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Full-scale pilot plant

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Occurrence, identification and removal of microplastics in a wastewater treatment plant compared to an advanced MBR technology: Full-scale pilot plant

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ABSTRACT

Microplastics are of increasing interest as one of the most important threats to the natural environment and aquatic life. One of the main pathways of microplastics entering the aquatic and terrestrial environment are wastewater treatment plants. The aim of this study was to investigate the occurrence and removal of MPs in both wastewater and sludge from an MBR-based and a WWTP. The focus is on the amount of microplastics emitted into the environment, the efficiency of removal in wastewater treatment plants and how their operation and design, could be improved to reduce the presence of these pollutants in the effluent. The results showed that the influent (SI) had mean concentration of 507 ± 70 MPs L^{-1}, in the reactor tank (SRS) the concentration increases to $1.77 \times 10^7 \pm 1.61 \times 10^7$ MPs kg-1 (dw) and in the permeate (SP) the estimated amount of microplastics decreased to 1.58 ± 1.08 MPs L^{-1}. This is a removal efficiency of 99.69%, with respect to the estimated average MPs. After the clarifier (SC) and sand filtration (SSF) a mean of 17.38 ± 4.71 MPs L^{-1} and 2.93 ± 1.50 MPs L^{-1} respectively were found, resulting in an efficiency of 96.58% and 99.42%, respectively, regarding the inlet water of the treatment plant. The two predominant forms in all samples (except for SCS) were fragments and fibers. In total 25 types of polymers were detected, and only 5 resulted in all types of samples, the most detected polymer families were Acrylates and Polyethylenes.

1. Introduction

Nowadays, plastics are highly present materials, as they are widely used for all kinds of purposes, including many fields, industrial or domestic, as they are simple compounds, cheap to produce and very versatile compounds. This has caused plastic to be one of the most discarded materials worldwide [1,2]. The plastics industry manufactured 367 Mt of plastics in 2020 [3]. Considering population growth and current plastic consumption and waste, plastic production is expected to double by 2025 and triple by 2050 [4].

Microplastics (MPs) are plastic particles with smaller than 5 mm in size. The importance of research related to the occurrence and fate of microplastics (MPs) in the aquatic environment has been increasing in all sectors in recent years [5,6]. Increased awareness of the problem and the development and improvement of methods to measure MPs facilitate their study. The problem of environmental MPs pollution is expected to persist for hundreds of years [7]. According to the World Health Organization (2019), the global production of plastics has increased almost exponentially since the 1950 s. Therefore, if not properly used and recycled, the release of MPs is expected to double or triple. MPs are released into the environment by plastics industries, the tearing and wearing of plastic items, the use of personal care products [8] and the washing of synthetic textiles [9].

One of the largest inputs of MPs into the environment is known to come from wastewater treatment plants (WWTPs) [10]. Many authors have presented results on the detection and quantification of MPs in WWTP effluents [11,12] and other authors have presented removal efficiencies of MPs in WWTPs. Although, conventional WWTPs can efficiently remove MPs (64–99%) [13], when considering the daily

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Nomenclature

EMMA	ethylene/propylene copolymer.
EVA	ethylene-vinyl acetate.
HDPE	high density polyethylene.
LDPE	low density polyethylene.
Mpart	microparticles.
MPs	microplastics.
OM	organic matter.
PA	polyamide.
PAM	polyacrylamide.
PE	polyethylene.
PEMA	poly (ethyl methacrylate).
PES	polyester.
PET	polyethylene terephthalate.
PEVA	poly (ethylene-vinyl acetate).
PHDA	poly (hexadecyl acrylate).
PHDMA	poly (hexadecyl methacrylate).
PMMA	poly (methyl methacrylate).
PODA	poly (octadecyl acrylate).
PP	polypropylene.
PS	polystyrene.
PU	polyurethane.
PUEA	poly (ester-urethane acrylate).
PVA	polyvinyl acetate.
PVC	polyvinyl chloride.
PVDC	polyvinylidene chloride.
PVME	poly (vinyl methyl ether).
PVS	poly (vinyl stearate).
SI	influent samples.
SRS	reactor sludge samples.
SP	permeate samples.
SC	clarifier samples.
SSF	sand filters samples.
SCS	concentrate sludge samples.
UTS	urea/thiourea/sodium hydroxide method.
WPO	wet peroxide oxidation.
WWTP	wastewater treatment plant.

discharge rate, this percentage would not be sufficient. The total amount of MPs would still be discharged daily into the environment; therefore, the final effluent can act as one of the main routes of entry of MPs into aquatic environments [14]. According to Liu et al. [15] the abundance of MPs in the influent ranged from 0.28 particles L^{-1} to 3.14×10^4 particles L^{-1}, while that in the effluent ranged from 0.01 particles L^{-1} to 2.97×10^2 particles L^{-1}. The high production of treated wastewater still contains a large amount of MPs particles, so further reduction is essential to protect the environment. Another study showed an initial analysis of the WWTP influent and determined the amount of MPs in the wastewater entering the plant with values between 185.4 and 897.6 MP L^{-1}; whereas in the WWTP effluent amounts between 12.2 and 64 MP L^{-1} were detected, indicating a removal efficiency of this pollutant of up to 97.1% [2].

The application of effective wastewater treatment technologies is necessary to prevent further spread of emerging micropollutants in the environment. The membrane bioreactor (MBR) is an association of adsorption, biodegradation and membrane separation processes that allows obtaining a high-quality effluent with low levels of total suspended solids (TSS), turbidity, biological oxygen demand and pathogens, since small particles are rejected by the membrane [16]. MBR technology has many advantages over classical activated sludge treatment, with higher sludge ages and higher sludge densities, which provide improved pollutant removal properties. The MBR process facilitates more efficient removal of particulate MPs pollutants from wastewater than traditional settling tanks [17]. On the other hand, the benefits of MBR technology are often accompanied by increased wastewater treatment costs and a potentially hydraulic risk related to fouling problems. Therefore, when designing the wastewater treatment plants of the future, it is very important to be clear about the pros and cons One of them, is the efficiency related to MPs removal.

The efficiency of different technologies for the treatment of MP contaminated wastewater effluents has been reported, although some of them at pilot scale or with short analysis periods [18]. Bayo et al. [18] reported that the mean concentration of microplastics was 4.40 ± 1.01 MP L^{-1} for the influent, 0.92 ± 0.21 MP L^{-1} for MBR permeate and 1.08 ± 0.28 MP L^{-1} for RSF (Rapid Sand Filter) filtrate. Other authors [19] report data of 99.9% removal of MPs during MBR treatment (from 6.9 to 0.005 MP L^{-1}). Cai et al. [20] reported data on the effluent of the MBR of 1.5×10^{13} MPs d^{-1} a 10.2×10^{11} MPs d^{-1}.

