

# Polymeric Membranes for Micronanoplastic Sampling and Removal from Water Effluents

Junkal Landaburu-Aguirre\* and Serena Molina

IMDEA Water Institute, Avenida Punto Com, 2, Alcalá de Henares, 28805 Madrid, Spain

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**\*Corresponding author:** Junkal Landaburu-Aguirre, IMDEA Water Institute, Avenida Punto Com, 2, Alcalá de Henares, 28805 Madrid, Spain

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## Abstract

Micro and Nano Plastics (MNPs) are pollutants of increasing concern that are found in water samples such as marine environment and freshwater. Wastewater Treatment Plants (WWTPs) have been identified as one of the main dominant sources of Microplastics (MPs) in freshwater. Primary and secondary wastewater treatments remove the majority of MPs, achieving removal efficiencies of 98-99%. However, these studies have mainly monitored relatively big size MPs leaving the small size MNPs aside. Consequently, the release of MNPs from WWTP to the aquatic environment might be much more problematic than known to this day. The implementation of advanced treatment processes such as membrane technology can contribute to overcoming these limitations, by implementing them not only as a tertiary treatment, but also as a sampling method. This minireview shows the latest works related to the separation and removal efficiency of MNPs using pressure driven microfiltration and ultrafiltration membranes. In addition, membrane fouling mechanism by MNPs is explained showing that the hydrophobic interaction and the relation between particle size and membrane pore size have the main influence on it.

**Keywords:** Polymeric membranes; Micronanoplastics; Wastewater treatment; Fouling

**Abbreviations:** MNPs: Micro-Nano Plastics; WWTPs: Wastewater Treatment Plants; FTIR: Fourier Transform Infrared; MF: Microfiltration; UF: Ultrafiltration

## Introduction

The plastic industry contributes to economic growth, having produced an output of 377 million Metric Tonnes (Mt) by 2020 [1]. This massive production has a great environmental impact. Around 78% of the plastics produced have been discarded either in landfills or elsewhere in the environment. Once in the environment, plastics undergo abiotic and biotic weathering processes that cause their degradation and fragmentation into smaller particles, commonly termed Microplastics (MPs; defined as fragments <5mm) and Nanoplastics (NPs, defined as fragments <1µm) [2,3]. The Micro-Nano plastics (MNPs) that are formed due to the fragmentation of larger plastics by physical, mechanical or biodegradation are called secondary MNPs. In addition, there are also primary MNPs, which are specifically manufactured in micro(nano)-size for use in personal care, cosmetics or synthetic textiles, etc. [4]. MP and NP particles are emerging pollutants of increasing concern. The ocean is estimated to already contain over 150Mt of plastics [5]. In addition, recent studies revealed that the abundance of MPs in freshwaters is comparable to that of marine environment [6]. Under this context, Wastewater Treatment Plants (WWTPs) have been identified as one of the main dominant sources of MPs in freshwater [7]. The MPs found in wastewaters consist for example of microbeads added in peeling lotions and toothpastes and synthetic fibers from textile and clothing [4]. In general terms, studies have indicated that wastewater treatment plants remove the majority of MPs, achieving removal efficiencies of 98-99% [8,9]. Among the conventional physico-chemical treatment methods used in the removal of these pollutants there are sand filtration [10], coagulation-flocculation [11], membrane bioreactor [12], electrocoagulation [13] and sorption [14]. Despite the high removal ability of the wastewater

treatment technologies studied, the research efforts have been mainly limited to the quantification of relatively big size MPs, leaving small size MP and NPs out of the studied size spectrum. The evaluation of the removal capacity of Micronanoplastics (MNPs) by advanced water treatment technologies has been limited due to the lack of standardized methods for sampling, identification and quantification of MNPs from wastewater treatments [15]. Among the existing techniques for MPs chemical identification Fourier Transform Infrared (FTIR) and Raman are the most commonly used techniques.  $\mu$ FTIR is capable of identifying MPs ranged between 20 $\mu$ m and 500 $\mu$ m, being the major drawback of this method that cannot identify particles <20 $\mu$ m [16]. On the other hand, because the laser beam in Raman spectroscopy is smaller than in FTIR, Raman spectroscopy can identify microplastics as small as a few micrometers. As an alternative, thermal degradation method based on a gas chromatographic mass spectrometer coupled with pyrolysis is established as a recognized method for qualitative and quantitative analyses of polymers capable of quantifying both MPs and NPs. During the sampling process, the choice of the used mesh size already limits the MNP size characterization and identification capacity of our methodology, with 20 $\mu$ m being the smallest screening mesh size mainly used until now [17]. As an example, Ben-David et al. [18] observed that including a finer mesh size of 0.45 $\mu$ m during the sampling method doubled the number of MPs found in the tertiary treatment effluents [18], showing the need of developing new sampling methods capable of capturing small MNPs. Polymeric Microfiltration (MF) and Ultrafiltration (UF) membranes can contribute to overcoming these limitations, by implementing them not only as a tertiary treatment, but also as a sampling method.

