 L/h, TCI = 25 °C were used in a batch concentration of 5 L of the same WW, the initial TOC concentration of which was 57.5 mg/L. To concentrate the feed WW further, it was recirculated through the MD module. The permeate was separated from the residual brine, which was therefore reducing its volume. Concentration experiments started when the first drop of permeate was collected and measured, and they finished when the minimum level of TOC was reached.

Feed WW was concentrated four times during the MD process, up to 50 g/L (equivalent to EC = 65.7 mS/cm). Permeate production was almost constant around 0.67 L/h, with a maximum variation of 2% due to the saline concentration increase along time. This demonstrated the high tolerance to salinity of the commercial MD membrane used, despite the presence of organic compounds in the feed. Besides, the hydrophobicity of the membrane avoided the accumulation of a permanent fouling layer on its surface, and thus the vapour flux was not worsened during the process due to that. Moreover, a maximum EC of 47.7 µS/cm was measured in the permeate, which is equivalent to a salt rejection factor of 99.83% and suggested that no pore wetting occurred.

Regarding the removal of organic compounds, Fig. 6 illustrates that the TOC in the permeate was reduced during the batch treatment, from 166.2 mg/L in the first sample to 5.2 mg/L in the last, after 2.7 h. With these results, the rate of TOC removal was 8.7 mg/h on average. In terms of COD, that reduction was from 448.7 to 14 mg/L.

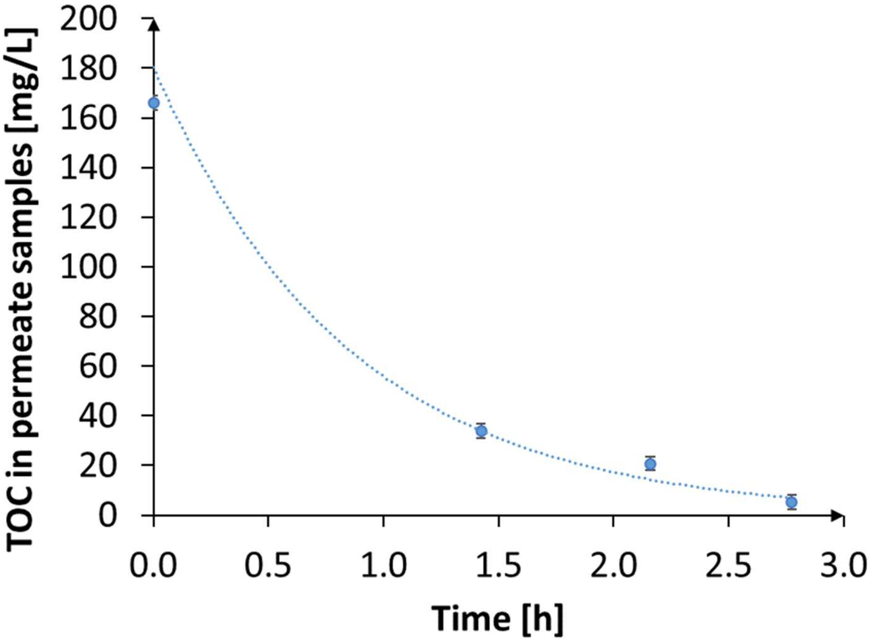

Fig. 6. Evolution of TOC in the permeate with the time of batch treatment (TEI = 80 °C, FFR = 150 L/h, TCI = 25 °C).

Taking into account the initial values of TOC in the feed WW volume, a reduction of 97% was estimated. This result is in accordance with that obtained previously by Davey et al., (2021) treating also real WW.

Figure 7 summarises the variation of the parameters measured along the whole train of operations.

