

Evaluation of membranes performance for microplastic removal in a simple and low-cost filtration system



Angela Raffaella Pia Pizzichetti^{a,b}, Cristina Pablos^{a,*}, Carmen Álvarez-Fernández^a, Ken Reynolds^b, Simon Stanley^b, Javier Marugán^a

^a Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan Carlos, C/Tulipán S/n, 28933, Móstoles, Madrid, Spain

^b ProPhotonix IRL LTD, 3020 Euro Business Park, Little Island, Cork, T45 X211, Ireland

ARTICLE INFO

Keywords:

Tap water
Dead-end microfiltration
Abrasion
Fouling
Polyamide
Polystyrene

ABSTRACT

The ubiquitous presence of microplastics (MPs) in the environment has become a major challenge in recent years. One of the main concerns is the eco-toxicological effect on marine ecosystems and the potential threat for human organs and tissues. This paper focuses on evaluating membranes performance in removing MPs within a simple, low-cost system that could be easily implemented in a domestic environment. The performance of polycarbonate, cellulose acetate, and polytetrafluoroethylene membranes with the same nominal pore size of 5 μm was evaluated in the removal of polyamide and polystyrene microparticles in the range of 20–300 μm . Their mass removal efficiency when filtering 100 mg/L of MPs was also calculated. A high mass removal efficiency of MPs above 94 was obtained with the three membranes. However, depending on the MPs' nature, they could either break through the membrane or break down into smaller particle sizes. Beside size-exclusion separation, the main competing mechanisms are membrane abrasion and fouling phenomenon. Their contribution depends on the membrane properties, MPs-membrane interaction, particles' irregularity, and transmembrane pressures employed. At comparable mass removal efficiency, the highest performing membrane material for long-term household system applications was found to be cellulose acetate.

1. Introduction

In recent years, there has been a growing awareness of novel pollutants affecting water quality. Microplastics (MPs), defined as plastic particles smaller than 5 mm, have been detected ubiquitously in freshwater systems and labelled as contaminants of emerging concern [1–5]. The impact of MPs' on the ecosystems and human health is still under study. One of the main concerns is that they attract on their surface other hydrophobic persistent organic pollutants (POPs), act as substrates for biofilms, and contain additives that can be dangerous for the human body [4,6,7]. At present, there are very few studies focusing on the technologies and their effectiveness for their removal from drinking water, and they mainly rely on expensive operations first developed for other purposes but also explored for MPs removal [8]. This study aims to tackle the problem of microplastics pollution in drinking water by exploring a low-cost tap water filtration system. To the best of the authors' knowledge, no previous studies have been published focusing directly on MP removal from tap water through microfiltration. This work presents the

evaluation of the performance of three commercial membranes of polycarbonate (PC), cellulose acetate (CA), and polytetrafluoroethylene (PTFE) with the same nominal pore size. The chosen membranes have different chemical features, allowing the study of the possible influence of the material on the effective removal of MPs and their long-term performance. The work is focused on microfiltration, the oldest membrane system for dead-end filtration [9]. In this process, suspended solids are separated from liquid depending on the membrane characteristics, such as material type, pore size, and operating parameters [10]. The primary mechanism is size-exclusion, but in the presence of electrostatic interaction, pore adsorption can also occur, resulting in higher fouling phenomenon [9,11,12].

Transmembrane pressure, water flux, and mass removal were calculated to assess and compare the performance of the studied membranes. According to the literature, on average, over 90% of microplastics in wastewater treatment plant effluents are smaller than 500 μm [1]. Therefore, a size range of 20–300 μm was chosen for the MPs particles to evaluate. The selected membranes' nominal pore size was 5 μm , looking

* Corresponding author.

E-mail addresses: cristina.pablos@urjc.es (C. Pablos), javier.marugan@urjc.es (J. Marugán).

for a compromise between the removal of the particles and the required transmembrane pressure. Finally, since most of the research published on MPs focus on polyethylene [13,14], this study analyses the removal of other two major MPs plastic constituents relevant from the environmental point of view, such as polyamide (PA) and polystyrene (PS) [15, 16].

2. Materials and methods

2.1. Materials

Polyamide nylon 6 (PA) and polystyrene (PS) particles were purchased from Goodfellow. The sieves of 300 μm , 20 μm , and a sieve pan were purchased from Scharlab. The size of the PS particles bigger than 300 μm was reduced by cryogenic milling (Biomet, Retsch).

2.2. Characterisation of PS and PA particles

The zeta potential of the PA and PS particles was measured with the NanoPlus HD sensor from Micromeritics. Deionised water from a Millipore Milli-Q system was used with a concentration of PA and PS of 500 mg/L each. Suspensions of the plastics were measured at several pH values, adjusting the amount of HCl and NaOH, respectively, for acid and basic solutions.