Circular economy (CE) is based on the concept that products, materials (and primary materials) should remain in the economy as much as possible, and that waste should be treated as secondary raw materials that can be recycled for processing and reuse [21]. WWTPs can be an important part of circular sustainability due to the integration of energy production and resource recovery during the production of clean water, they must become "ecologically sustainable" technological systems [22]. Due to that current trend of circular economy in WWTPs [23] and water reuse, it is necessary to achieve a high-quality final effluent, to be able to reuse the effluent for agriculture, industry, municipality or even discharge the effluent to the water receiver. In order to avoid environmental pollution from insufficiently treated wastewater discharged into the environment or subsequently reused in the environment, the European Union has approved a regulation concerning minimum requirements for water reuse where, in Annex II, it is stated that depending on the results of the risk assessment there would be additional requirements [24]. Therefore, the importance of knowing the amount and type of MPs in reclaimed water prior to its reuse or discharge is emphasized, being one of the potential micropollutants in wastewater to be taken into account [25]. One of the current problems is that despite reuse regulations, MPs are not yet regulated so there are no limit values for microplastics in the effluent before discharge or in water for reuse.

The aim of this study was to investigate the occurrence and removal of MPs in water and sludge from a MBR-based WWTP compared to conventional WW treatment. Specifically, the objectives were: (1) to analyze the concentration of MPs in the inlet of a WWTP located in Jutland, Denmark, (2) to evaluate the difference in form and composition of MPs in the MBR feed (Reactor Sludge Samples; SRS) and permeate samples (SP) over a period of 2 months working continuously, (3) to evaluate the presence and form of MPs in different locations of the WWTP, such as the inlet (SI), in the clarifier (SC), after sand filtration (SSF) and in the concentrated sludge before polyelectrolyte addition (SCS) and (4) to evaluate the removal performance of MPs by the above mentioned technologies. Evaluating how the different systems perform in parallel and throughout the WWTP simplifies the information on an approach to deal with the microplastics problem; it is also important to know how the MBR systems operate with respect to the size and, specially, the shape of the plastics.

2. Materials and methods

2.1. Description of the WWTP

Søholt wastewater treatment plant is located at Ege Allé in Silkeborg (Denmark, GPS coordinate 56.175203, 9.583300). The plant was built in 1976 and is continuously being expanded. The WWTP collects both

urban and industrial wastewater and, has a treatment capacity of 105.000 PE (Person Equivalents). The different treatment units that compose it consist of a biological tank for nitrification and denitrification, chemical phosphorus removal, a clarifier and a sand filtration system, in addition to the sludge line. In 2009 an anaerobic digester for the sludge treatment and biogas production were installed and used for self-energy, making the treatment plant approximately 20% self-sufficient.

2.2. MBR system

A pilot-scale 250 L aerobic immersed MBR with a submerged hollow-fiber ultrafiltration membrane module, located after the primary treatment, was installed in the plant to treat wastewater. This treatment was installed in the WWTP to evaluate and compare the effectiveness of the treatment within the WWTP itself. The membrane module was a laboratory scale ZeeWeed ZW500–4 M supplied by SUEZ. The size was of 0.9/1.9 mm with a 0.02–0.04 mm pore size with a hydrophilic and non-ionic surface consisting of a polyvinylidene fluoride active layer. The membrane module was continuously aerated to minimize fouling, this was combined with a recirculation line from the permeate tank to the membrane module, which periodically refluxed to remove fouling layers. The MBR system was prepared for a period of 3 weeks prior to the experiments. Before and during the experiments, the physical and chemical parameters of pH, conductivity, suspended solids, total solids and COD were analyzed to evaluate the effectiveness of the MBR system.

The MBR was fed with the primary treatment effluent for the three months of operation. In order to develop biomass, a high solid retention time was kept at 1750 d during this time, while hydraulic retention time was kept at 20.8 h. The working flow rate was approximately of 10 L h^{-1}.

To evaluate the separation efficiency by the membrane, the retention coefficient of the membrane (R) was carried out based on the following Eq. (1).

$$R = 1 - Cp/Cf \quad (1)$$

where Cp is the concentration in permeate (SP), and Cf is the concentration in the MBR reactor (SRS).

Assuming the WWTP influent (SI) as the membrane feed water, the observed membrane retention coefficient (R_{obs}) would follow the Eq. (2).

$$R_{obs} = 1 - Cp/Cf_{inlet} \quad (2)$$

where Cp is the concentration in permeate (SP), and Cf_{inlet} is the concentration in the WWTP influent (SI).

2.3. Experimental design and sampling

Samples were collected at the Silkeborg WWTP every two weeks between October 14, 2021 and December 6, 2021. Prior to sample collection, from September 2021, the MBR was prepared and turned on until stable operating was achieved. Also, sampling methods were optimized to mitigate potential sample contamination during on-site operations, sample transfer and laboratory analysis.

Water samples were filtered through 100 mm (4-inch) diameter stainless steel sieves of one to three mesh sizes (1 mm, 355 and 100 μm). For the analysis of MPs, a 5 L water sample was collected in the WWTP influent (SI), in addition to a 110 g of wet weight sludge from the reactor sludge (SRS) (the sludge had a moisture content of 99.2% ± 0.2%, dry weight (dw) of the samples were between 0.9 ± 0.2 g dw). In the case of the permeate, a tank was used to collect and accumulate the week's water in order to obtain a composite sample. The amount of water collected for MPs analysis in the permeate (SP) was of a 100 L per sample, 30 L for the clarifier samples (SC) and a 100 L for the sand filters (SSF). Finally, for the concentrated sludge (SCS), from the treatment plant's sludge line, 30–50 g was sieved, depending on the wet weight of the sample (the sludge had a moisture content of 96.9% ± 0.2%, the dw of the samples was between 1.2 ± 0.3 g dw). A summary of the sampling points is shown in Fig. 1. The volume of samples varies according to the organic load at each sampling point, which can interfere with the correct analysis.

The permeate and sand filters samples were collected with the sieves in situ, always carrying an extra sieve of the same size in parallel, to collect any possible environmental contamination. The field blank samples were subjected to the same pretreatments as samples in the laboratory. The influent and sludge samples were processed in the laboratory. Samples were immediately poured into glass beakers. All containers were sealed with aluminum foil and transferred to the laboratory in coolers and stored at 4 °C and in the dark until further treatments.

