# Microplastics in marine environment – sources, classification, and potential remediation by membrane technology – A review

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## Abstract

Presence of microplastics in marine environment has been a pollution problem for years but only recently people have become aware of it, similarly as happened in the las few decades with global warming due to greenhouse gases. Microplastics are pollutants highly stable to complete biodegradation and there is a high risk that they can enter in the food chain (e.g. fish or agriculture products) because of the fact that secondary plastics (in principle, as small as monomers and oligomers) generated from the evolution of primary ones (those directly spread in the environment) require more specific separation processes for their removal. In this review, firstly, we focussed on the classification and potential remediation technologies to be applied depending on the microplastics size. Secondly, membrane technologies (microfiltration, ultrafiltration and nanofiltration) are presented in the context of microplastics removal, revealing their suitability for the task and a future path of research and development to be carried out to mitigate the problem.

## 1. Introduction

Plastics are very attractive materials. They were created as a solution for scarce and expensive raw components such as ivory, tortoiseshell and animal bones. The creation, development and further improvement of plastics exceeded the anticipated results and modern plastics are characterized by durability, transparency, light weight, strength, versatility and hygiene (in biomedical applications) just to name a few.[1] Such exceptional properties resulted in their massive manufacture in the last decade, rising to an annual worldwide production in 2018 of 359 Mt of plastic (i.e. ca. 48 kg per earth inhabitant and year).[2] Plastic demand in Europe in 2018 divided into the following sectors: packaging (39.9%), building and construction (19.8%), automotive (9.9%), electrical and electronic (6.2%), agriculture (3-4%), household, leisure and sports (4.1% altogether) and others (16.7%) that include appliances, mechanical, engineering, furniture, medical applications, etc.[2]

While the social benefits of plastics are clear, this asset has been the subject of raising environmental concern. Nowadays, only about 32.5% of plastic waste is recycled, 42.6% is used as an energy recovery and 24.9% ends up in a landfill[2], and it is unacceptable that the waste ends up in rivers, lakes or the oceans. If the trend is not stopped, it is estimated that by 2050 ca. 12,000 Mt of plastic waste will be in landfills or in the natural environment.[3]

The first reports of plastic pollution in the oceans appeared in the 70s and did not drive huge attention.[4, 5] As it was mentioned before, the biggest amount of plastics in Europe comes from packaging applications. The most common polymers used for packaging are: polypropylene (PP), poly(ethylene terephthalate) (PET), polyethylene (PE), polystyrene (PS), and poly(vinyl chloride) (PVC)[1], thus, it is the most frequent to find such materials as a pollution in the oceans. There are many consequences of large plastic litter (macroplastic) in the ocean, however, the effect on the marine animals seem to be the most obvious and straightforward. Such impact includes: suffocating of the seabed and thus preventing the gas-exchange, injury and death of marine mammals, birds and fish as a result of plastic ingestion and entanglement.[6, 7] After ingestion of plastics, the animals die from starving or from inflammation of their stomachs. Over 250 marine species are impacted by plastic ingestion.[8] An increased influx of plastic litter into the oceans is a result of modification in demographics (more people migrate to coastal regions), extensive fishing or recreational and maritime uses of the ocean to name a few.[1] We have to also consider as an important factor the extreme consumerism of current society aggravated by false sensations of security when, for instance, plastic biodegradability is claimed suggesting that certain materials and utensils could be thrown off and magically disappear without a trace in a short period of time as true organic waste. Actually, what are called biodegradable plastics are solids that may have half-lives of a few years that increase in marine environments, due to relatively low temperature and near-neutral pH, approaching those of in principle more stable plastics. For instance, the specific degradation rates of PLA (polylactic acid) and HDPE (high density polyethylene) are similar under marine environmental conditions.[9]

As long as it is relatively easy to spot a macroplastic piece floating in the ocean or accumulating on the beach it is very difficult to distinguish and separate another type of plastic litter that is called microplastic. Recently, there is an increasing environmental interest and concern about microplastics mainly because they present different properties than their macro counterparts.[10] In fact, lower particle size of a plastic litter causes higher bioaccumulation in the marine animals resulting in very high risk to the marine biota, such as:[11] decreased food consumption, false satiation, reproductive complications and blocked enzyme production. The potential impact on humans (via for example fish or sea salt ingestion) includes respiratory irritation, obesity, cardiovascular disease, asthma and cancer. This is mainly due to the high surface area to volume ratio that microplastics possess. Because of that, microlitter can become heavily contaminated with for example persistent organic pollutants (POPs) as a result of microplastics ability to concentrate hydrophobic POPs on their surface. This process is very intensive mainly due to POPs greater affinity to the hydrophobic surface of plastic compared to for example seawater.[8] Moreover, there is also an emerging concern of microplastic pollution in freshwater and seas.[11] Recently, it has been identified that even the Arctic Sea is a reservoir with some microplastic contamination.[12] Microlitter was also found in lakes and rivers and, due to the wind and river-driven transport, the plastic litter reaches the coast and the ocean.[11, 13-15]

It is believed that the vast majority of plastic ever made is still present in the environment in some form.[16].[3] It has been observed in some highly polluted areas that plastic litter can fuse together or combine with the natural elements of the environment such as rocks, soil or organic materials creating plastic rock-like forms. It is suggested that, due to the enormous influence of human on even the most fundamental processes on earth, we are moving from Holocene to "Anthropocene" epoch.[16]

Even though there is an extensive work on microplastics in the marine and fresh waters there are still some challenges to consider: i) standard quantification procedure (establishing a clear and standard size definition measure), ii) understanding and evaluating of sources and behaviour of microlitter in fresh water, iii) possible remediation technique for removal of micro or nanoplastics from water, and iv) in the future, with the appropriate technology the plastics recovered from the sea could become a source of raw material or fuel.[17, 18] In this article we propose membrane technology as a solution for the removal of practically invisible plastic debris. This separation technology offers almost unlimited tuning of membrane properties allowing manipulation of pore size and its distribution, mechanical resistance as well as type of material that will be used for plastic and water separation. All these issues will be addressed in this article, since we believe that membrane technology will pave the way to both the removal of microplastics and their potential reuse.

## 2. Classification of microplastics

### 2.1. Classification according to size

Since the first reference to microplastics in academic literature[19], a significant number of authors have further studied their characteristics and origin. Despite being the first to report them, Thompson et al.[19] did not mention any size criteria to consider a fragment of plastic as a microplastic. However, many other authors since that publication have established a limit of size between the so-called macroplastics (regularly discarded plastic fragments easily observable with the naked eye, even when they are surrounded by other particles such as sand or gravel) and microplastics (see the criteria in Table 1**¡Error! No se encuentra el origen de la referencia.**).

*Table 1 Size criteria for microplastics in the academic literature*

| **Author and Year** | **Size criteria** | **Reference** |
|---|---|---|
| Graham and Thompson, 2009 | < 10 mm | [20] |
| Ryan et al., 2009 | < 2 mm | [21] |
| Andrady et al., 2011 | 0.06-0.5 mm | [1] |
| Costa et al., 2010 | < 1 mm | [22] |
| Eriksen et al., 2014 | > 0.2 mm | [23] |
| Law et al., 2014 | < 5 mm | [12] |
| Horton et al., 2017 | < 5 mm | [16] |
| Auta et al., 2017 | < 5 mm | [24] |
| European Commission (2017, 2019) | < 5 mm | [25, 26] |
| EPA, the United States, 2017 | < 5 mm | [27] |
| Hale et al., 2020 | < 5 mm | [28] |

This criterion is essential mainly because it establishes the limits between the *small* macroplastics that have low physical dimensions, thus, they are easily characterized using simple techniques, and the microplastics: those fragments that usually need to be characterized using optical instruments due to their small size.[22] The dimensions of microplastics are responsible for the challenges in terms of collection, characterization and estimation of their real presence in the environment. For this reason, from the 80s, a considerable number of academic publications and different institutions have focused on the plastic debris in general[29, 30], but a distinction between microplastics and macroplastics was not considered. However, in the last decade, a new consensus in the science community has attempted to establish a size criterion for plastic debris.

IUPAC (International Union for Pure and Applied Chemistry) considers microparticles of dimensions between 0.1 and 100 μm,[31] as Table 1 shows. However, in the last years, the scientific community has agreed on defining the microplastics as plastic fragments whose longest dimension is below 5 mm. Consequently, the European Commission,[25, 26] the EPA (United States Environmental Protection Agency)[27] and the countries from the Asian Pacific region,[28] advised by scientists in recent reports regarding microplastics, adopted this criterion, and so did the European chemical industry so far.[32] This criterion, then, is the upper size limit we will use in the present publication for microplastics.

Even though the concept of microplastics as a pollution of the oceans is the most extended and the most explored, other authors also introduced in 2011 the concept of nanoplastics as particles of size between 200 nm and 2 μm that are the products of the degradation of microplastics.[1] A few years later in 2015, Jambeck et al.[33] established the upper size limit of nanoplastics being 100 nm. This restriction is significant, since particles below such limit, in contrast to microplastics, may be capable of disrupting the cell membrane.[34] Moreover, the few recent authors investigating this issue agree on this size limit criterion.[35-37] Unfortunately, it is challenging to establish a clear size criteria as well as the impact of nanoplastics on health and environment since the literature on this topic is not numerous yet.

### 2.2. Classification according to the origin

The microplastics have been divided into primary microplastics and secondary microplastics depending on whether they were fabricated as microplastics in origin (primary microplastics), or they appeared as a physicochemical degradation of bigger plastic debris (secondary microplastics).[6] This section addresses both types of particles, considering that the term “microplastics” represents both microplastics and nanoplastics.