2.3. Filtration experiments

The filtration setup system is detailed and schematised in Fig. S1 (Supplementary Information). It includes a glass container with a bottom exit of 5 L, a needle valve, temperature, pressure, and flow rate sensors, and a centrifugal pump (model TP 78/A, Calpeda) connected to a variable-frequency drive (RS510, RS Pro) to regulate its power. The membranes are held in a stainless-steel filter holder of 47 mm diameter (16254, Sartorius). Distilled water from Millipore TANKPE100 was used in all the experiments to avoid any other contamination or uncontrolled effects on the comparison of the performance of the different membranes.

The studied membranes, shown in Table 1, are commercially available and provided by Filter-Lab: PC, CA, and PTFE, all with 47 mm diameter and nominal pore size of 5 μm . The hardness of the membranes was measured with a shore durometer (P. G. 812, Amsler W Testor), type A.

Polycarbonate and cellulose acetate are both negatively charged membranes, with zeta potential of -11.5 mV at pH \sim 7.4 [17], and -35 mV at pH \sim 6 [18], respectively. Therefore, the CA membrane has a stronger negatively charged surface compared to the PC membrane. Most of the commercial membranes available currently in the market are negatively charged [19]. The exception includes positively charged nylon membranes which were not suitable in our case study as it could have influenced the probe MPs removal.

2.4. Analysis of the removal efficiency of the membranes

Glass microfiber filters of 0.70 μm (provided by Filter-Lab) were employed to quantify the mass removal efficiency of the different membranes. The details are described in the Supplementary Information.

Table 1
Membranes' characteristics.

Membranes	Pore size	Properties	Shore Hardness
Polycarbonate (PC)	5 μm	Hydrophilic	71.0 \pm 2.7
Cellulose acetate (CA)	5 μm	Hydrophilic	62.7 \pm 0.6
Polytetrafluoroethylene (PTFE)	5 μm	Hydrophobic	76.3 \pm 3.2

3. Results and discussions

3.1. Zeta potential and surface charge of microplastics in water

Plastic is a hydrophobic material, but in water is found to enhance the adsorption of hydroxide ions, which affects the particle charge depending on the particle size and can induce electrostatic interaction when both particles and membranes are charged [10,11,20]. Zeta potential (ζ) depends on the particle's environment and, more precisely, corresponds to the potential difference between the dispersion medium and the stationary layer of the fluid attached to the particle [21,22]. PA's and PS's zeta potential changes from negative to positive when changing from basic to acid conditions, where the points of zero charge are at pH 6.5 and pH 4, respectively, according to Fig. 1. At neutral pH 6.5, common drinking water conditions, PA particles show a high degree of aggregation and hydrophobic behaviour. In contrast, PS particles reveal a slightly negative potential with a magnitude of 20 mV, which means incipient instability and a slightly negative surface charge.

3.2. Microfiltration: membranes performance with PA and PS particles

The membranes' performances were studied as a function of time and with a known initial concentration of microplastics (100 mg/L). The results of transmembrane pressure (TMP) and flow rate for PA and PS measurements are shown in Fig. 2. Temperature values (not shown) were constant at room temperature during the experiments. At the beginning of each experiment, the pump was manually set to operate at 0.5 bar of TMP. Due to their high hydrophobicity, the working pressure of the PTFE membranes was set to 1.5 bar.

To ensure that the observed effects are significant, for each membrane, at least five replicates of the filtration experiments were performed to evaluate the experimental errors. Table 2 shows the average TMP drop and the average flux for each membrane after 10 min of the system operation.

3.3. Mass removal efficiency

A considerable variation in concentration and particle size emerged from previous studies mainly due to the use of different sample collection and analysis methods, which affected the final quantification and the identification [4,23]. Simon et al. [24] also underlined the error arising from reporting the measurements based on particle number only as the continuous breaking down of the particles in the environment could

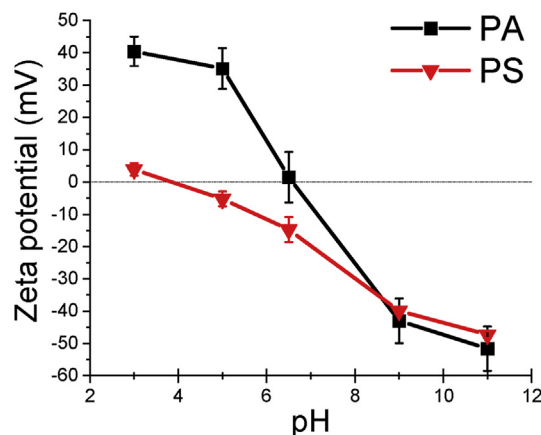


Fig. 1. Zeta potential curves of 500 mg/L of PA (black squares) and PS (red triangles) particles of size between 20-300 μm as a function of pH. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