2.4. Microplastics isolation

Once the samples were sieved, the material was collected using distilled water in beakers and allowed to dry in an oven at 75 ºC. After the samples were dried, for microplastics insolation, the wet peroxide oxidation (WPO) method was used [26]. In this case, 20 mL of 0.05 M Fe (II) and 20 mL of 30% v/v hydrogen peroxide (H_2O_2) were added to the dry sample. Then, a magnetic stirrer was added, and samples were covered with a watch glass to avoid any possible external contamination. The samples were then placed on a magnetic stirring device, set at 75 ºC and 200 rev/min for 30 min. Finally, the samples were filtered through 53 μm mesh sieve to remove excess reagents, collecting the samples in the same beakers. For this purpose, there were collected with as little ultrapure water as possible so that the next step of cellulose removal could be performed correctly. If a considerable volume of ultrapure water was needed for collection, it was dried again in the 75 °C oven.

To remove cellulose, 40 mL of a solution of urea 8%, sodium hydroxide 8% and thiourea 6.5% (by weight) were added for every 100 mg of dry sample. The method is called UTS because of the acronym of its reagents (Urea/Thiourea/Sodium Hydroxide). The UTS method has already been used by authors in other works with good results [27]. The beakers were placed in the freezer at − 20 °C for 40 min and then placed in agitation until room temperature was reached. After that, the samples were passed through a 53 μm mesh sieve and washed 15 times with 30 mL of ultra-pure water. Finally, the samples were recovered in the same beakers.

For influent and sludge samples, the process (WPO+UTS) was repeated up to three times, in order to reduce organic matter (OM) and cellulose so there could be no interference with the analysis of microplastics. For the permeate samples, the WPO method was performed only once, without the need to apply the UTS. Once the organic matter and cellulose were removed from the samples, the density separation step was performed. In this case, 40 mL of 5 M NaCl was added and allowed to decant overnight. Finally, the samples were filtered through a 0.8 μm pore size polycarbonate filter with a diameter of 45 mm and then

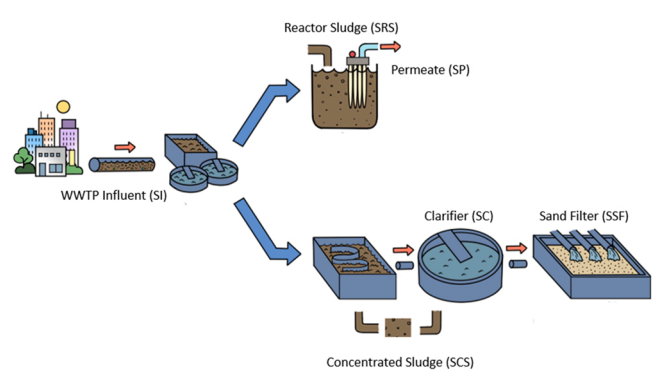

Fig. 1. Sampling points.

dried for approximately 2 h at 40 °C.

2.5. Physical and chemical analysis

Physical and chemical characterization of microplastics was carried out. In the case of physical characterization, the filters were analyzed using a Carl Zeiss Axio Imager M1m optical microscope. Considering the filter area, according to the principle of random fields to avoid bias and assuming that microparticles are randomly distributed on the filter surface [28], a certain number of pictures were taken of each sample and a particle count was performed. After quantification, the total number of microparticles (Mpart) was calculated by estimation on all samples. At the same time, the Mpart were classified into four categories according to their shape: fiber, filament, fragment, and sphere. On the other hand, the chemical characterization consisted on the identification of the polymers by with the use of a PerkinElmer Spotlight 400 and Spectrum 3 Fourier Transform Infrared Spectroscope (ATR-FTIR) in attenuated total reflection mode. FTIR measurements were performed for MPs determination of the MPs, generating a spectrum for each particle analyzed. A total of 922 suspected particles were analyzed of which 681 were microplastics. A similar number of particles were selected in each filter analyzed, considering that each sample had several filters due to the size separation performed. The obtained spectra were compared with the polymer spectra library, and the type of MPs was determined when the match rate was higher than 70% (Joint Research Centre, Institute for Environment and Sustainability [29]). To improve the reproducibility of the work and the cross-referencing of the FTIR peaks, several examples of FTIR spectra of the most identified polymers can be found in the supplementary material (Appendix A. Supplementary data).

2.6. Reagents and chemical products used

Iron II sulphate 7-hydrate purissimum (99.5%), sulphuric acid (95–98%), thiourea (98.5%), sodium hydroxide extrapure and hydrogen peroxide (30% v/v) were supplied by Panreac (Barcelona, Spain). The pure urea pearls (98.5%) and extra-pure sodium chloride were provided by Scharlau (Barcelona, Spain). Filters (0.8 μm polycarbonate filters PC membrane 47 mm) were purchased from Isopore™ (Darmstadt, Germany) and Petri Slide were provided by Millopore^{M} (Darmstadt, Germany). Hypochlorite de sodium was supplied by Novadan (Kolding, Denmark).

2.7. Quality assurance and quality control (QA/QC)

Monitoring contamination throughout the process is important for the analysis of MPs. Attention should be given to implementing consistent QA/QC practices from the beginning and throughout the study process, including study design, sampling and collection, extraction, in addition to analysis, in order to strengthen the reliability and comparability of microplastic data [30].

According to Rochman et al. [31], all plastics should be removed from the surface of field or laboratory equipment prior to use. Strong cleaning practices are important when one is concerned about possible contamination, which is why, in this study, all glassware and stainless steel was washed with a concentrated detergent and rinsed up to 5 times with ultrapure water [32].

All equipment used for sampling and in the laboratory was prewashed with distilled water several times and covered with aluminum foil. The sampling material was transported in closed coolers that preserved the isolation before, during and after sampling. Cotton coat and gloves were worn during sampling and analysis to avoid contamination by plastic fibers. For blank controls, sieves were placed at the sampling points to collect contamination in situ and were treated similarly in the laboratory. Also, reagents were filtered prior to use and blanked with ultrapure water in a similar way to the samples. Samples of the stainless steel sieves from the airborne contamination generated in the on-site sample collection and treated similarly with the same reagents, in addition to the reagent blanks, were analyzed as samples.

3. Results and discussion

3.1. Abundance of microplastics and removal efficiency

Despite the different organic matter and cellulose removal treatments, not all particles collected in the samples are plastic [33]. A total of 922 suspected particles were analyzed of which 681 were microplastics. Fig. 2 shows the proportions of MPs in relation to the total Mpart found in each sample (SI, SRS, SP, SC, SSF and SCS). Non-plastic particles were identified as additives, particulate hormones, cellulose, inorganic particles, or polymers with a search match of less than 70% (Joint Research Centre, Institute for Environment and Sustainability [29]) which were discarded from the final MPs data as required.