**Primary microplastics**

Primary microplastics are particles added to the products that are frequently used as scrubbers in facial cleansers, cosmetics and air-blasting media. However, there are other existing products that are primary microplastics themselves. These are, for example, plastic pellets and vectors for drugs.[6] Other authors have even gone further in the research of microplastics origins. Auta et al.[24] mentioned products with microplastics used as shower/bath gels, peelings, eye shadows, deodorants, blush powders, makeup foundation, mascara, shaving cream, baby products, bubble bath lotions, hair colouring, nail polish, insect repellents and sunscreens. In fact, in 2017 the European Commission published a report where a panel of specialists researched all primary microplastics fabricated in Europe (see Table 2**¡Error! No se encuentra el origen de la referencia.**).[25]

*Table 2 Main markets where primary microplastics are added in Europe, estimation of mass production in tonnes/year in 2017 and main polymer types fabricated per market* [25]

| **Product** | **Tonnes/year (2017)** | **Main polymer types** |
|---|---|---|
| Cosmetics/personal care | 714 | Polyurethane (about 50% of all microplastics in cosmetics), polyethylene, cellulose acetate, polylactic acid, Nylon-11 |
| Paints and coatings | 220 | Acrylic polymers, fibers of polyamide, polyacrylonitrile |
| Detergents | 142 | Polyurethane, polyester, polyamide, acrylic, PMMA, PET glitters, rheology modifiers, polyethylene |
| Oil and gas industry | 2 | Additives, cross-linking agents, wax inhibitors |
| Agriculture | Difficult to estimate | Used as coatings to form pills and control the release of fertilizers, polysulfone, polyacrylonitrile, cellulose acetate |
| Industrial abrasives | Difficult to estimate | PMMA particles, rubbers, polyethylene |
| Minor industries | 1.6 | - |

From Table 2 we can extract the conclusions that the personal care market is the most prominent fabricant of products with primary microplastics added in Europe and that the polyurethane is one of the most fabricated polymers in the form of microplastic. In 2017 the polyurethane primary microplastics represented at least half of the total production of microlitter in the cosmetics and personal products market as well as it was present in detergency market (the third biggest producer of primary microplastics). However, the report published by the European Commission also included alternative microparticles to substitute microplastics, which, in combination with previous and future prohibitions of use of these particles in different markets in Europe and other countries all over the world, have probably decreased the presence of microplastics in nowadays products.[25] Some of these alternatives include the use of particles of seaweed or fruit hard shells, silica or clay for personal care products, glass beads for paints (as those frequently used in paints for roads), silica for detergents or silicon carbide as abrasives.

In North America, there are plenty of reports about microplastic presence, production and fate in some industrial sectors, but there are no reports summing up the overall production of primary microplastics. The EPA published a report about microplastics in 2017, where several experts evaluated the available information about microplastics production and their presence in the environment. Nevertheless, they did not give any production estimation.

Although, the International Union for Conservation of Nature (IUCN) communicated a rough number of primary microplastics release to seas and oceans in the USA. That number would be 260,000 tonnes/year, compared to 240,000 in Europe.[38] However, these numbers are not in agreement, at least in the case of Europe, with those given in Table 2. One reason is that the IUCN considers the whole European continent, while the report of the European Commission considers only the countries of the European Union. The other reason is that Table 2 shows the total primary microplastics produced, while the IUCN gives the total primary microplastics wastes. To illustrate this difference, we can look at the specific example of primary microplastics in paints. According to the report of the European Commission mentioned, the total primary microplastics production in the paints market is 220 tonnes/year (see Table 2), but the total tonnes of primary microplastics contained in the total building paint sold in the European Union is higher (22,000-38,000 tonnes/year).[25] This huge difference may come from the fact that part of the primary microplastics contained in the paint used in the European Union is fabricated in the territory, while the rest may be imported.

As Kentin and Kaarto informed in 2018, since 2016 several European and non-European countries started to forbid the use of microplastics in personal care products, being South-Korea the first. [39] Besides, the European Union is likely going to block throughout 2020 any kind of microplastic intentionally added to the products in all European markets. [32, 40]

## Secondary microplastics

### *Definition and properties*

The secondary microplastics are defined as a microlitter derived from the breakdown of larger plastic debris through physical, biological and chemical processes.[6] First of all, to interpret the behaviour and fate of microplastics in the water environment it is crucial to understand the polymer degradation processes that can be divided into different types: i) biodegradation (action of living organisms such as microbes), ii) photodegradation (action of light - usually sunlight; one of the fastest degradation processes), iii) thermooxidative degradation (slow oxidative breakdown at moderate temperature), and iv) hydrolysis (reaction with water).[1] Essentially, the process of extreme reduction of the average molecular weight of the polymer is called plastic degradation resulting in plastic pieces becoming brittle or powdery.[41] The degradation process that autocatalyses itself (autocatalytic degradation) can occur with the presence of oxygen where the molecular weight of the polymer is diminished followed by generation of oxygen-rich functional groups in the polymer. UV solar radiation is the fastest and most efficient degradation process to plastic litter especially exposed in air or lying on the beach.[1]

The plastic breakdown processes usually take place in beaches and off-shore, where the plastic debris is exposed to harsher conditions than in continental lands and in-land water bodies. Nevertheless, those conditions, such as intense UV radiation, corrosion and erosion,[6] tend to be especially critical in beaches because of the higher oxygen concentration and the presence of sand, which acts as a scrubber when it is windy. Off-shore, plastic debris experiences continuous exposure to UV radiation and high oxygen concentration even when they float. Nevertheless, the same type of UV radiation is not so powerful anymore if the objects are floating in seawater. This is mainly due to the decrease of the temperature in the sea as well as lower oxygen concentration in water in comparison to open air beach.[42]

Moreover, low-density polymers, such as for example polyethylenes, tend to float, while high-density polymers, such as PVC, sink. Low-density polymers, when they were fabricated as continuous thin films (i.e. plastic bags) that are floating in the sea for a prolonged time are suitable for biological surface fouling, which is characterized by coverage with biofilm, algae adhesion followed by a colony of invertebrates.[1] Consequently, as the microorganisms grow on the plastic film, this becomes heavier, thus it sinks.[8] Afterwards, the piece of plastic is defouled by foraging organisms, so they gain buoyancy again, and they return to the water column surface. Here, the cycle starts again. While the plastic debris is on top of the water column, it breaks down, but when it is underwater, the breakdown stops.[8]

It is important to mention that even though there are many degradation processes that can occur in the water and coast environment, however, common plastics used in everyday applications do not biodegrade at a fast enough velocity that could be beneficial. The reason for that is that, together with those above mentioned related to temperature and pH of sea water, the microbial species that are able to metabolize polymers are rare in nature. Nevertheless, there are some examples of biopolymers which can be biodegraded such as: chitins,[43] chitosan[44] and a few synthetic polymers such as aliphatic polyesters do biodegrade rapidly in the sea.[45]

The fouling-defouling phenomenon and the different densities of plastic debris take part in the complexity when dealing with the secondary microplastics in oceans: they are heterogeneously distributed along the whole water column. That complexity is what makes it extremely challenging to detect and remove them from water reservoirs.[8]

Several companies have already started to manage microplastics in water bodies. The Ocean Cleanup, a non-profit organization, created by several Dutch scientists started to manage the plastic rubbish dispersed at the surfaces of the Oceans and the most full-flowing rivers of the world.[46-48] Ocean Cleanup attempts to clean the Oceans as well as rivers from the plastic litter since the company claims that the majority of plastic debris present in marine waters comes from smaller reservoirs such as rivers or lakes. Nevertheless, this company removes only macroplastics from the surface of the water. It has to be considered that except the problem of microplastic pollution there is also a rising concern that microplastics can be further broken down to smaller particles creating nanoplastics. At the same time, Draper, a highly technological company from the United States, researched several techniques, in collaboration with the EPA to detect microplastics in oceans and rivers.[49]

Even though many organizations would remove around 90% of all plastic litter,[48] there will still be more plastic debris and microplastics in deeper areas and sediments of the oceans, including nanoplastics too. Those plastics will be more challenging to manage, as in a cleaning process the fauna and flora can be hardly damaged.

*Origin, quantification and types of secondary microplastics worldwide*

As a gross estimation, it is considered that around 80% of plastic debris present in seas and oceans comes from terrestrial sources. As these plastic wastes degrade, they become secondary microplastics. However, the macroplastics degradation not only occurs in seas and oceans since microlitter was also found in lakes and rivers due to: i) nearby plastic manufacturers, ii) wastewater treatment plants, iii) fishery, iv) beach litter, v) cargo shipping and harbours, and vi) inland sources (sewage sludge, runoff from urban agricultural places, touristic and industrial areas) [11, 13-15]. What follows that, due to the wind and river-driven transport, the plastic litter is moved, reaching the coast and eventually the ocean.[8]

The above percentage of 80% is a mixture of mismanaged plastic litters and intentionally added microplastics in manufactured products or small fibers from our textiles after washing.[50] [33] In case of Europe, 9.8 Mt out of the 61.8 Mt of plastic produced in 2018 was recycled (around

19%), but in the specific case of the European Union, that percentage was significantly higher (32.5%). The rest of the plastic litters are either used for energy recovery (42.6%) or deposited in landfills (24.9%).[2] There is a missing percentage that is related to the mismanaged plastic litters that finish in the oceans, which is, according to Jambeck et al.,[33] around 2% of all plastic residue. These are mainly plastic litters thrown away, wind-blown and mismanaged by mechanical or human error.

The USA, according to the EPA, recycled around 8.4% of the plastics they produced, while 15.8% and 75.8% were used for energy recovery or deposited in landfills, respectively.[51] As in the European Union, those numbers sum up to 100%, so the quantity of mismanaged plastic litters is also likely to be low in relative terms.[2] In case of the far Asian region, the top plastic producer in the world, it is difficult to have an updated estimation of the amount of plastic wastes mismanaged. Nevertheless, it is known that in terms of plastic production, the European countries produced that year 17% of all plastics used worldwide,[2] while 18% was produced in the USA and 51% in Asia. This means that Europe and USA seem to contribute equally to the plastic pollution in oceans, beaches, seas worldwide, but the plastics production in Asia is likely to have a bigger impact on the environment than both USA and Europe together (see Figure 1).

Additionally, Jambeck et al.[33] estimated the percentage of waste that is plastic and the percentage of plastic waste that is mismanaged using data of the mass of waste generated per capita annually collected in 2010, considering only population living within 50 km of a coast worldwide (people generating waste that can potentially enter the oceans). It was observed that China and Indonesia are the main mismanaged plastic waste contributors worldwide (20.7% and 10.1%, respectively) which in the case of China corresponds to the 76% of the total plastic waste they produced.[33] Even though that number is not comparable to the one given by the European Union or the USA (the estimations in the EU and USA were based on the total plastic produced, not the total plastic waste), it still gives an idea of which regions are the most significant worldwide contributors of plastic litter, and in consequence of secondary microplastics.