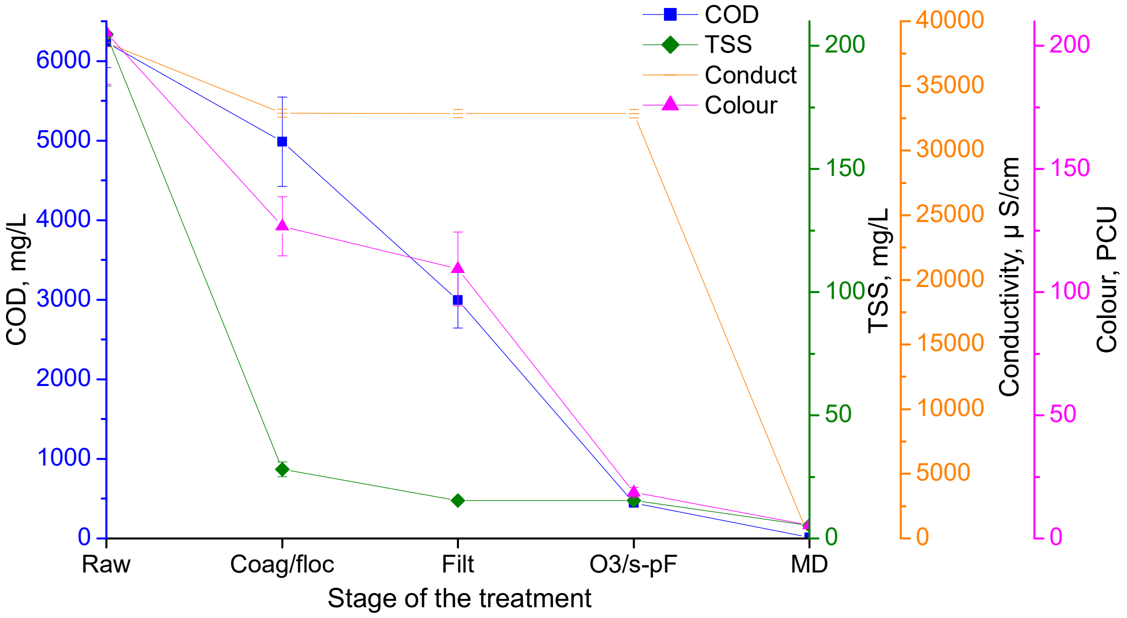

Fig. 7. Changes in TSS, COD, electrical conductivity and PCU of the wastewater. Error bars represent the standard deviation of the results (n = 3)

Finally, Fig. 8 shows pictures of the change in the appearance of the WW along the treatment processes carried out. It is possible to see a significant improvement in the quality of the water after the different treatments.