As shown in Fig. 2, the SI and SCS samples have the least non-plastic particles, 79.35% and 96.41% of plastics, respectively, compared to SRS, SP, SC and SSF with 48.49%, 65.71%, 58.37% and 42.19%, respectively. These results are similar to those found by Franco et al. [13] in the influent waters of the WWTP of Cadiz, southern Spain with a total of 72% of MPs. The SRS samples underwent the same WPO and UTS cycles as SI and SCS (between 2 and 3 times), however, due to the concentration of particles produced in the reactor, more OM was observed in the samples once the treatments were carried out. Samples from the SP, SC and SSF were only treated once with WPO as they have less OM concentration.

Table 1 shows the average concentrations of both systems (WWTP and MBR system).

Comparing the yields obtained between the treatment proposed for the elimination of MPs (MBR) and those currently existing at the WWTPs, in a single technology such as the MBR it is possible to achieve equal or even higher yields than those achieved by the whole system including the biological reactor, decanter and sand filtration. This would reduce the space required for the WWTPs, in addition to obtaining a concentrated sludge that can be treated using other technologies. Furthermore, all removed MPs are concentrated in the sludge, in contrast to a conventional plant in need of a tertiary treatment, where MPs are in both sludge and the sand filter. In terms of energy consumption, it can be more efficient to have an MBR than all the conventional treatment units. Fig. 3 shows how the membrane system (SP) operates more efficiently than the clarifier (SC) and slightly superior to the sand filter (SSF).

Table 2 shows the results obtained from the 5 samplings analyzed at each of the different location studied (SI, SP, SC, SSF, SRS, SCS). In SI, SP, SC and SSF (the most aqueous matrices) data is presented in MPs L^{-1} while for sludge samples (SRS and SCS), results are shown in MPs kg^{-1} (dw). Taking into account the behavior of the MBR reactor, Table 1 shows that the influent water from the treatment plant (SI) has an

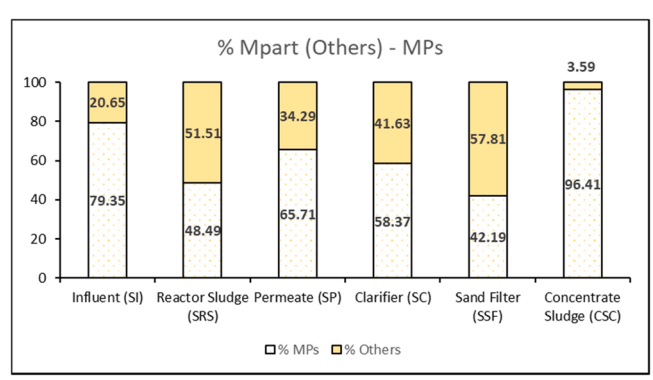

Fig. 2. Percentage of Microplastics with respect to total Microparticles analyzed.

Table 1
Average concentrations of both systems (WWTP and MBR system).

	WWTP	MBR	Units
Influent (SI)	507 ± 70	507 ± 70	MPs L^{-1}
Clarifier effluent (SC)	17.38 ± 4.71 MPs L^{-1}	–	MPs L^{-1}
After Sand filter (plant effluent) (SSF)	2.93 ± 1.50	–	MPs L^{-1}
Permeate (MBR effluent) (SP)	–	1.58 ± 1.08 MPs L^{-1}	MPs L^{-1}
Sludge (SCS and SRS)	$4.60 \times 10^6 \pm 1.51 \times 10^6$	$1.77 \times 10^7 \pm 1.61 \times 10^7$	MPs kg^{-1} (dw)
Removal efficiency	99.42	99.9	%

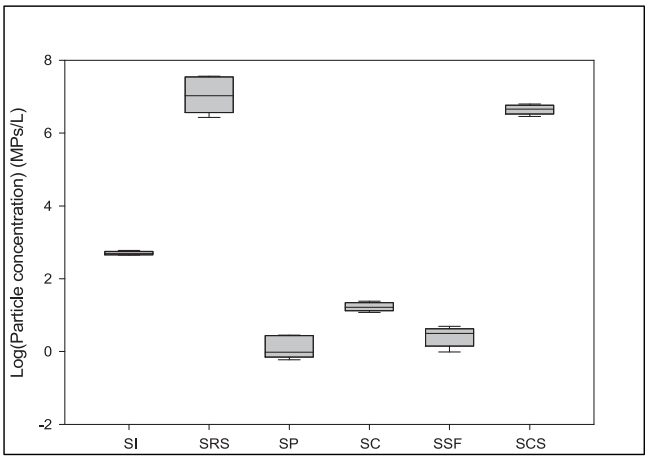

Fig. 3. Log-Normal distribution to particle concentration (MPs L^{-1}) in Influent (SI), Reactor Sludge (SRS), Permeate (SP), Clarifier (SC), Sand Filter (SSF) and Concentrate Sludge (SCS).

Table 2
MPs L^{-1} estimated in SI, SP, SC and SSF and MPs kg^{-1} (dw) estimated in SRS and SCS, during the 5 samplings carried out.

Samples Code	SI (MPs L^{-1})	SRS (MPs kg^{-1})	SP (MPs L^{-1})	SC (MPs L^{-1})	SSF (MPs L^{-1})	SCS (MPs kg^{-1})
1	447.41	5.01×10^6	2.83	23.97	3.59	3.90×10^6
2	457.13	3.37×10^7	2.69	11.80	0.97	2.89×10^6
3	528.59	3.63×10^7	0.60	19.90	4.90	6.29×10^6
4	596.71	2.69×10^6	0.84	14.72	2.06	5.39×10^6
5	502.25	1.06×10^7	0.96	16.49	3.13	4.52×10^6

average concentration of 507 ± 70 MPs L^{-1}, in the reactor tank (SRS) the concentration increases to $1.77 \times 10^7 \pm 1.61 \times 10^7$ MPs kg^{-1} (dw) and in the permeate (SP) the estimated amount of microplastics decreases to 1.58 ± 1.08 MPs L^{-1}, and therefore a removal efficiency of 99.69%, with respect to the average MPs estimated at the inlet of the treatment plant (SI) is obtained. The higher concentration of MPs in SRS compared to SI reflects the high SRT of the MBR. If we consider the concentration of MPs in the reactor, we can say that it is higher than 99.9%.