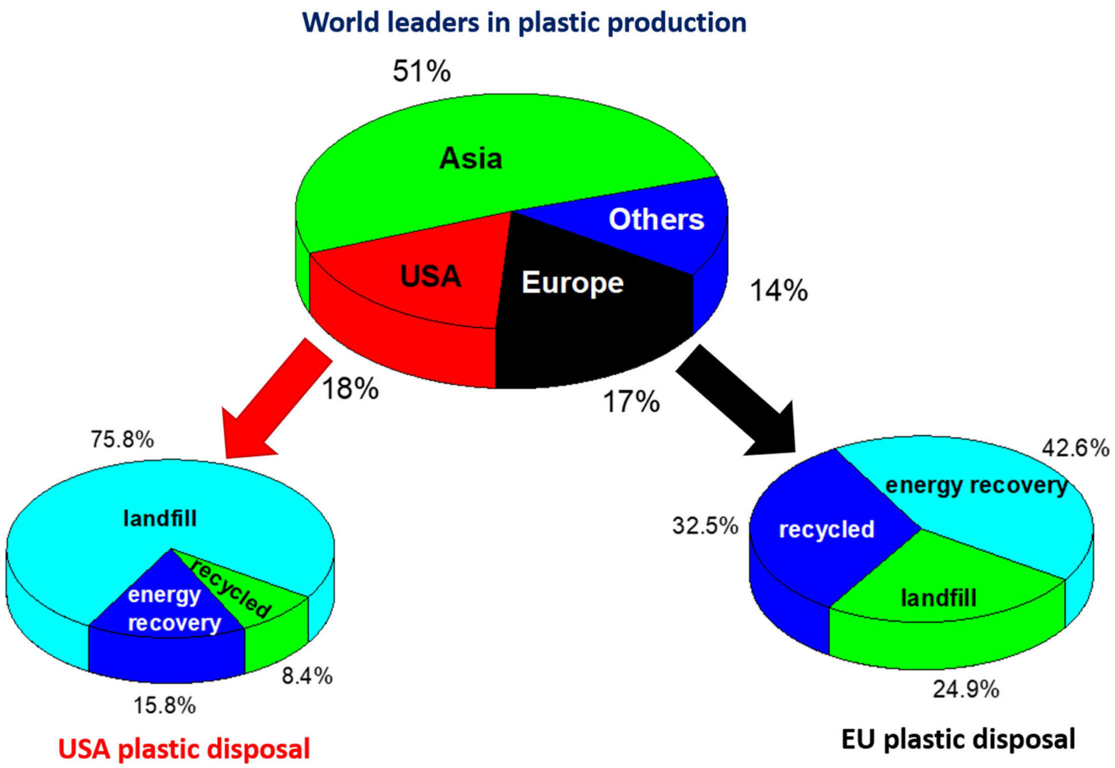

*Figure 1 World leaders in plastic production and their plastic disposal management*

In 2015, around 36.3% of the total production of plastic worldwide belonged to polyethylene (20% for low-density polyethylene and 16.3% for high-density polyethylene), 21.0% to polypropylene, 7.6% to polystyrene, 11.8% to PVC, 10.2% to polyethylene terephthalate, 8.2% to polyurethane and 4.9% to the rest of polymers (Figure 2)[3].

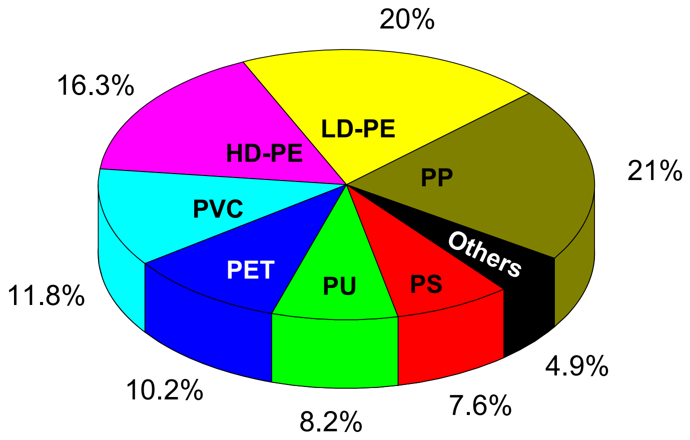

*Figure 2 Visual representation of the percentage of plastics produced worldwide*

As China is the biggest plastic manufacturer[3], and considering that they mismanage around 76% of the plastic wastes [33], we can roughly estimate that half of the plastic litter that finishes in the oceans is likely to float. This assumption is quite reasonable since polyethylene, polypropylene and polystyrene (which sum up more than 50% of the total plastic production[3]) are buoyant plastics, and they are widely used in packaging, the biggest industrial user of polymers worldwide.[52]

Finally, the last origin of microplastics in fresh and marine waters is the washing process where synthetic clothing, such as nylon or polyester (PES) might lose thousands of fibers into wastewater. Microplastics can bypass the waste water treatment plant (WWTP) and enter directly to the aquatic water bodies.[50]

## 3. Detection and characterization of microplastics

The microplastics detection as well as their characterization methods are still not standardized. Variety of different techniques are used depending on the microplastics occurrence, size and type. This may result in a difficulty in comparing such wide range of measurements with so many variables.

### 3.1. Sampling methods and processing

In order to effectively process the samples, they have to be efficiently collected. Nevertheless, the existing techniques are in general unable to identify all particles and are quite time consuming. The main challenges of microplastic detection in water consist of: i) plastic type identification mainly due to discolouration, abrasion and fragmentation (e.g. disappearing or losing the plastic identification code), ii) separation of different types of plastics in one sample (low-density, high-density), and iii) capturing of microplastic fragments from water or sediment.[53]

There are three general sampling methods as described by Thiel et al.[54]:

- Selective – direct extraction of larger objects.
- Bulk – entire volume of the sample (when it is hard to distinguish by a naked eye).
- Volume – reduced (where only the portion of interest is preserved).

Depending on the zone where the sample is taken from, the sampling methods may vary. The cross section of the ocean can be divided into three segments: 1) sediment, 2) water column, and 3) water surface. The samples that are taken from the sediments are usually collected by tweezers, tablespoons, trowels or picked by hand [54-57], while the water column or water surface samples are collected by nets or big reservoirs.[54, 58] Figure 3 shows the schematic representation of the sampling methods depending on the section of the water body considered.

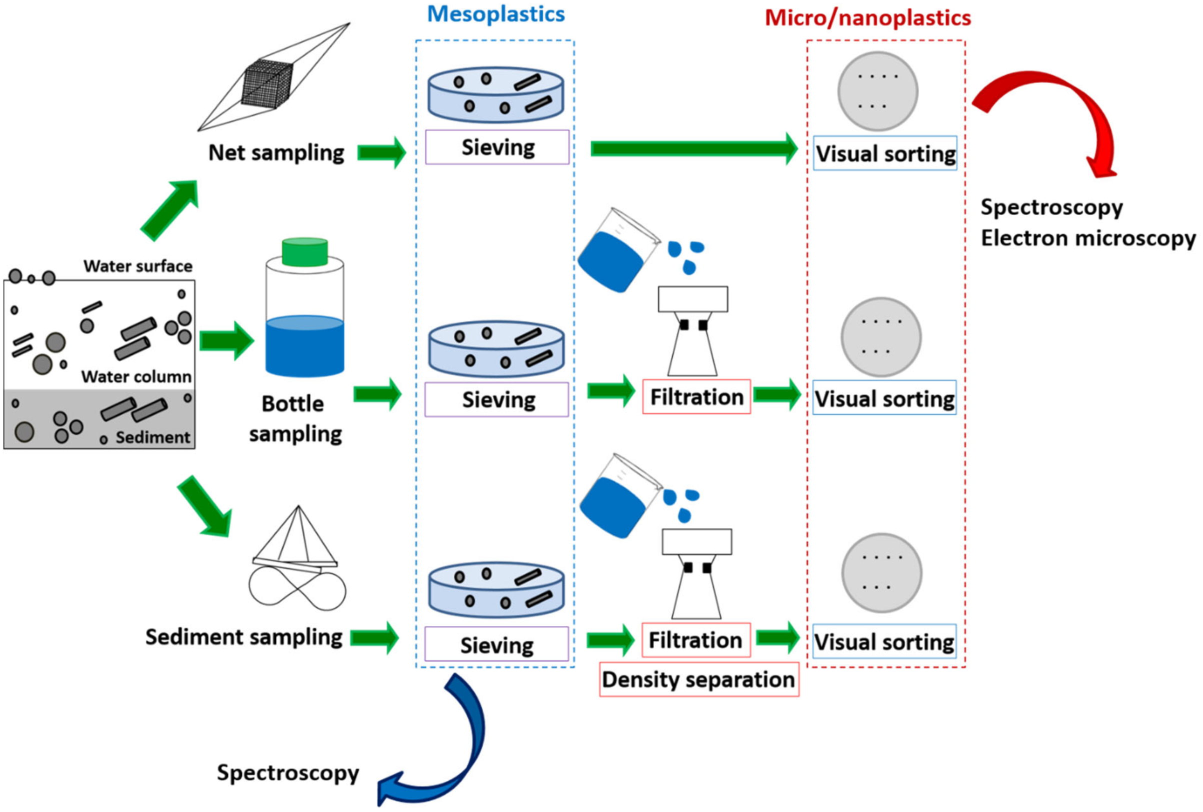

*Figure 3 Different sampling methods depending on the section of the Ocean*

On the other hand, sampling from the wastewater is different and mainly consists of: container collection, separate pumping, filtration and autosampler collection.[50] Collected water from any type of aquatic reservoir is usually filtered. Hence, the mesh/pore size of sieves and filters is extremely important to ensure the comparability of different measurements.

When the samples are effectively collected they should be processed. There are main four different sample processing techniques[54]:

- Density separation – to separate the plastic that floats in the sediment sample.
- Filtration – usually by vacuum.
- Sieving.
- Visual-sorting – by naked eye and a microscope.