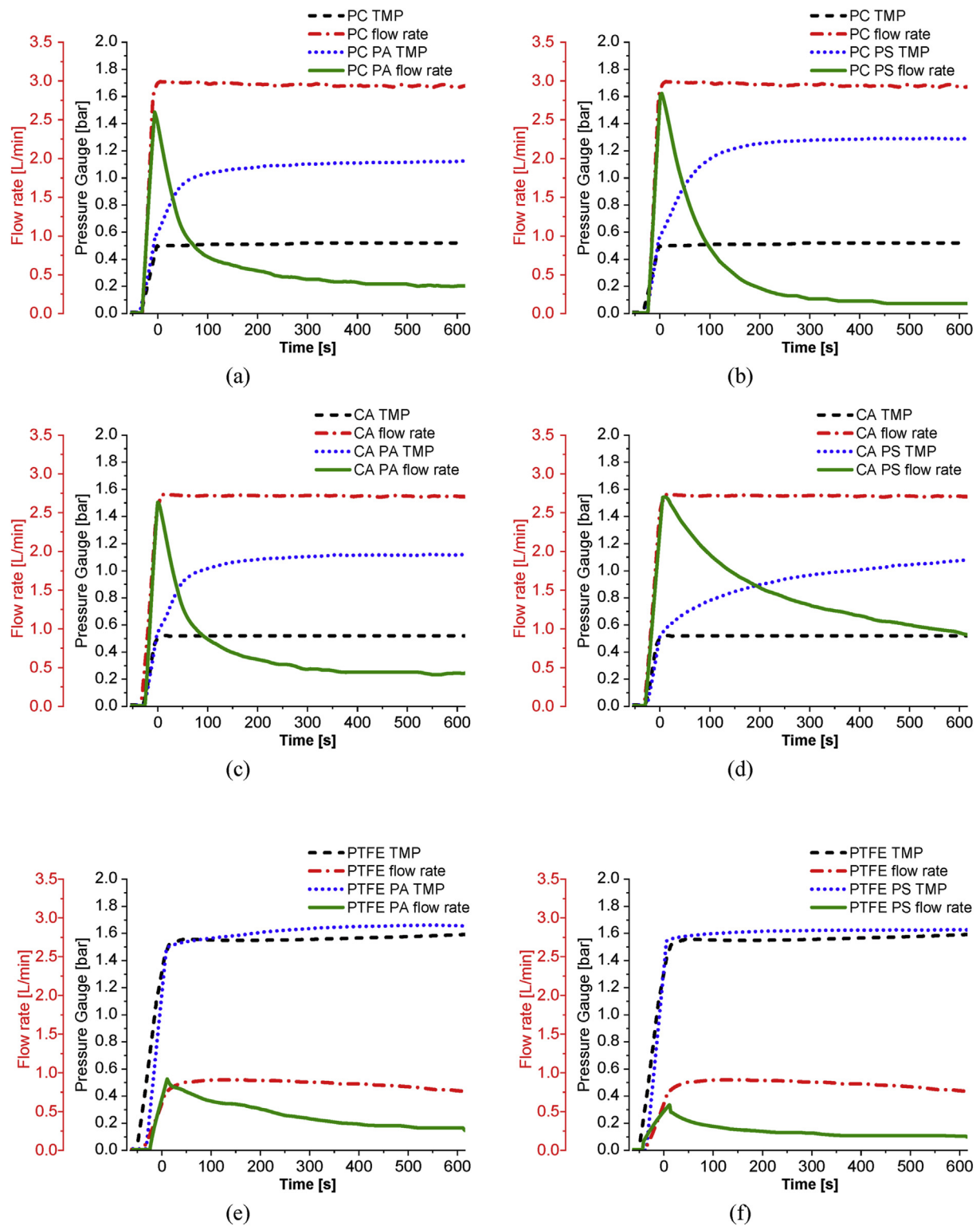


Fig. 2. Results of transmembrane pressure (TMP) and flow rate of PC, CA, and PTFE membranes for PA (a, c, and e) and PS (b, d, and f) filtration. The dash-dash (black) and the dash-dot (red) curves correspond to the behaviour of the membranes when filtering pure water, TMP and flow rate, respectively. The dot-dot (blue) and the straight-line (green) curves correspond to the membrane's behaviour when filtering water with 100 mg/L of PA and PS, TMP and flow rate, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

result in a potential overestimation of their concentration. The particle number is not a conserved base quantity; therefore, we reported the mass removal efficiency to help provide comparable results with other studies. The mass removal efficiency ($MRE\%$) was calculated as follows:

$$MRE\% = \left(1 - \frac{Fm_{MPs}}{Im_{MPs}}\right) \cdot 100$$

Where Im_{MPs} corresponds to the initial mass of the MPs entering the

Table 2

Average transmembrane pressure drop (Δ TMP) and flux (J) after 10 min of operation of the studied membranes during 100 mg/L of PA and PS filtration.