Talvitie et al. [19] obtained a removal efficiency of 99.9% using MBR while Cai et al. [20] yields resulted in a 93.2%. Other authors reported that the MBR permeate contained 0.4 MP L^{-1} compared to the final process effluent in a conventional WWTP (1.0 MP L^{-1}) with influent samples and digested sludge values of 57.6 ± 12.4 MP L^{-1} and 170.9 ± 28.7 MPs g^{-1} dw (1.7090×10^5 MPs kg^{-1}), respectively [6]. Bayo et al. [18] reported that the average microplastic concentration was of 4.40 ± 1.01 MP L^{-1} for the influent, and 0.92 ± 0.21 MP L^{-1} for MBR. There is a risk of MPs release from the polymeric membrane in all systems, Table 2 shows how the accumulation of MPs in SP is higher during the first weeks. This may be due to the washing of the membrane itself, which can increase the concentration of polymers in the permeate. Also, [34] have shown how contaminant particles, such as MPs, can damage the membrane surface by enlarging the surface pores, creating new pores and decreasing the membrane thickness through excessive direct contact, which can compromise the integrity of a membrane [35].

Additionally, Table 2, shows the increase of MPs from day 1–3 in SRS. After taking sample 3, the sludge was purged from the MBR reactor, and the membrane was cleaned, which resulted in a decrease in the concentration of MPs in sample 4, which once again increased its concentration in sample 5. This shows that the system is working correctly, and the MPs are being retained in the reactor tank and are becoming more concentrated. In addition to obtaining a permeate better than the biological and same/better quality than after the sand filter (tertiary treatment). The MPs was concentrated in a smaller volume of sludge which is beneficial for subsequent disposal.

Considering the conventional treatment available at the WWTP, Table 1 shows that in the SC and SF samples a mean of 17.38 ± 4.71 MPs L^{-1} and 2.93 ± 1.50 MPs L^{-1} respectively were found, obtaining an efficiency of 96.58% and 99.42% into the clarifier and sand filtration respectively regarding the inlet water of the treatment plant. For the clarifier of a WWTP located in the city of Sari, on the south coast of the Caspian Sea, it was 96.7% (423 ± 44.9 MP m^{-3}) [36]. These values are in line with those given by other authors. Funck et al. [37] reported that only 79% of MPs smaller than 100 μm, 50 μm and 10 μm are removed by tertiary sand filtration of WWTPs. Hidayaturrahman and Lee [38] showed that primary and secondary treatment processes effectively remove microplastics from wastewater with efficiencies ranging from 75% to 91.9%. The removal efficiency increased to > 98% after tertiary treatment using rapid sand filtration.

In WWTPs, most MPs (>95%) are transferred from the liquid phase in the activated sludge [39]. Table 2 shows that, in this study, in SCS the amount of estimated MPs remains stable ($4.60 \times 10^6 \pm 1.51 \times 10^6$ MPs kg^{-1} (dw)), while other authors reported in a review that the number of plastics in the sludge samples ranged from 510 to 76,300 particles per kg wet weight (ww) and from 1000 to 240,300 MPs kg^{-1} (dw) [40].

Table 3 shows the estimated value of MPs per day that would be discharged to the medium by the WWTP in general (SCS and SSF) and permeate flow. In this case, taking into consideration the outflow of the WWTP itself, it was considered that the SSF and SP flow rate would be the same. Moreover, since it is difficult to consider the different variations in the flow during the day and the recirculation's of the plant itself, it has been estimated that Qinlet is based on the two outlets provided by the plant, that is, the flow that is discharged after sand filtration and the sludge that is finally removed from the WWTP (Qinlet = QSCS+QSSF). Considering the CAS mass balance, it is observed that the MBR reactor discharges a lower concentration of MPs ($2.35 \times 10^7 \pm 2.01 \times 10^7$ MPs d^{-1}) compared to $4.08 \times 10^7 \pm 2.37 \times 10^7$ MPs d^{-1} in SSF and, as shown in Table 2, the reactor sludge resulted more concentrated in MPs. The mass balance in the WWTP is observed as most of the MPs end up in the sludge, starting from $6.96 \times 10^9 \pm 1.09 \times 10^9$ MPs d^{-1} in SI, $4.08 \times 10^7 \pm 2.37 \times 10^7$ MPs d^{-1} in SSF, and concentrating up to $3.97 \times 10^{10} \pm 1.01 \times 10^{10}$ MPs d^{-1} in SCS. Therefore, this effect is of great importance for future applications, such as soil amendments and similar applications, where the sludge is returned to the medium, and eventually become a risk for the environment [41].

3.2. Occurrence and distribution of MPs

3.2.1. Distribution by particle morphology

Morphology categories and definitions are not standardized, this makes comparisons between studies very difficult [42]. In this study, the distribution of the shapes was based on previous work by the authors [43] where 5 types of shapes were selected. However, due to the impossibility to clearly differentiate some fragments from flakes, these two shapes were unified under the name of fragments, leaving finally 4

Table 3
MPs day^{-1} estimated in SI, SCS, SSF and SP during the 5 samplings carried out.

	Sample code	1	2	3	4	5
Mass balance of CAS	SI MPs d^{-1}	8.7×10^9	6.0×10^9	6.6×10^9	7.3×10^9	6.2×10^9
	SCS MPs d^{-1}	3.09×10^{10}	3.01×10^{10}	5.30×10^{10}	4.71×10^{10}	3.77×10^{10}
	SSF MPs d^{-1}	6.9×10^7	1.2×10^7	6.0×10^7	2.5×10^7	3.8×10^7
	SP MPs d^{-1}	5.4×10^7	3.4×10^7	7.3×10^6	1.0×10^7	1.2×10^7

categories: fragments, fibers, flakes and spheres.

As it can be seen in Fig. 4, the two predominant forms in all samples (with the exception of SCS) were fragments and fibers, with 70.12% and 23.82% in SI, 46.21% and 42.22% in SRS, 29.94% and 67.91% in SP, 45.82% and 41.84% in SC and 45.18% and 49.30% in SSF, respectively. Fragment is the predominant form in all samples, with the exception of permeate where fibers were detected with the highest percentage. The third predominant form is filaments, with spheres being practically non-existent (0.16% in SI, 0.13% in SRS, 1.61% in SC, 0.41% in SSF, 0.07% in SCS and not detected in SP. In SCS the two predominant forms are fragments and filaments with 73.43% and 20.21% respectively, with fibers accounting for 6.33% of the forms studied. The fact that fibers are not predominant in SCS is in accordance with the fibers found in SC and SSF which represent almost 50% of the total, may indicate that the fibers pass all the WWTP treatments and are discharged as they are not deposited in the sludge.