Density separation technique is based on the differences in densities of plastics (ranging from 0.8 to 1.4 g $cm^{-3}$) and sediments (typically 2.65 g $cm^{-3}$).[54] Generally, a saturated solution of NaCl (1.202 g $cm^{-3}$ at 25 ºC) is mixed with the sediment sample. It is anticipated that the lighter plastics will float to the surface while the heavier sand and other sediment particles will settle to the bottom. Even though NaCl is the most commonly used salt for the solution concentration there are some examples where sodium polytungstate was used as well;[59] this can be dissolved in water to adjust the density from ca. 1 to 3.10 g $cm^{-3}$ at saturation.[60] Nevertheless, the mass of the sample that can be analysed by this method is limited mainly because sodium polytungstate is quite expensive.[61] Nuelle et al.[61] developed a new analytical approach to extract microplastics from sediments. This method allows to process approximately 1 kg of sediment sample. First, the air-induced overflow method was used to pre-extract 1 kg of sediments. It was then possible to reduce the volume of sodium iodide used for the flotation step because the original sediment mass was reduced by approximately 80%. Finally, the sediment samples were stored in $H_2O_2$ solution during one week and 92% of biogenic material had dissolved completely resulting in pure microplastics samples [61]. Another density separation method is Munich Plastic Sediment Separator. In this approach, higher density of a separation fluid is applied and it allows to separate plastic particles in the size of mesoplastics (5-20 mm) and large microplastics (1-5 mm) as well as small microplastics (<1 mm).[62]

Density separation is frequently followed by a simple filtration method where micro- and macroparticles are separated by passing over a filter with the pore sizes from 1 to 2 μm usually with the help of a vacuum.[63]

Sieving is another alternative approach for the separation of plastic particles. Variety of mesh sizes, ranging from 0.038 to 4.75 mm, are used allowing to distinguish different size categories of microplastics (see section 2.1). The particles that pass through the sieve are discarded while those that remain are collected and sorted.[54]

Finally, visual sorting and separation is done to examine the plastic materials and distinguish them from organic debris (dried algae, animal parts, seagrasses, shell fragments, wood, etc.) and other materials (glass, tar, metal). Such examination is usually done either by the naked eye or with dissecting microscope. Moreover, it is very important to keep in mind that the plastic samples should be dried and stored in a temperature-controlled and dark space in order to decrease the degradation during storage.[54, 64] A schematic representation of the sample processing steps is presented in Figure 4.

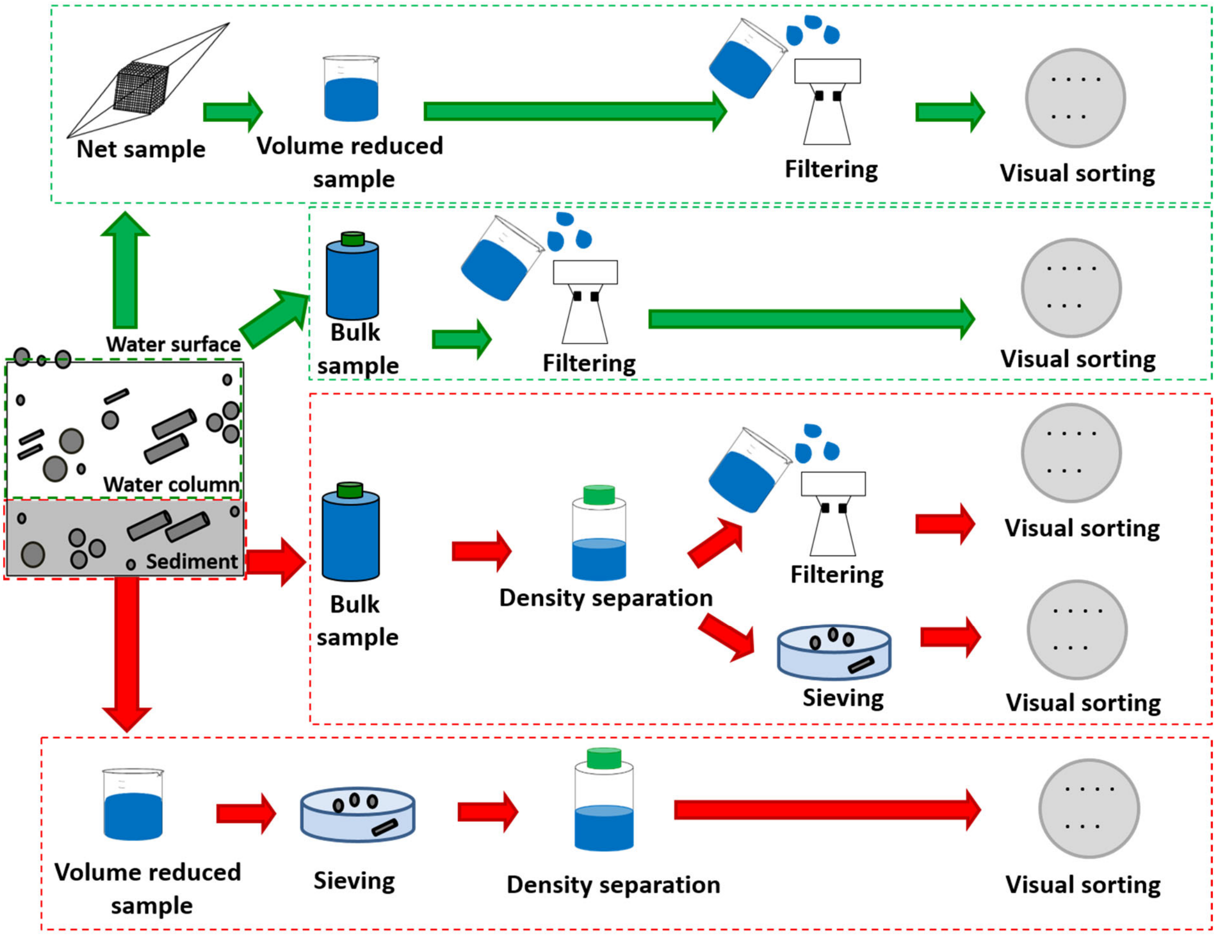

*Figure 4 Different steps of sample processing depending on the section of the Ocean*

Once more, the wastewater samples, especially those from WWTPs, are treated in a different way, mainly because they contain high concentration of inorganic solids or organic matter. It is necessarily to purify the microplastic pieces from this pollution in order to be able to characterize them properly. One of the common method is catalytic wet peroxidation (WPO), using NaClO, $H_2O_2$ or Fenton reagents,[50] or alkaline and acid treatments.[65]

On the other hand, the MPs accumulation in soil and sludge should not be forgotten. In the work of Li et al. an additional pre-digestion procedure with 30% $H_2O_2$ to the standard separation methods was investigated. It was demonstrated that this additional pre-digestion procedure significantly increased MPs (mainly small fibres) extraction in soil (420-1290 MP items/kg) and sludge (5553-13460 MP items/kg).[66]

Nonetheless, there is still a need for improvement of detection and sampling methods in order to: i) develop a cost effective method, ii) have simple methods to guarantee sufficient replication, iii) spread the methods that will reduce the contamination, and iv) ensure accurate and precise techniques.[53]

## 3.2. Microplastics characterization methods

Once the microplastics are collected and separated they should be characterized. Generally, the microplastics characterization can be divided into physical and chemical types of analysis. Physical analysis refers to the microplastics size, shape and colour, while chemical characterization deals with the chemical composition of the plastic litter.[50]

Stereomicroscope is the most widely used technique for the physical characterization even though it still shows some limits connected with the lack of automatization and difficulty to distinguish all polymer types.[50] Moreover, it has to be taken into account that plastics undergo various chemical and physical modifications, especially after a prolonged residence at sea. For instance, one of the parameters that can be modified is the specific density of plastic particles. As it was observed by Moret-Ferguson *et al.*, the density of pellets decreased from 0.85 to 0.81 g $cm^{-3}$ for HDPE and from 1.41 to 1.24 g $cm^{-3}$ for polystyrene (PS).[67] This suggests some leaching and the subsequent incorporation of small plastic particles to the water. Another indication of the prolonged residence at sea is the shape of the plastic edges. Smooth edges are believed to be old fragments that have been polished by sand, rocks, waves, sediments or other particles. While, on the other hand, sharp edges are usually associated with a recent introduction into the sea.[4, 54] It is also worth to mention that nanotoxicology and colloid science are two disciplines that have shown the potential in standard methods for measurements of the surface properties, size and stability of microplastics.[16]

Normally, the chemical composition of microplastics is identified by Raman spectroscopy (giving an additional information about the crystalline structure of the polymer), infrared (IR) spectroscopy (infrared spectrophotometer, Fourier transform infrared spectroscopy – FT-IR, near-infrared spectrometer – NIR), electron scanning microscopy (SEM) or differential scanning calorimeter (DSC).[68] A reference material and a measured sample are put under a given temperature in DSC to determine the polymers that the microplastics are made of thanks to the characteristic smoke during combustion and temperature of degradation of the material.[54, 69, 70] Nevertheless, a combined and complementary approach is needed for efficient characterization methods for microplastics.

Moreover, it has to be taken into account that microplastics can undergo a photo-transformation or photo-aging process. Recent studies have shown that the reactive oxygen species (ROS), such as hydrogen peroxide ($H_2O_2$), singlet oxygen ($^1O_2$), superoxide radical anion ($O_2\bullet^-$) and hydroxyl radical (OH●) exhibit great potentials to accelerate the aging process of MPs in the aquatic system.[71] It was indicated that the photo-aging of, for example, PVC microplastics depended on the particle size. Moreover, the aging reaction could be facilitated in the presence of low-molecular-weight organic acid (LMWOA) and LMWOA-Fe(III) complex under natural as well as simulated sunlight irradiation and ambient conditions.[71] Furthermore, Liu et al. tried to understand the long-term natural aging of MPs in aquatic environment with polystyrene and high-density polyethylene MPs as examples. Heat-activated $K_2S_2O_8$ and Fenton treatments were used to induce MPs aging. Thanks to this study the correlation model of the O/C ratio or carbonyl index (CI) versus alteration time was developed and compared to the natural alteration mechanisms. This important work is helpful in predicting the weathering degree and accumulation of for example hydrophilic antibiotics onto aged MPs as well as in developing strategies that would accelerate the aging reactions using advance oxidation processes.[72] A complementary work was conducted by Zhou et al. who investigated the effect of discharge plasma oxidation, that was used to stimulate the radical oxidation of MPs, on the aging behaviour and mechanisms of MPs. The aged MPs (PVC in this case) was characterized by higher hydrophilicity and higher crystallinity as well as it possessed more O-containing functional groups. Interestingly, the aged PVC MPs had more affinity to adsorb tetrabromobisphenol that lead to unexpected toxic effects. This important study showed the potential environmental risk as a result of aging microplastics.[73]

## 4. Potential remediation technique based on plastic particles removal with membrane technology

In the last decade several authors have analysed the efficiency of the current methods to eliminate microplastics in WWTPs,[74-76] while others have suggested novel methods to improve the standards. Primary treatment methods, such as skimming and settling, remove most of the microplastics present at the inlet effluent, whereas tertiary treatment methods are needed to remove more than 95% of them.[77] Novel investigations are followed by an increasing interest of water professionals in microplastics, mainly boosted by a report of Norwegian Environmental Agency (NEA) published in 2015.[78] NEA addressed the effect of microplastics on the environment looking at the emission of these plastic particles to the environment via domestic and industrial wastewater. By the end of the decade, the increasing attention to microplastics gave rise to new investigations that proved the presence of worrying plastic pollution in drinking water, and a rising concern about plastic debris in seas and oceans.