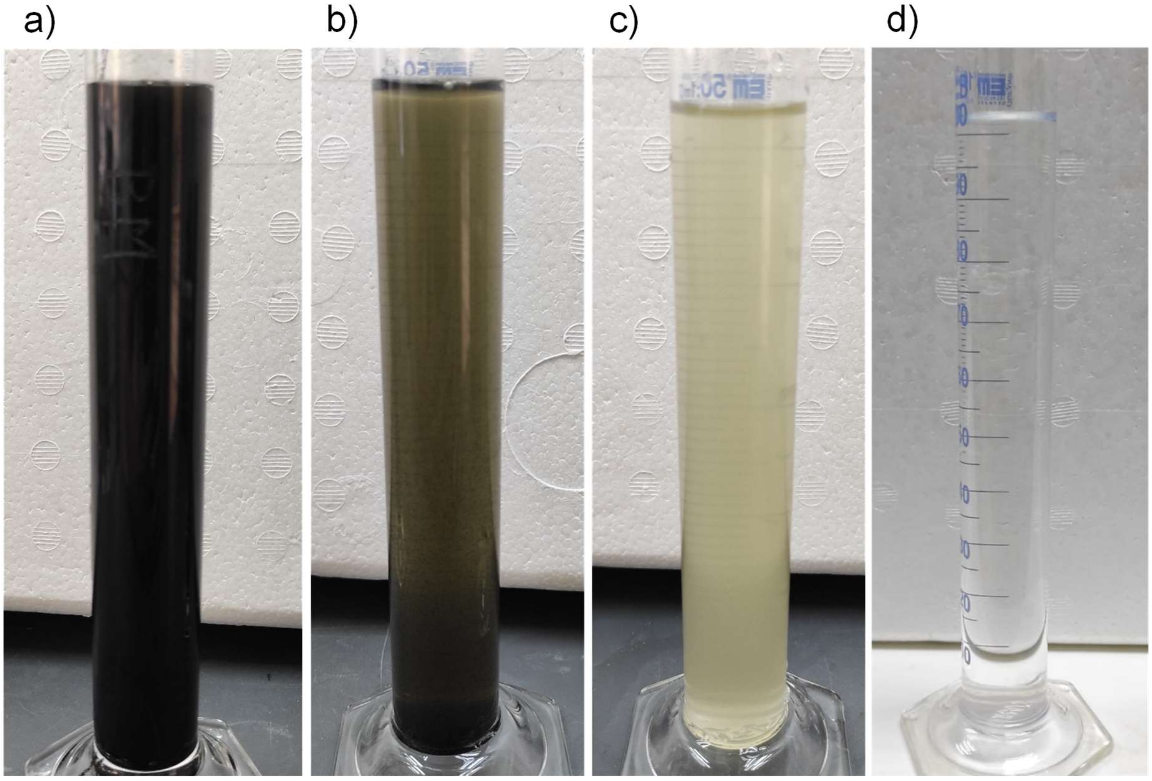

Fig. 8. Pictures of the sample of WW: a) raw; b) after coag/floc; c) after O_3/s-pF and d) after the membrane distillation process

4.- Conclusions

In this work, a novel process line to remove pollutants in wastewater coming from an industrial culture of scallops has been assessed. This line includes coagulation-flocculation, an advanced oxidation process based on solar photo-Fenton, and finally a membrane distillation step, which yields freshwater with very reduced TOC and a concentrated brine.

The coagulation/flocculation process carried out using $FeCl_3$ did not produce any change in TSS and colour in the water. However, the use of a cationic polyelectrolyte had a significant impact on TSS, COD, and colour, obtaining a removal of 85.9%, 20.0% and 38.3%, respectively. The filtration process allowed a removal of TSS, COD and colour of 45.2%, 39.9% and 13.6%, respectively. With the O_3/s-pF process the TSS in WW did not suffer any change, however removals of COD and colour of 85.0% and 82.9%, respectively, were achieved. These treatments allowed improving the quality of the highly polluted wastewater, enough to remove suspended solids and organic matter. However, the WW still contained salts that required the use of a separation process for removal.

MD was demonstrated as a suitable final operation to separate freshwater from the feed WW coming from the AOP, and to obtain simultaneously a concentrated residual brine with reduced volume, easier to process. Commercial MD membrane used (made in PE) showed excellent applicability in removing salts from the WW solution, not only from seawater or saline sources free of hard contaminants, as it is commonly described in the state of the art. Besides, the high hydrophobicity of the membrane pores contributed to avoid wetting and permanent fouling during the process. This demonstrated that specific membrane designs with special features do not seem to be necessary in principle to remove contaminants in WW coming from aquaculture. Values of TOC removal up to 97% were estimated using the commercial MD membrane. The AGMD operational mode showed less permeate productivity and lower thermal efficiency than V-AGMD, but higher rejection of TOC, which is the main aim of this concept proof. Because of that, subsequent studies dealing with upscaling this WW treatment process must take into account the trade-off between the thermal efficiency of MD and the organic matter level of the resulting freshwater. Moreover, a subsequent cost analysis will be necessary to increase the scale and the degree of maturity of the process, in order to determine the most convenient operating conditions of each individual operation.

The integration of the pretreatments, the O_3/s-pF and the MD processes achieved a significant removal of all the measured pollutants present in the WW, allowing to clean a very contaminated industrial wastewater, and permitting its recovery for different uses, demonstrating that it is a very useful strategy for dealing with the climate crisis and water scarcity.

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