It has been estimated that a single wash of one set of synthetic fiber clothing can release more than 1900 fiber debris [9]. Fibers are highlighted as the most difficult MPs to remove due to an approximately smooth surface and a high length-to-width ratio that prevents them from being captured by small pore sizes [19]. Studies show that fibers are mostly the leftover MPs in WWTP effluents [33,44–46]. According to De Falco et al. [47] the most abundant fraction of detached microfibers was retained by filters with a pore size of 60 μm, with an average length of 360–660 μm and an average diameter of 12–16 μm. Edo et al. [48] showed that in the primary effluent, the projected fiber sizes ranged, in length, from 104 to 4000 μm and, in width, from 5 to 34 μm. In the secondary effluent, it ranged from 144 to 1824 μm in length and 8–89 μm in width. The fibers of the wet sludge were in the range of 213–4716 μm in length and 5–34 μm in width, while the figures for the heat-dried sludge were 71–2224 μm in length and 7–58 μm in width. Considering the authors' average length and width, it is shown that even if the membrane size is between 0.9 and 1.9 mm with a pore size of 0.02–0.04 mm (20–40 μm), fibers can pass through the membrane if they are correctly oriented.

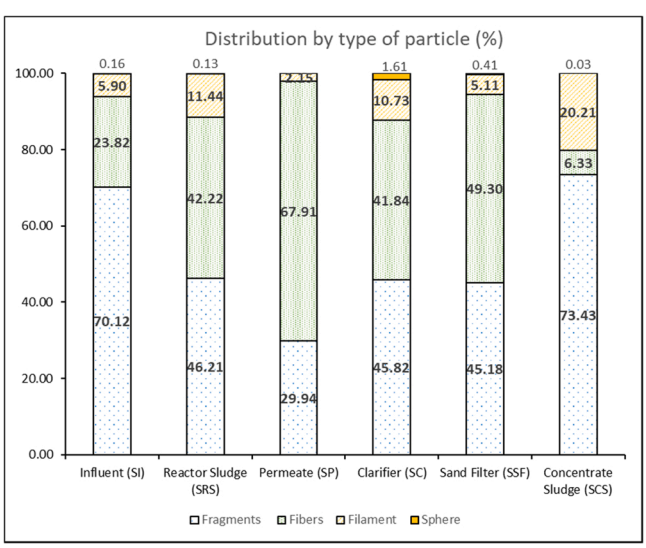

Fig. 4. Distribution by particle morphology (%) in Influent (SI), Reactor Sludge (SRS), Permeate (SP), Clarifier (SC), Sand Filter (SSF) and Concentrate Sludge (SCS).

Fibers accounted in the clarifier by Petroody et al. [36] were 77.5% of the total number of MPs. Long et al. [45] claimed that WWTPs were not effective in removing fibers, where the concentration of fibers in the influent increased significantly from 17.7% to 30.4% in the effluent, these values are slightly lower than those reported in Fig. 4 for both SI and SC. For SP, other authors found that the fraction of fibers remained is the most abundant accounting for 40%, whereas that of fragments and films was approximately of 28% and 32%, respectively [49].

3.2.2. Size distribution

The size distribution was monitored for SI, SRS and SCS samples, which result of greater interest, because the largest fraction of microplastics removed in a conventionally WWTP is trapped in the sludge [50].

Fig. 5 shows that in the 3 types of samples SI, SRS and SCS, half of the particles (50.20%, 49.70% and 52.97% respectively) correspond to the smallest particles, those between 100 and 355 μm, in accordance with what has been described by other authors [13]. It should be noted that for SRS, particles > 1 mm and those between 1 mm and 355 μm are both around 25% (24.84% and 25.46% respectively), while for SI and SCS, 15.47% and 10.22% are of particles > 1 mm and 34.33% and 36.81% for those between 1 mm and 355 μm, respectively. This may be due to the fact that thin and smaller particles such as fibers pass more easily through the membrane while the medium-sized particles remain in the tank and concentrate, thus obtaining a higher percentage of these larger particles in the MBR. It is noted that the pore size should not allow such large particles to pass through, but it is obvious that some do, perhaps due to leakage, and in the case of fibers because of their thickness which is much smaller than their length, as discussed in Section 3.2.1. It is the hydrodynamic particle size that is measured, and the minimum length (shortest distance of the particle) might be much lower than the actual measured size. Approximately 50% of plastic particles identified in sludge samples were between 100 and 500 μm, over 20% were between 10 and 100 μm, and over 10% were between 500 and 1000 μm [40].

3.3. Determination of polymer types

Different types of polymers were detected in the different samples,

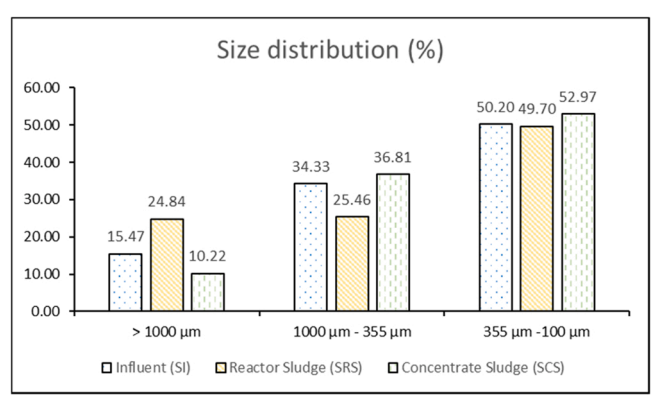

Fig. 5. Relative size distribution (%) in Influent (SI), Reactor Sludge (SRS) and Concentrate Sludge (SCS) (> 1000 μm, 1000 – 355 μm and 355–100 μm).

with a total of 25 types (Copolymers less common, EMMA, EVA, HDPE, LDPE, PA, PAM, PE, PEMA, PES, PET, PEVA, PHDA, PHDMA, PMMA, PODA, PP, PS, PU, PUEA, PVA, PVC, PVDC, PVME and PVS). The most abundant polymer families were Acrylates and Polyethylenes. Considering each of the sampling locations, the number of different polymers that were identified and confirmed with FTIR were 15 for SI, 10 for SRS, 8 for SP, 12 for SC, 11 for SSF and 15 for SCS. Among the 25 polymers identified only 5 (PHDA, PVS, PE, PP and PS) were present in all sample types (SI, SRS, SP, SC, SSF and SCS). This may be because in the different routes of the WWTP, MPs can be released into the environment through pipes and other entry routes such as different equipment used, clothing and environmental contamination [51,52]. Furthermore, it should be considered that these are point samples taken at different stages and that water retention times can vary from hours to days at different stages of the WWTP.