There are plenty of improvements carried out on WWTPs to remove microplastics more efficiently. Only a few of them were applied to primary and secondary treatments, such as anaerobic digestion, thermal drying and lime stabilization on the amount of microplastics present in the sludge. The majority of those improvements appeared in the form of advanced treatments in which membranes are usually involved.[77, 79]

In this part of the report, we analyse the role of membranes in the removal of microplastics from wastewater, drinking water and seas and oceans, and how can we use membrane technology to remediate the plastic pollution from those media.

Membrane technology is one of the possible remediations to remove plastic litter from water mainly because membrane-based operations have the potential to replace energy-intensive conventional technologies due to their low energy consumption, operation flexibility and simplicity, good stability, easy control and scale-up, and can handle enormous amounts of water (e.g. as those involved in sea and brackish water desalination). Membrane separation processes differ based on the separation mechanism and size of the separated particles, including microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis, dialysis and gas separation.[80-82]

*Wastewater*

Wastewater is an important contributor of microplastics to seas and oceans,[74, 78, 83] mainly because thanks to the small size of primary microplastics it is unlikely to remove them by existing, standard screening methods. However, this could be easily avoidable since wastewater is treated and controlled in most of the countries in the world. In fact, there is a strong correlation between water treatment and income of countries with 70, 38 and 28% treatment of the generated wastewater in case of high-, upper-middle- and lower-middle-income countries, respectively.[84] This suggests that eventual regional policies for microplastics capture should have to be afforded with cheap and highly efficient technologies accessible to all the economies.

In the specific case of WWTPs, it is already known that pretreatments, primary treatments and secondary treatments (see Figure 5 to see the four WWTP stages), already remove around 75% of microplastics contained in wastewater, being the primary treatments the most effective.[77] However, around 98% of all microplastics presented in wastewater are nowadays already removed in current stations (with tertiary treatments included); the other 2% are considered to be microplastics with sizes below 20 μm and nanoplastics.[85, 86] That efficiency boost from 75%

to 98% was given by the application of tertiary treatments (see Figure 5), among which membranes have huge future potential.[87]

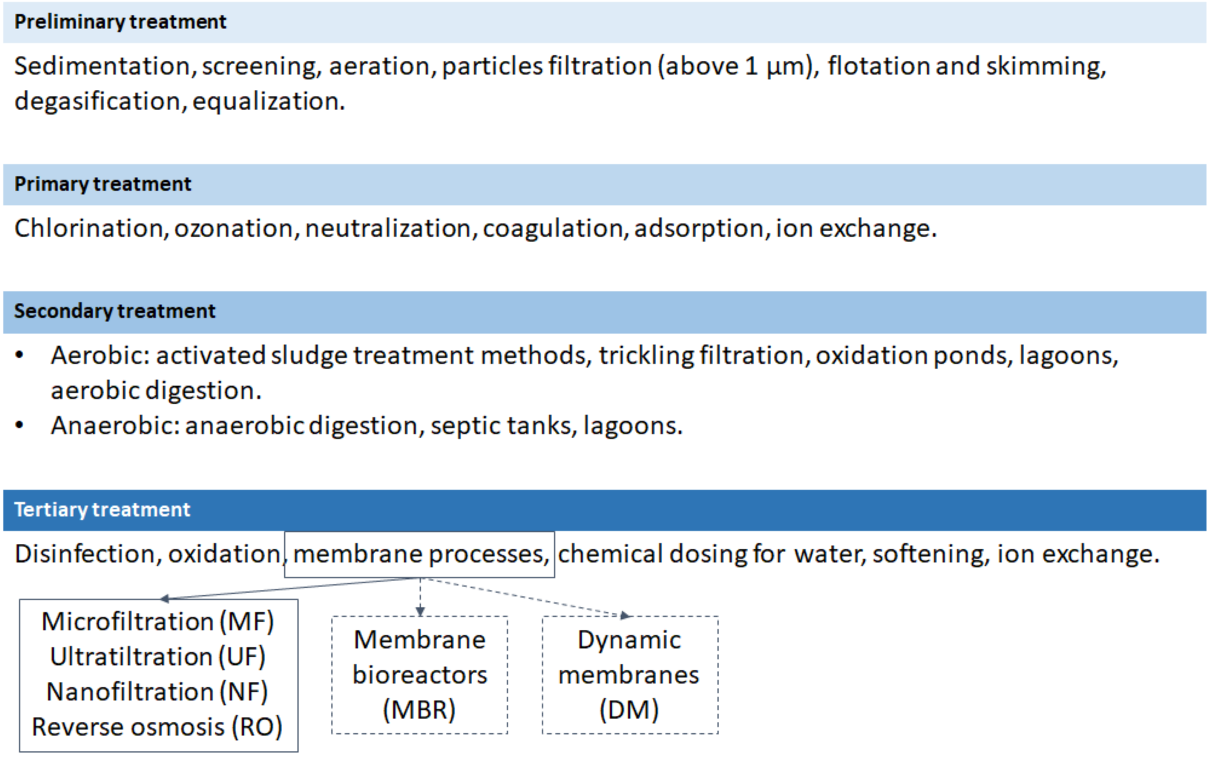

*Figure 5 The four stages of a WWTP, the membrane processes being one of the tertiary treatments with highest potential in the removal of microplastics*

Ultrafiltration (UF) membranes with pore sizes between 1 and 100 nm are usually combined with coagulation steps to remove most of the organic matter present in wastewater and the microplastics contained. Nevertheless, they are not efficient enough in the removal of the fraction of plastic particles that remains in the final effluents.[74, 75] In fact, the degradation of plastics can yield low molecular weight polymer fragments such as monomers and oligomers [88] which claims further investigations on their efficient removal; UF and eventually nanofiltration (NF) membrane applications being the proper tools for this purpose.

In 2016, for instance, Mason et al.[75] studied effluents from 17 different WWTPs, all of them in the United States. They took 90 samples in total, some of them in intermediate stages of a part of the WWTPs studied. Some of the facilities that were studied had even tertiary treatments in their installations, which gave the researchers the chance to observe their effectivity to remove microplastics. As the researchers concluded, a significant concentration of microplastics in the shape of fibers were found in the WWTP effluents, even if there were tertiary treatments. However, they also admitted that, due to their sample analysis method, they could have counted biological origin fibers as microplastics.

Interestingly, Mason et al.[75] did not find any clear correlation between the use of tertiary treatments, as advanced filtration methods, and a most effective removal of microplastics in WWTPs. However, they analysed the microplastics content before and after membrane filtrations in one of the seventeen WWTPs, and they detected a reduction of 15%. All in all, this is only a preliminary study, and, as the authors indicate in the publication, further studies on the tertiary treatments effectiveness to remove microplastics are needed.

In 2017, Talvitie et al.[74] suggested several ways to rise up that rejection to 99.9% using membrane bioreactors, which would substitute the traditional coagulation-precipitation methods after the aeration with the activated sludge (secondary treatment).[78] The drawback of this investigation was that only microplastics with sizes above 20 μm were considered, when nowadays, it is well known that there is plastic litter far smaller: such as nanoplastics even below 100 nm,[87] the above mentioned monomers and oligomers, and also plastic additives used during their fabrication, with potential sizes of only a few nanometers.

Other authors have also investigated the use of other membrane-based technologies, such as the dynamic membrane (DM) technology.[89, 90] This system consists of using a highly permeable membrane with big pores to let the formation of a cake-layer with large suspended solids to obtain a selective barrier. This DM system requires low pressures (even lower than UF and microfiltration - MF) and no extra chemicals are needed, as in the case of coagulation steps. Li et al.[76] studied the use of this type of membranes in the removal of microplastics, demonstrating that DM systems can deal with this kind of particles. Besides, they observed that the turbidity of the feed dropped dramatically. However, they did not further analyse the size of the microplastics retained, even if they thought that around 90% of all microplastics retained had particle sizes below 90 μm. Consequently, although the DM systems can be more efficient than UF membranes in some of the operation parameters, they cannot substitute the latter because 90 μm is considerably higher than the 40 nm particles the UF membranes can reject.

*Drinking water*

Several studies have found microplastics in inland water bodies such as rivers and lakes of different countries worldwide.[91-94] This issue is likely more severe in countries that depend on surface water to obtain drinking water since groundwater is naturally filtered at some level, and surface water is unprotected. In consequence, open-air waterbodies are sensitive to mismanaged plastic wastes, usually air-blown, that at harsh conditions would break down into smaller pieces of plastics and, eventually, microplastics.

As microplastics appear into the drinking water, they can be removed by agglomeration and precipitation using Fe and Al-based salts, but UF membranes can be far more effective, as some authors evidenced.[95] In addition, removal by catalytic processes may give rise to organic by-products difficult to follow, suggesting the separation way as superior. Ma et al.[95] actually demonstrated that UF and coagulation-precipitation methods can be complementary, even though fouling effects could be significantly aggravated. Last but not least, it has been reported that 0.5-10 μm in size microplastics can be present at concentrations of ca. 650 μg/L in the drinking water contained in polymeric bottles.[96]

*Secondary microplastics*

Removing secondary microplastics is highly challenging, as we can conclude from the fact that these are usually distributed along the water column of inland water bodies, seas and oceans, and they can be of much smaller size, having even a micropollutant character as dissolved plastic monomers. Consequently, it seems evident that the organizations created worldwide that aim at cleaning the oceans are rather focused on removing the big plastic debris (sources of the secondary microplastics), than the secondary microplastics themselves. The Ocean Cleanup claims to be able to remove plastic debris from a few millimetres to big plastic wastes,[48] but as we indicated in this review, there are pieces of plastic quite smaller. Removing microplastics from the sea is too expensive and challenging, but it is even more in the case of nanoplastics. However, the impact of microplastics on the health of marine animals (with effects related to decreased food consumption, false satiation, decreased growth rate, reproductive complications, behaviour, oxidative stress, decreased immune response, weight loss, pathological stress and blocked enzyme production[97]) and humans (via ingestion of fish) is important enough as to not to discard the future need of massive plastic removal from ocean water (as it happened with carbon dioxide from the atmosphere). Karbalei et al.[97] have summarized the potential impacts for humans in case of exposition to microplastics including respiratory irritation, dyspnea, coughing, obesity, increasing phlegm production, cardiovascular disease, asthma and cancer. As the particle size of microplastics decreases, their removal becomes more complicated and costly and their effects on human beings tend to be higher at molecular scale with mechanisms similar to those of micropollutants. This is one of the reasons to include cancer as an important potential effect of this type of pollution.