### Polymeric Microfiltration and Ultrafiltration Membranes

In MF and UF membranes pressure is applied to overcome the hydraulic resistance of the membrane for the mass transfer. MF membranes work in a pore size range between 0.1-10 $\mu$ m, which means that they require a relatively low operating pressure (0.1-2 bar) and UF membranes have a pore size between 0.01-0.1 $\mu$ m, operating at pressures between 2-6 bar. The small pore sizes of these membranes make them viable for the separation of small MNPs (<20 $\mu$ m) [19,20]. The separation of these micropollutants can be conducted with different purposes such as:

- A. Water purification: undesired MNP pollutants are removed from wastewaters by implementing MF and UF membranes as a tertiary treatment in WWTPs.
- B. Concentration: small size MNPs can be present in water environmental samples in low concentrations, making their detection and identification difficult. A concentration step would be required, where the solvent (water) is removed retaining the desired compound (MNPs) in the concentrate part.

The process performance of membrane separation processes is evaluated in terms of their selectivity, represented by the rejection

coefficient (R, %), and the permeate flux (J, L/m<sup>2</sup>h) calculated with the following equations (Eq. 1 and Eq. 2):

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \cdot 100 \quad \text{Eq. (1)}$$

where  $C_p$  and  $C_f$  (g/L) are the concentrations of permeate and feed solutions, respectively

$$J = \left(\frac{V}{A\Delta t}\right) \quad \text{Eq. (2)}$$

where V (L) is the volume of permeated water, A (m<sup>2</sup>) is the membrane area, and  $\Delta t$  is the permeation time at 25 °C temperature. Kook et al. [21] analyzed the removal efficiency and behavior of MNPs (PS and PE; 0.1 and 1.0 $\mu$ m) in membrane-based wastewater treatment, comparing polymeric and ceramic membranes. They observed that 1.0 $\mu$ m PS microplastic was successfully removed, obtaining 99.6% removal by all membranes, although they observed a slightly lower retention of over 96.0% for the 0.1 $\mu$ m PS microplastics. This was an expected result since the evaluated membrane had a pore size around 0.1 $\mu$ m. In order to improve the selectivity of the membranes towards the MNPs, other studies have been focused on preparing tailor made membranes for such purpose. Wang et al. [22] studied the removal efficiency of modified electro-spun membranes with controlled surface charge towards three different sizes of PS nanospheres (500nm, 100nm, 50nm). They observed that the positively charged membranes boosted the retention rate of the PS nanosphere to almost 100% due to the electrostatic interaction occurring between the charged membrane and the Nano plastic. Wan et al. [23] also prepared nanofibrous membranes to remove NPs in a gravity-driven membrane filtration process. The three types of studied NPs (range 107-1450nm) were successfully removed (92%) using the nanofibrous membranes in a gravity-driven mode, an energy-saving method because the required pressure is lower than the operating pressure of UF membranes. In addition, they showed that when diameter of NPs is bigger than the diameter of the membrane pore size, the NPs were rejected by the membrane pores via size- exclusive effect.

However, when diameter of the NPs is smaller than the diameter of the membrane pores, the NPs were adsorbed in the nanofibrous membranes by electrostatic attraction and hydrophobic interactions. During the filtration process, fouling remains one of the main issues that directly affect the membrane process performance in terms of reducing the permeate flux, changing the membrane selectivity or permeate quality, and increasing the membrane maintenance and replacement costs [24]. The fouling mechanism in the membrane is determined by the ratio of the foulant size ( $d_f$ ) to membrane pore size ( $d_{pore}$ ) as following: (i) if  $d_f < d_{pore}$ , the foulant can be adsorbed onto the membrane surface or pore walls, or pass through the membrane; (ii) if  $d_f = d_{pore}$ , the foulant tend to form a gel/cake layer or block the external or internal membrane pores; and (iii) if  $d_f > d_{pore}$ , the foulant typically blocks the membrane surface pores or forms gel/cake layers at the membrane surface [24]. Enfrin et al. [25] studied the process performance

of UF (PES; 30kDa) membranes towards a broad size distribution plastic particle from 12.5 to 689.6nm that were extracted from a cosmetic product used for facial scrub. They observed that during the filtration experiments, the water flux declines 38% due to the hydrophobic interactions between the NPs and the membrane, causing the adsorption of the NPs onto the pores and surface of the membrane. More specifically, they assumed that the fouling occurs first by intermediate pore blocking before all the pores get covered and then, the NPs accumulate forming a cake layer on the whole membrane surface. This kind of work is crucial to develop appropriate filtration and cleaning procedures, enhancing the membrane process performance. Therefore, further research on understanding the membrane fouling mechanism by MNPS is highly important.

## Conclusion

MNPs are an emerging environmental challenge that has gained an outstanding interest in the past few years increasing the research effort to understand their identification and quantification, fate, impact as well as mitigation strategies. Membrane technology is a mature technology capable of eliminating small MNPs (<20µm) efficiently. However, research studies related to this application are scarce. This might be due to the lack of standardized processes and to the lack of efficient quantification and sampling methods for small MNPs that hinder a real evaluation of treatment technologies such as membrane technology. Further research on implementing membrane technology for the concentration and removal of small MNPs, gaining a deep understanding of the separation and fouling mechanism of these micropollutant should be encouraged.

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