As it can be seen in Fig. 6 the most abundant polymer found in most samples, except for SSF and SC, was PHDA (57.07% in SI, 52.81% in SRS, 27.27% in SP and 69.23% in SCS). In the case of SSF the most abundant polymer was PE (21.43%) and in the case of SC, PVS (32.94%). PHDA was found in 18.82% in SC and 3.57% in SSF. This may indicate that during the settling process the PHDA is trapped in the sludge (SCS). Phase change materials (PCMs) have lately become a subject of active research for storing thermal energy and adjusting temperature. PCMs have been used for energy-efficient buildings, waste

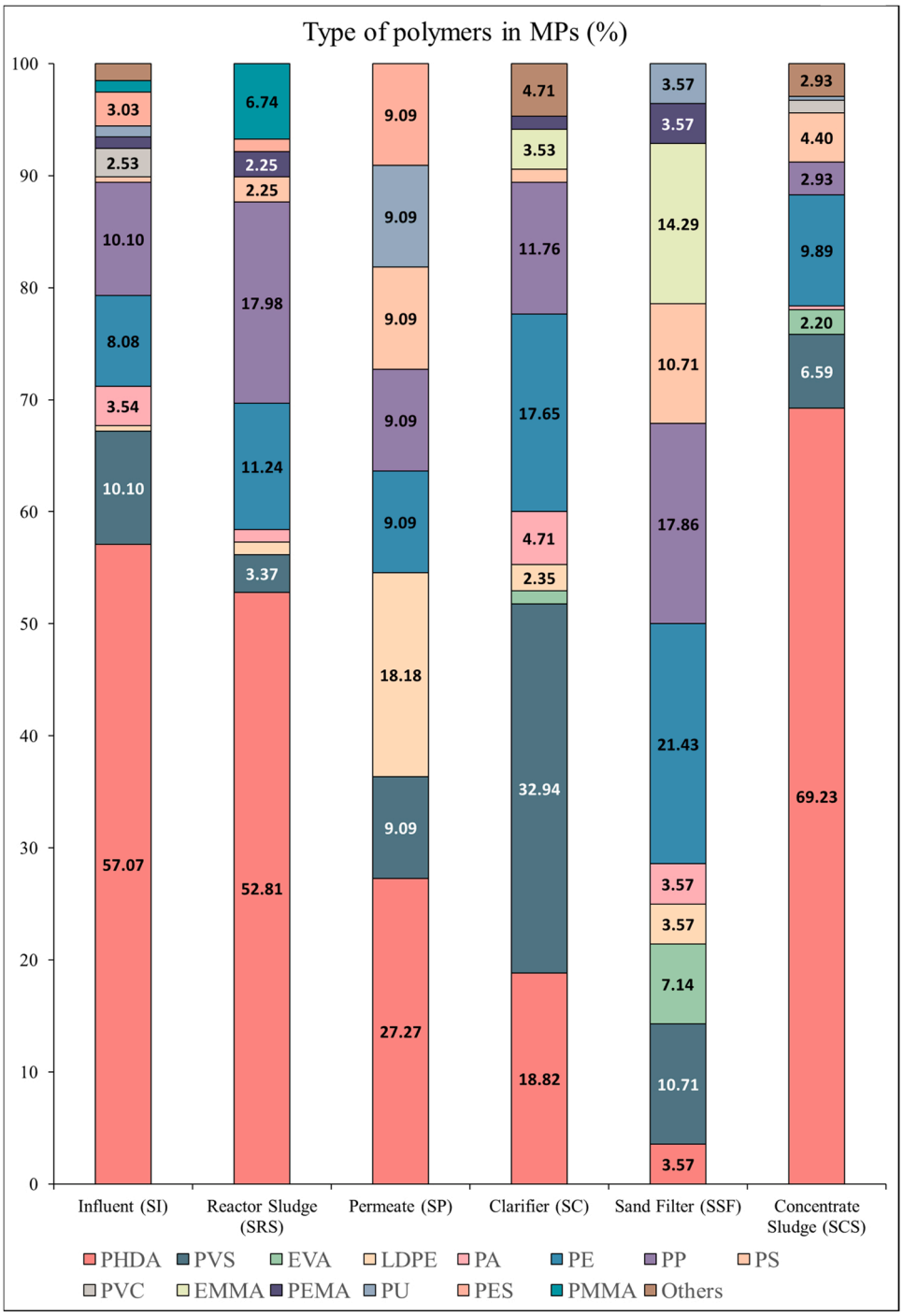

Fig. 6. Type of polymer in MPs (%) in Influent (SI), Reactor Sludge (SRS), Permeate (SP), Clarifier (SC), Sand Filter (SSF) and Concentrate Sludge (SCS).

heat recycling, and thermo-regulating fibers, etc. Hexadecyl acrylate (HAD) is a type of PCM, which has superior properties such as high latent heat or appropriate phase transition temperature [53].

Another polymer of note is PP, present in all samples with percentages ranging from 10.10% to 17.98%, except for SCS (2.93%). PP and PE are two of the most widely used polymers in domestic and industrial use, hence their abundance [54,55]. Sol et al. [56] reported the presence of PP with values between 13% and 39% in the influent of WWTPs and between 3% and 19% in the effluent of several WWTPs with different treatments including clarifiers and sand filtration.

Focusing on the MBR system and its future applications, it is observed that of the 15 polymers detected in SI (PHDA, PVS, HDPE, LDPE, PA, PE, PP, PS, PVC, PEMA, PU, PES, PET, PMMA and PVA) and 10 in SRS (PHDA, PVS, LDPE, PA, PE, PP, PS, PEMA, PES and PMMA) only 8 were detected in SP (PHDA, PVS, LDPE, PE, PP, PS, PU and PES). HDPE, PA, PVC, PEMA, PET, PMMA and PVA were not detected. This may indicate which polymers are more susceptible to membrane rejection. Furthermore, it is important to consider that PHDA had been detected as 57% and 53% of plastics in SI and SRS, dropping to 27% in SP, so we could say that PHDA, despite being the most found polymer in SP, is rejected by the membrane in a high percentage. The opposite happens with PVS with 9% in SP and 10% and 3% in SI and SRS respectively. Results show that despite having a smaller amount of this polymer in the feed, it is found in a higher percentage in the permeate particles. PP and PE behave in the same way, with 18% and 11% in SRS and 9% and 9% in SP, respectively. The lowest rejections are observed for LDPE, PS, PU and PES. Considering that the forms that obtained the lowest rejection were fragments and fibers, it can be observed that PES tends to occur mostly in synthetic fibers from apparel. In addition, LDPE can come from the different plant connections and permeate water collection tanks, since even though we try to avoid as much contamination as possible, there can always be a risk. In the aquatic environment, microplastics (PS, PA, PVC, PUR, PES) that are denser than water tend to sink, while low-density microplastics (PE, PP) may remain afloat or sink under the action of various environmental factors [57]. As a result, they may be retained in the reactor sludge and the WWTP itself and not enter the water line or the membrane itself or enter in smaller quantities.