Some studies, such as the published by Woodall et al.[98], proved the presence of a significant amount of micro and nanoplastics in deep-sea areas all over the world. In the specific case of the mentioned study, the sample collection method would unlikely lead to a feasible estimated concentration of microplastics in the areas considered. Nevertheless, it illustrates the complexity of the issue.

The scientific literature is focused on methods to remove microplastics and nanoplastics from wastewater and drinking water, rather than from open-air water bodies, because it is not technically viable and doable. In fact, it is already known that membranes can be very useful for removal of those plastic particles. But to remove micro and nanoplastics present in sea sediments and soils, first they must be extracted from those places.[99]

*Limitations in the removal of microplastics by membrane technology*

Recent publications have highlighted the necessity of improving the removal of microplastics with sizes below 100 μm, and moreover, those in the range of nanoplastics (< 100 nm).[77] But that is not all: there are improvements that must be done in the performance of membranes in terms of fouling phenomena, which highly limits the effectiveness of the separation in a long term.[100]

In that way, Ziajahromi et al.[65] studied the effectiveness of reverse osmosis (RO) membranes in the removal of microplastics as part of the tertiary treatment of a WWTPs. RO membranes remove all particles present in the feed due to the very dense polymeric barrier that acts as the actual membrane, but a few plastic particles were unexpectedly detected in the permeate stream. As the authors pointed out, this is necessarily explained by the appearance of pores on the membrane surface, the selective membrane material, other kind of imperfections or simply small gaps between pipework. However, as these are unavoidable imperfections inherent to any kind of technical process, RO is in principle the most effective membrane to remove microplastics and nanoplastics from water.

But there is still a big drawback in membrane technology, and that is fouling. Fouling phenomenon is one of the main limitations of membrane separations since they worsen the membrane performance at both long term and short term. As it is widely known, fouling can be reversible or irreversible: after filtration, a backwashing process is applied, so the solutes that cause the reversible fouling are removed, but not those that cause the irreversible fouling. Fouling is usually related to the hydrophilicity of the membrane surface. This should be promoted, since hydrophobic surfaces favour the interaction with the organic species responsible for fouling. Hydrophilicity can be enhanced through the composition of the membrane materials, particularly the membrane skin layer exposed to the filtering solution, with hydrophilic fillers such as zeolites,[101] graphene oxide[102] or certain MOFs.[103]

Both industry and academy know the impact of common solutes in MF, UF and RO processes, so they can design some strategies to avoid this limiting phenomenon such as fouling. However, there is not yet enough information about the behaviour of microplastics and nanoplastics in membrane processes. In other words, they are expected to cause fouling, but the mechanism is still unknown.[104] For this reason, in 2020 some authors investigated this mechanism filtrating polyethylene microplastics that were intentionally added on a commercial facial scrub. They performed several UF experiments, where they observed a decrease in the water filtration rate of 38% in 48 h, with a recovery of approximately 70% after a backwashing process. As they indicated, the micro and nanoplastics caused fouling because they are adsorbed on the internal pores of the UF membrane, clogging the cavities, and therefore leading to a progressive reduction in the water permeation and solute rejection. This experiment gave significant reasons to continue the research on fouling of microplastics and nanoplastics.

### *Future solutions from membrane technology to deal with plastic pollution*

Both in this review and in the literature, the main solutions to remove microplastics using membranes laid on MF and UF, RO and different derivatives of them all, such as membranes bioreactors (MBR) or dynamic membranes (DMs) systems. The main advantage of membrane technology is the fact that membranes are highly efficient in the removal of low-molecular weight contaminant such as small microplastics (<100 μm) and nanoplastics. In fact, Hu et al.[77] previously mentioned improvements on microplastics removal efficiency (>99%) when using membrane separation methods in WWTPs, and Freeman et al.[79] registered removal tests in WWTPs from different countries higher than 90% when tertiary treatment (with membranes usually involved) were applied. Besides, in this last publication several new methods with and without membranes involved are mentioned. Some of them, such as DMs are potentially effective to remove microplastics, while others such as MBR are proved to be highly effective for rejecting all microplastics (>99.9%) except for those smaller than 20 μm).[79]

These technologies seem to eliminate most of the plastic particles, but not all.[87] Moreover, some researchers suggested to combine RO membranes with UF membranes, giving rise to an almost total removal of microplastics and nanoplastics, except for those who found preferential pathways created by several defects.[65] However, RO membranes have a number of drawbacks apart from fouling: they are extremely dense, so the water permeation and therefore the membranes productivity are very low. This is one of those situations where the nanofiltration (NF) becomes very useful.

As explained many times in the literature,[105-107] NF membranes have intermediate UF-RO characteristics. Some areas of them have pores, while others are dense. Theoretically, the transport model that explains the mass transfer across NF membranes is a mixture between the pore-flow model (typical in UF membranes) and the solution-diffusion model (typical in RO membranes). In fact, some authors hypothesized that NF membranes might be dense, as RO membranes, but with wider intermolecular distances between the polymer chains.[107, 108]

The consequences of these small differences are a slightly higher solvent permeation through NF than through RO membranes, but a higher molecular weight cut-off (MWCO) in the latter than in the first. For instance, RO membranes can reject up to 99.9% of NaCl dissolved in water, but NF membranes rarely reject more than a 50% of that salt. However, NF membranes are highly effective rejecting divalent ions (such as Mg based salts) and light organic molecules (active principles, dyes, for example) from water, without creating high transport resistance.[106]

Then, it would be interesting to carry out investigations to observe whether NF membranes can remove as much of micro and nanoplastics as RO membranes do, but with significantly higher permeances. According to many investigations of the last decade, there are heavy reasons to think NF would be an efficient method.

Many research groups all over the world have developed highly permeable membranes effective in the removal of light organic molecules or salts that, at first glance, should be smaller than the vast majority of micro and nanoplastics (Table 3). These, then, are promising membranes in the treatment of plastic pollution: very high retention, high filtered water production, and low clean water production costs. However, some of these membranes developed at lab-scale are too far from being fabricated in industry yet, so in spite of their potential, they are not an immediate solution for the plastics issue.

*Table 3. NF membranes performances measured in scientific publications. All membranes were fabricated and measured at lab-scale during the investigations referred in the last column. TFC and TFN stand for thin film composite and thin film nanocomposite membranes, respectively; they consist of typical membrane structures suitable for NF and RO.*

| **Membrane type** | **Permeance ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)** | **Solute** | **Rejection (%)** | **Ref** |
|---|---|---|---|---|
| TFC | 2.2 | Acridine Orange | 90.6 | [109] |

| | | | | |
|---|---|---|---|---|
| TFC | 3.6 | NaCl | 59.0 | [110] |
| TFC | 6.0 | Sucrose | 77.0 | [111] |
| TFC | 6.9 | Sucrose | 94.9 | [112] |
| TFN | 3.3 | NaCl | 95.3 | [113] |
| TFN | 6.1 | NaCl | 94.3 | [114] |
| TFN | 14.8 | Congo Red | 99.6 | [115] |
| Bilayered membrane | 33.1 | Diclofenac | 99.5 | [116] |

That is not the case of those membranes already being sold by large manufacturers, as Filmtec (DuPont), Nitto Group and Koch Membranes, which in addition to other smaller membrane producers (Polymem Membrane Manufacturer, Synder Nanofiltration or Lanxess, for instance), fabricate nanofiltration membranes with outstanding performances highly interesting for nanoplastic removal. As it is seen in Table 4, several membranes combine a high permeance and high rejection of solutes such as $MgSO_4$, far lighter than nanoplastics or any other organic compound that would be released from the plastic degradation. This implies that for the purpose envisaged in this review the membrane structure should be optimized to enhance the water permeance, while keeping high rejections of nanoplastics larger in size than the solutes in Table 4 and because of that easier to be efficiently separated.

*Table 4. Permeance and rejection values of commercial NF membranes manufactured by three major producers (Filmtec, Nitto Group and Koch Membranes).*[117]

| **Manufacturer** | **Membrane model** | **Permeance ($L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$)** | **Solute** | **Rejection (%)** |
|---|---|---|---|---|
| **FILMTEC** | NF-2540 | 6.3 | $MgSO_4$ | 99.0% |
| | NF-4040 | 7.1 | | 99.0% |
| | NF-400 | 6.5 | | 99.0% |
| | NF90-400/34i | 8.9 | | 97.0% |
| | NF90-2540 | 8.7 | | 97.0% |
| | NF90-4040 | 8.7 | | 97.0% |
| | NF200-400 | 6.0 | | 3.0% |
| | NF345HP-370 | 8.7 | | 98.5% |
| | NF270-2540 | 10.7 | | 97.0% |
| | NF270-4040 | 10.9 | | 97.0% |
| | NF270-400/34i | 11.0 | | 97.0% |
| **NITTO GROUP** | ESNA1-LF-LF-4040 | 6.6 | $CaCl_2$ | 92.0% |
| | ESNA1-LF2-LD | 8.6 | | 86.0% |

|  |  |  |  |  |
|---|---|---|---|---|
|  | ESNA1-LF-LD | 6.9 | $MgSO_4$ | 92.0% |
|  | ESNA1-LF2-LD-4040 | 8.2 |  | 90.0% |
|  | NANO-BW | 5.2 |  | 99.7% |
|  | NANO-BW MAX | 5.2 |  | 99.7% |
|  | NANO-SW | 5.2 |  | 99.8% |
| **KOCH MEMBRANES** | 8040 MPS-34-NYHN | 2.0 | NaCl | 35.0% |
|  | 8040 MPS-34-ZYHN | 2.0 |  | 35.0% |
|  | MPS-34 2540 A2X | 2.0 |  | 35.0% |
|  | MPS-34 2540 A2Z | 2.0 |  | 35.0% |
|  | MPS-34 4040 A2X | 2.6 |  | 35.0% |
|  | MPS-34 4040 A2Z | 2.0 |  | 35.0% |
|  | 8040 MPS-36-NYHN | 6.7 |  | 10.0% |
|  | 8040 MPS-36-ZYHN | 6.8 |  | 10.0% |

*Polymeric membranes reuse and recycling*

A suggesting implication in the context of microplastics deals with the reuse and recycling of polymeric membranes. Poerio et al.[87] collected several publications that explored the environmental impact of the growth of the industrial sector of membranes, and therefore of the manufacture of membrane modules, as well as possible ways to reuse or recycle used membranes.[118, 119] According to these studies, almost 70% of the membranes are recyclable, and the use of recycled membranes can save around 85% of the expenses of acquiring new commercial membranes.[120]

It is interesting how those investigations could be combined with another study carried out by He et al.[18], who reused microplastics combining them with clay to fabricate composite particles (CPs). They used these CPs in a fluidized bed bioreactor to treat septic tank wastewater of low chemical oxygen demand to nitrogen ratio, and they compared the results with commercial composite particles. The authors concluded that the CPs with reused microplastics had big potential, at least, for this application.

It would be of great importance to do efforts in the future to explore strategies to manufacture materials but also membranes using microplastics collected from the environment. It may be difficult, since to prepare a membrane with the conventional methods all microplastics collected should be either soluble in the same solvent (as the used in membranes production, such as DMF, DMSO and NMP) or they should be separated first, which would likely be challenging. Assuming someone can prepare casting solutions out of these materials, probably only MF membranes could be fabricated. This is because MF membranes are highly porous, so the presence of huge spaces or pores or even imperfections (that would probably form as a result of a highly complex, and likely uncontrolled, phase inversion), may not be critical.

## 3. Conclusions and outlook

Due to their prevalence as stable pollutants in both soil and water, microplastics have constituted in a global worry comparable to that of global warming generated by excess greenhouse gas $CO_2$ in the atmosphere. The governs have to take drastic actions to control the production and release of plastics but also think of remediation policies since the presence of microplastics polluting oceans but also surface water and agriculture soil is creating a big problem of animal and human health. Moreover, there is a serious risk of falling in a cycle in which humans receive indirectly microplastics from the food extracted from the sea or generated through the use of polluted water and soil. Another important issue regarding the technologies to be implemented for microplastic remediation deals with the so called secondary microplastics. These are much smaller particles (at the limit they are additives, monomers, oligomers) becoming true micropollutants that may require at the end the membranes with molecular separation abilities as those presented here. This means that besides macroseparators, micro and ultrafiltration membranes, nanofiltration membranes, as this review proposes, it is necessary to remove the smallest secondary microplastics generated by degradation of primary microplastics.

As said, microplastics are a formidable problem regarding global pollution of our planet and several issues remain as challenges dealing with their assessment and removal. 1) The existing characterization tools available for polymers must be adapted for quick and accurate assessment of the presence of secondary microplastics in water, as they can eventually evolve to micropollutants, impossible to be detected with naked eye. 2) This will allow proper awareness of the problem since the use of polluted water for growing animals and vegetables establishes a closed cycle that humanity must avoid. 3) The estimation of up to 12,000 Mt of cumulative plastic waste in landfills or in the natural environment by 2050,[3] given at the beginning of this paper, implies a huge amount of waste (ca. 1.6 tonnes per earth inhabitant) that could find application as source of recycled matter or fuel, first if adequate use and recycling had been carried out, and second once recovered from their inacceptable current places. 4) Membrane technology, comprising micro-, ultra- and nanofiltration applications, is the most suitable to remove secondary microplastics from waste water treatment plant effluents or eventually from seawater. It is obvious that the latter case is unapproachable with the current media and technologies, but a parallel situation can be found in the case of carbon capture when recent researches propose the direct capture of $CO_2$ from the atmosphere.[121] 5) For the treatment of the immense amounts of polluted water that the previous point would require, membranes with ultrahigh permeance should be available, which means ultrathin selective membranes, for instance, as those recently proposed for gas separation based on the use of single-layer graphene (with ca. 12000 GPU of selective $CO_2$ permeance).[122]

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References:

1. A. L. Andrady, *Marine Pollution Bulletin*, 2011, **62**, 1596-1605.
2. PlasticsEurope.
3. R. Geyer, J. R. Jambeck and K. L. Law, *Sci. Adv.*, 2017, **3**, e1700782.
4. E. J. Carpenter and K. L. Jr. Smith, *Science* 1972, **175**, 1240-1241.
5. E. J. Carpenter, S. J. Anderson, G. R. Harvey, H. P. Miklas and B. B. Peck, *Science*, 1972, **178**, 749-750.
6. M. Cole, P. Lindeque, C. Halsband and T. S. Galloway, *Marine Pollution Bulletin*, 2011, **62**, 2588-2597.
7. M. R. Gregory, *Philosophical Transactions of the Royal Society B: Biological Sciences*, 2009, **364**, 2013-2025.
8. S. L. Wright, R. C. Thompson and T. S. Galloway, *Environmental Pollution*, 2013, **178**, 483-492.
9. A. Chamas, H. Moon, J. Zheng, Y. Qiu, T. Tabassum, J. H. Jang, M. Abu-Omar, S. L. Scott and S. Suh, *Acs Sustainable Chemistry & Engineering*, 2020, **8**, 3494-3511.
10. L. Lv, X. Yan, L. Feng, S. Jiang, Z. Lu, H. Xie, S. Sun, J. Chen and C. Li, *Water Environment Research*, 2019, 1-11.
11. M. Wagner, C. Scherer, D. Alvarez-Muñoz, N. Brennholt, X. Bourrain, S. Buchinger, E. Fries, C. Grosbois, J. Klasmeier, T. Marti, S. Ridriguez-Mozaz, R. Urbatzka, A. Dick Vethaak, M. Winther-Nielsen and G. Reifferscheid, *Environmental Science Europe*, 2014, **26**, 1-9.
12. K. Lavender Law and R. C. Thompson, *Science*, 2014, **345**, 144-145.
13. C. J. Moore, G. L. Lattin and F. Z. A, *Long Beach: Algalita Marine Research Foundation*, 2005.
14. F. Dubaish and G. Liebezeit, *Water Air Soil Pollut*, 2013, **224**, 1352.
15. K. A. Zubris and B. K. Richards, *Environmental Pollution*, 2005, **138**, 201-211.
16. A. A. Horton, A. Walton, D. J. Spurgeon, E. Lahive and C. Svendsen, *Science of the Total Environment*, 2017, **586**, 127-141.
17. UNESCO, *Wastewater. The Untapped Resource. Facts and Figures*, 2017.
18. X. He, H. Li and J. Zhu, *Biochemical Engineering Journal*, 2019, **151**, 107300.
19. R. C. Thompson, Y. Olsen, R. P. Mitchell, A. Davis, S. J. Rowland, A. W. G. John, D. McGonigle and A. E. Russell, *Science*, 2004, **304**, 838-838.

20. E. R. Graham and J. T. Thompson, *Journal of Experimental Marine Biology and Ecology*, 2009, **368**, 22-29.
21. P. G. Ryan, C. J. Moore, J. A. van Franeker and C. L. Moloney, *Philosophical Transactions of the Royal Society B: Biological Sciences*, 2009, **364**, 1999-2012.
22. M. F. Costa, J. A. Ivar do Sul, J. S. Silva-Cavalcanti, M. C. B. Araújo, Â. Spengler and P. S. Tourinho, *Environmental Monitoring and Assessment*, 2010, **168**, 299-304.
23. M. Eriksen, L. C. M. Lebreton, H. S. Carson, M. Thiel, C. J. Moore, J. C. Borerro, F. Galgani, P. G. Ryan and J. Reisser, *PLOS ONE*, 2014, **9**, 1-15.
24. H. S. Auta, C. U. Emenike and S. H. Fauziah, *Environmental International*, 2017, **102**, 165-176.
25. S. Bintein, *39168*, 2017, **European Commission**, p 220.
26. J. Bujnicki, P. Dykstra, E. Fortunato, N. Grobert, R. Rolf-Dieter, C. Keskitalo and P. Nurse, *Scientific Opinion 6/2019*, 2019, **European Commission**, p. 64.
27. M. Murphy, *EPA office of Wetlands*, 2017, **Oceand and Watersheds**, p. 37.
28. R. C. Hale, M. E. Seeley, M. J. La Guardia, L. Mai and E. Y. Zeng, *Journal of Geophys. Res. Oceans*, 2020, **125**.
29. M. R. Gregory, *Marine Environmental Research*, 1983, **10**, 73-92.
30. M. Claessens, S. D. Meester, L. V. Landuyt, K. D. Clerck and C. R. Janssen, *Marine Pollution Bulletin*, 2011, **62**, 2199-2204.
31. M. Vert, Y. Doi, K-H. Hellwich, M. Hess, P. Hodge, P. Kubisa, M. Rinaudo and F. Schué, *Pure and Applied Chemistry*, 2012, **84**, 377-410.
32. *European Chemical Agency*.
33. J. R. Jambeck, R. Geyer, C. Wilcox, T. R. Siegler, M. Perryman, A. Andrady, R. Narayan and K. L. Law, *Science*, 2015, **347**, 768-771.
34. B. Nguyen, D. Claveau-Mallet, L. M. Hernandez, E. G. Xu, J. M. Farner and N. Tufenkji, *Acc. Chem. Res.*, 2019, **52**, 858-866.
35. C. Barría, I. Brandts, L. Tort, M. Oliveira and M. Teles, *Marine Pollution Bulletin*, 2020, **151**, 110791.
36. M. Shen, Y. Zhang, Y. Zhu, B. Song, G. Zeng, D. Hu, X. Wen and X. Ren, *Environmental Pollution*, 2019, **252**, 511-521.
37. L. Rubio, R. Marcos and A. Hernandez, *Journal of Toxicology and Environmental Health, Part B*, 2020, **23**, 51-68.
38. J. Boucher and D. Friot, *IUCN International Union for Conservation of Nature*, 2017.
39. E. Kentin and H. Kaarto, *RECIEL*, 2018, **27**, 254-266.
40. A. Neslen, *The Guardian*, 2019, **Brussels**.
41. A. L. Andrady, *Macromol. Sci. R. M. C*, 1994, **34**, 25-75.
42. A. L. Andrady and J. E. Pegram, *Journal of Applied Polym. Sci.*, 1990, **39**, 363-370.
43. M. Poulicek and C. Jeuniaux, *Biochem. Syst. Ecol.*, 1991, **19**, 385-394.
44. A. L. Andrady and J. E. Pegram, *David Taylor Research Center. US Department of the Navy*, 1992.
45. J. M. Mayer and D. L. Kaplan, *ACS Symposium Series 627ACS*, 1996.
46. A. M. https://theoceancleanup.com.
47. *The Ocean Cleanup*, 2019.
48. *The Ocean Cleanup*, 2019.
49. *Draper*, 2019.
50. J. Sun, X. Dai, Q. Wang, M. C. M. van Loosdrecht and B.-J. Ni, *Water Research*, 2019, **152**, 21-37.
51. *United States Environmental Protection Agency*, 2017.
52. , 2019.
53. D. Eerkes-Medrano, R. C. Thompson and D. C. Aldridge, *Water Research*, 2015, **75**, 63-82.
54. V. Hidalgo-Ruz, L. Gutow, R. C. Thompson and M. Thiel, *Environmental Science and Technology*, 2012, **46**, 3060-3075.
55. K. Ashton, L. Holmes and A. Turner, *Marine Pollution Bulletin*, 2010, **60**, 2050-2055.