Analyzing the predominant type of MPs in SI exposed previously, 15 polymers were detected (PHDA, PVS, HDPE, LDPE, PA, PE, PE, PP, PS, PVC, PEMA, PU, PES, PET, PMMA and PVA); those found in SC, 12 types (PHDA, PVS, EVA, LDPE, PA, PE, PP, PS, EMMA, PEMA, COPOLYMER and PUEA) and for SSF, 11 types (PHDA, PVS, EVA, LDPE, PA, PE, PP, PP, PS, PUR, PVME, EMMA and PEMA). In addition to the amount of MPs discharged in the comparison of the MBR System and the SSF, a decrease in the type of polymers from 11 to 8 is observed between the SSF and the SP.

In the present study, the color of each polymer was not analyzed, as done by other authors [58], since Parashar et al. [59] confirmed that black, white, and transparent MPs predominated in all samples of the WWTPs studied. This can be explained by the existence of degradation processes such as prolonged soaking of MPs in different WWTP treatment processes, in addition to an extended exposure to UV radiation that can cause oxidation, leaching and discoloration of paints/dyes and turn them into light colors.

3.4. Rejection coefficient for the membrane

The results obtained for R considering the RSR and SP values as a function of the particles (Mpart kg^{-1} (dw) and Mpart L^{-1}) are shown in Table 4. It can be observed that all values are at R = 0.99, reaching a value of R= 1 for the spherical form, since none were found in the membrane permeate. This coefficient again shows how, although to a lesser extent, fibers offer the lowest rejection of all particles and spheres the most, but all types of MP are almost fully retained by the membrane.

The estimation of R, according to the type of polymer, considering the number of MPs kg estimated in SRS and MPs L estimated in SP are shown in Table 5. Table 5 shows that for each type of polymer, values are equal or greater than 0.99. These results are in accordance with the above, where the polymers with the highest resistance to rejection are LDPE and PES. By calculating the log reduction, it is easier to see the difference in rejection, but the conclusion is the same.

Table 4
Rejection Coefficient for the Membrane according to particle morphology in SRS and SP.

Morphology	R	-log (Cp/Cf)
Fragments	0.99999981	6.72
Fibers	0.99999962	6.42
Filament	0.99999994	7.22
Sphere	1	–

Assuming that the feed to the membrane reactor was only the inlet wastewater, R values resulted in 1 for spheres, 0.997 and 0.996 for filaments and fragments, respectively, and 0.978 for fibers (Table 6) In this case R has a lower value than the R calculated from SRS since the concentration of MPs in SI is much lower than that found in SRS.

Despite not being the feed of the MBR system as such, it can be seen in Table 7 that the results obtained for R in SI and SP are like those shown in Table 5, for R in SRS and SP. These results are in agreement with the previous results, where the polymers with the highest rejection resistance are LDPE and PES.

Data shows that membranes demonstrate a high retention of MPs, of almost 100%. Due to MPs concentration in the bioreactor with a factor of 100, the removal is lower but still very high. The R_{obs} is higher than 94% despite for LDPE.

4. Conclusions

After analyzing and comparing the different current WWTP treatments with the MBR system, the results showed that the influent water of the treatment plant (SI) had an average concentration of 507 ± 70 MPs L^{-1}, in the reactor tank (SRS) the concentration increased to $1.77 \times 10^7 \pm 1.61 \times 10^7$ MPs kg^{-1} (dw) and in the permeate (SP) the estimated amount of microplastics decreased to 1.58 ± 1.08 MPs L^{-1}. This represents a removal of a 99.69% with respect to the average MPs estimated at the inlet of the treatment plant. While in the clarification (SC) and sand filtration (SSF) samples an average of 17.38 ± 4.71 MPs L^{-1} and 2.93 ± 1.50 MPs L^{-1} were found, respectively, obtaining an efficiency of 96.58% and 99.42%, respectively, with respect to the water entering the treatment plant. Thus, the removal by membrane filtration is higher than the removal rate of microplastic after biological treatment and a clarifier and comparable or better than the removal efficiency after tertiary treatment (sand filter).

Considering the form and type of microplastics found in each of the systems, the two predominant forms in all samples (except SCS) were fragments and fibers. Different types of polymers were detected in the samples. In total 25 types of polymers were detected, and only 5 were

Table 5
Rejection Coefficient for the Membrane according to type of polymer estimated of MPs in SRS and SP.

Type of polymer	R	-log (Cp/Cf)
PHDA	0.99999995	7.30
PVS	0.99999976	6.62
LDPE	0.99999855	5.84
PA	1	–
PE	0.99999993	7.15
PP	0.99999995	7.30
PS	0.99999964	6.44
PEMA	1	–
PES	0.99999927	6.14
PMMA	1	–

Table 6
Rejection Coefficient for the Membrane according to particle morphology in SI and SP.

Morphology	R_{obs}	-log (Cp/Cf_{inlet})
Fragments	0.99678774	2.49
Fibers	0.97855377	1.67
Filament	0.99725686	2.56
Sphere	1	–

Table 7
Rejection Coefficient for the Membrane according to type of polymer estimated of MPs in SI and SP.

Type of polymer	R_{obs}	-log (Cp/Cf_{inlet})
PHDA	0.998509292	2.83
PVS	0.997192253	2.55
HDPE	1	–
LDPE	0.888791214	0.95
PA	1	–
PE	0.996490317	2.45
PP	0.997192253	2.55
PS	0.944395607	1.25
PVC	1	–
PEMA	0.971922534	1.55
PU	0.971922534	1.55
PES	0.990640845	2.03
PET	1	–
PMMA	1	–
PVA	1	–

present in all sample types (SI, SRS, SP, SC, SC, SSF and SCS), with the most detected polymer families being Acrylates and Polyethylenes. The most difficult microplastics to remove with the MBR system were fibers and LDPE. In the case of fibers, this may be due to the narrow fiber width, which may be smaller than the membrane pore size.

CRediT authorship contribution statement

Ágata Egea-Corbacho: Conceptualization, Methodology, Investigation, Writing – original draft. **Ana Pilar Martín-García:** Methodology, Investigation. **Ana Amelia Franco:** Term, Data curation. **José María Quiroga:** Founding, Term and Conceptualization. **Rune Røjgaard Andreasen:** Conceptualization, Writing – review & editing. **Mads Koustrup Jørgensen:** Conceptualization, Methodology, Investigation, Writing – review & editing. **Morten Lykkegaard Christensen:** Founding, Term, Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The authors do not have permission to share data.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.109644.

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