56. D. A. Cooper and P. L. Corcoran, *Marine Pollution Bulletin*, 2010, **60**, 650-654.

57. Y. Mato, T. Isobe, H. Takada, H. Kanehiro, C. Ohtake and T. Kaminuma, *Marine Pollution Bulletin*, 2001, **35**, 318-324.

58. K. L. Ng and J. P. Obbard, *Marine Pollution Bulletin*, 2006, **52**, 761-767.

59. P. L. Corcoran, M. C. Biesinger and M. Grifi, *Marine Pollution Bulletin*, 2009, **58**, 80-84.

60. G. L. Skipp and I. K. Brownfield, *Improved density gradient separation techniques using sodium polytungstate and a comparison to the use of other heavy liquids*, U.S. Geological Survey, 1993.

61. M-T. Nuelle, J. H. Dekiff, D. Remy and E. Fries, *Environmental Pollution*, 2014, **184**, 161-169.

62. H. K. Imhof, J. Schmid, R. Niessner, N. P. Ivleva and C. Laforsch, *Limnol Oceanogr Methods*, 2012, **10**, 524-537.

63. F. Noren, *KIMO report*, 2007.

64. L. M. Rios, P. R. Jones, C. Moore and U. V. Narayan, *Journal of Environmental Monitoring*, 2010, **12**, 2226-2236.

65. S. Ziajahromi, P. A. Neale, L. Rintoul and F. D. L. Leusch, *Water Research*, 2017, **112**, 93-99.

66. Q. Li, J. Wu, X. Zhao, X. Gu and R. Ji, *Environmental Pollution*, 2019, **254**, 113076.

67. S. Moret-Ferguson, K. L. Law, G. Proskurowski, E. K. Murphy, E. E. Peacock and C. M. Reddy, *Marine Pollution Bulletin*, 2010, **60**, 1873-1878.

68. L. Lv, L. He, S. Jiang, J. Chen, C. Zhou, J. Qu, Y. Lu, P. Hong, S. Sun and C. Li, *Science of the Total Environment*, 2020, **728**, 138449.

69. F. Murray and P. R. Cowie, *Marine Pollution Bulletin*, 2011, **62**, 1207-1217.

70. J. G. Shiber, *Marine Pollution Bulletin*, 1979, **10**, 28-30.

71. C. Wang, Z. Xian, X. Jin, S. Liang, Z. Chen, B. Pan, B. Wu, Y. Sik Ok and C. Gu, *Water Research*, 2020, **183**, 116082.

72. P. Liu, L. Qian, H. Wang, X. Zhan, K. Lu, C. Gu and S. Gao, *Environmental Science & Technology*, 2019, **53**, 3579-3588.

73. L. Zhou, T. Wang, G. Qu, H. Jia and L. Zhu, *Journal of Hazardous Materials*, 2020, **398**, 122956.

74. J. Talvitie, A. Mikola, A. Koistinen and O. Setälä, *Water Research*, 2017, **123**, 401-407.

75. S. A. Mason, D. Garneau, R. Sutton, Y. Chu, K. Ehmann, J. Barnes, P. Fink, D. Papazissimos and D. L. Rogers, *Environmental Pollution*, 2016, **218**, 1045-1054.

76. L. Li, G. Xu, H. Yu and J. Xing, *Science of the Total Environment*, 2018, **627**, 332-340.

77. Y. Hu, M. Gong, J. Wang and A. Bassi, *Rev Environ Sci Biotechnol*, 2019, **18**, 270-230.

78. P. Sundt, P.-E. Schulze and F. Syversen, *Norwegian Environmental Agency: Norway, 2015*, 2015.

79. S. Freeman, A. M. Booth, I. Sabbah, R. Tiller, J. Dierking, K. Klun, A. Rotter, E. Ben-David, J. Javidpour and D. L. Angel, *Journal of Environmental Management*, 2020, **266**, 110642.

80. H. Strathmann, *Journal of Membrane Science*, 1981, **9**, 121-189.

81. H. Strathmann, *AIChEJ*, 2004, **47**, 1077-1087.

82. J. R. Werber, C. O. Osuji and M. Elimelech, *Nature Reviews Materials*, 2016, **1**, 16018.

83. S. A. Carr, J. Liu and A. G. Tesoro, *Water Research*, 2016, **91**, 174-182.

84. T. Sato, M. Qadir, S. Yamamoto, T. Endo and A. Zahoor, *Agricultural Water Management*, 2013, **130**, 1-13.

85. A. B. Silva, A. S. Bastos, C. I. L. Justino, J. P. da Costa, A. C. Duarte and T. A. P. Rocha-Santos, *Analytica Chimica Acta*, 2018, **1017**, 1-19.

86. J. P. da Costa, P. S. M. Santos, A. C. Duarte and T. Rocha-Santos, *Science of the Total Environment*, 2016, **566-567**, 15-26.

87. T. Poerio, E. Piacentini and R. Mazzei, *Molecules*, 2019, **24**, 4148.

88. B. Gewert, M. M. Plassmann and M. MacLeod, *Environmental Science: Processes & Impacts*, 2015, **17**, 1513-1521.

89. J. Ma, Z. Wang, Y. Xu, Q. Wang, Z. Wu and A. Grasmick, *Chemical Engineering Journal*, 2013, **219**, 190-199.

90. J. Ma, Z. Wang, X. Zou, J. Feng and Z. Wu, *Process Biochemistry*, 2013, **48**, 510-516.

91. A. R. A. Lima, M. F. Costa and M. Barletta, *Environmental Research*, 2014, **132**, 146-155.

92. S. S. Sadri and R. C. Thompson, *Marine Pollution Bulletin*, 2014, **81**, 55-60.

93. S. Zhao, L. Zhu, T. Wang and D. Li, *Marine Pollution Bulletin*, 2014, **86**, 562-568.

94. M. Di and J. Wang, *Science of the Total Environment*, 2018, **616-617**, 1620-1627.

95. B. Ma, W. Xue, C. Hu, H. Liu, J. Qu and L. Li, *Chemical Engineering Journal*, 2019, **359**, 159-167.

96. *Water Research*.

97. S. Karbalaei, P. Hanachi, T. R. Walker and M. Cole, *Environmental Science and Pollution Research*, 2018, **25**, 36046-36063.

98. L. C. Woodall, A. Sanchez-Vidal, M. Canals, G. L. J. Paterson, R. Coppock, V. Sleight, A. Calafat, A. D. Rogers, B. E. Narayanaswamy and R. C. Thompson, *R. Soc. open sci.*, 2014, **1**, 140317.

99. Z. Wang, S. E. Taylor, P. Sharma and M. Flury, *PLOS ONE*, 2018, **13**, e0208009.

100. Z. Zhang and Y. Chen, *Chemical Engineering Journal*, 2020, **382**, 122955.

101. L-x. Dong, H-w. Yang, S-t. Liu, X-m. Wang and Y. F. Xie, *Desalination*, 2015, **365**, 70-78.

102. C. Ma, J. Hu, W. Sun, Z. Ma, W. Yang, L. Wang, Z. Ran, B. Zhao, Z. Zhang and H. Zhang, *Chemosphere*, 2020, **253**, 126649.

103. C. Echaide-Górriz, M. Navarro, C. Téllez and J. Coronas, *Dalton Transactions*, 2017, **46**, 6244-6252.

104. M. Enfrin, J. Lee, P. Le-Clech and L. F. Dumée, *Journal of Membrane Science*, 2020, **601**, 117890.

105. R. W. Baker, *Membrane Technology and Applications*, John Wiley & Sons, Ltd.

106. P. Vandezande, L. E. M. Gevers and I. F. J. Vankelecom, *Chemical Society Reviews*, 2008, **37**, 365-405.

107. K. Kosutic, *Journal of Membrane Science*, 2000, **168**, 101-108.

108. Y. H. See-Toh, F. C. Ferreira and A. G. Livingston, *Journal of Membrane Science*, 2007, **299**, 236-250.

109. C. Echaide-Górriz, M. Malankowska, C. Téllez and J. Coronas, *AIChEJ*, 2020, aic. 16970.

110. S. P. Sun, S. Y. Chan, W. H. Xing, Y. Wang and T. S. Chung, *Acs Sustainable Chemistry & Engineering*, 2015, **3**, 3019-3023.

111. S. Verissimo, K. V. Peinemann and J. Bordado, *Desalination*, 2005, **184**, 1-11.

112. H. Z. Zhang, Z. L. Xu, H. Ding and Y. J. Tang, *Desalination*, 2017, **420**, 158-166.

113. D. C. Ma, S. B. Peh, G. Han and S. B. Chen, *Acs Applied Materials & Interfaces*, 2017, **9**, 7523-7534.

114. B. Khorshidi, T. Thundat, B. A. Fleck and M. Sadrzadeh, *Sci Rep*, 2016, **6**, 22069.

115. M. Liu, Q. Chen, K. Lu, W. Huang, Z. Lü, C. Zhou, S. Yu and C. Gao, *Separation and Purification Technology*, 2017, **173**, 135-143.

116. L. Paseta, D. Antoran, J. Coronas and C. Tellez, *Industrial & Engineering Chemistry Research*, 2019, **58**, 4222-4230.

117. https://www.lenntech.es/products/membrane/romembranes.htm.

118. -. r. https://www.globalmarketers.biz/report/chemicals-and-materials/global-membranefiltration-market-2019-by-manufacturers, -type-and-application,-forecast-to-2024 Global Membrane Filtration Market 2019 By Manufacturers, Regions, Type And Application, Forecast to 2024.

119. A. Lejarazu-Larrañaga, S. Molina, J. M. Ortiz, R. Navarro and E. García-Calvo, *Journal of Membrane Science*, 2020, **593**, 117423.

120. https://www.water.imdea.org/news/2018/achievements-and-conclusions-life-transfomemproject-recycling-disposed-membranes, 2019.

121. E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas and C. W. Jones, *Chem. Rev.*, 2016, **116**, 11840-11876.

122. G. He, S. Huang, L. F. Villalobos, J. Zhao, M. Mensi, E. Oveisi, M. Rezaei and K. V. Agrawal, *Energy & Environmental Science*, 2019, **12**, 3305-3312.