	PA filtration		PS filtration	
	Δ TMP _{10min} [bar]	J _{10min} [L·s ⁻¹ ·m ²]	Δ TMP _{10min} [bar]	J _{10min} [L·s ⁻¹ ·m ²]
PC	0.54 ± 0.09	4.70 ± 0.75	0.69 ± 0.05	1.73 ± 0.63
CA	0.51 ± 0.24	4.66 ± 1.00	0.59 ± 0.05	9.67 ± 0.20
PTFE	0.13 ± 0.07	3.17 ± 0.72	0.11 ± 0.05	1.61 ± 0.34

system, calculated from the initial concentration of MPs in water (100 mg/L) and the total volume of water filtered in the experiment, and $F_{m_{MPs}}$ is the final mass of MPs recovered on the glass microfiber filter after vacuum filtration. Table 3 shows the estimated total number of particles per litre that had not been removed by the membranes (NT_{MP}), the particles' average diameter (D_{MP}), and the mass removal efficiency. Other measured data can be found in the Supplementary Information under the section Analysis of the Removal Efficiency.

The membrane performance is also affected by the abrasion of its surface due to the solid particles in the flow. This phenomenon is enhanced in dead-end filtration, when MPs have irregular shapes and when high pressures are applied [11]. In this case, PS particles have higher shape irregularity than PA particles, since the PS spherical particles greater than 300 μ m were first ground down to reach the desired size range. In comparison, PA particles were manufactured with sizes below 300 μ m. From one side, cryogenic milling by inducing internal cracks could produce greater brittleness of the PS particles [25]. On the other side, their irregular shape could result in more significant damage to the membranes, a phenomenon even more enhanced when high pressures are employed. Furthermore, the error for PS removal is more prominent for all the membranes due to the larger size and the irregularity of particles not retained, which led to a less precise estimation.

3.3.1. PC membrane

The glass microfiber filter, used in vacuum filtration with the water gathered from the PC membrane filtration, has a substantial PA particles' presence estimated at 127,000 particles/L but with an average size smaller than the defined range employed. We can consider that the impact of the particles on the membrane induced them to further breakdown into smaller particles to pass more easily through the 5 μ m pore size membrane. Similar conclusions could be drawn for PS particles, where even larger particles could pass through the membrane, probably this time due to the membrane abrasion mechanism discussed previously. The average diameter of the PS particles was around 37.40 μ m, with particles in the range of 10–100 μ m, compared to 15.66 μ m obtained for the PA particles, with size between 2–50 μ m.

PC membranes suffered higher fouling with PS particles than PA particles. This behaviour can be explained as PC, other than being a plastic itself, is hydrophilic and more likely to interact with other hydrophilic plastics, like polystyrene. This interaction may be prevalent compared to the repulsion between two surfaces negatively charged; indeed, their zeta potential absolute value is very little. Although higher fouling occurred, because of the abrasion mechanism of both the particles and the membrane, this did not result in significantly higher mass removal efficiency.

3.3.2. CA membrane

After PA filtration, the presence of 27,000 particles/L was estimated for the CA membrane, almost one fifth the amount compared to the PC membrane, with an average diameter of 20.58 μ m, varying in the range 7–70 μ m. From the shore hardness measure, CA membranes showed the lowest hardness value in a dry environment. The CA membrane is hydrophilic and wets easily, although it loses part of its hardness when it is wet, resulting in being more prone to abrasion. The impact of the PA particles with the membrane induced less break down of the particles but

Table 3

Total number of unremoved microplastic particles per litre (NT_{MP}), average size (D_{MP}), and mass removal efficiency (MRE%) of each membrane when filtering water with 100 mg/L of PA and PS.

Membrane	MPs	NT_{MP} [particles/L]	D_{MP} [μ m]	MRE%
PC	PA	127,000	15.66	99.6 ± 0.4
	PS	33,000	37.40	96.8 ± 4.5
CA	PA	27,000	20.58	99.8 ± 0.1
	PS	8,000	75.51	94.3 ± 5.1
PTFE	PA	46,000	21.72	99.6 ± 0.3
	PS	47,000	29.49	96.0 ± 4.6

more abrasion of the membrane. Therefore, bigger PA particles were able to pass through the CA membrane but much less than those that could pass through the PC membrane. In the presence of 100 mg/L of PS, the flux remained relatively high, around 9.67 ± 0.20 L·s⁻¹·m⁻² after 10 min, where the curve had not yet reached a fairly constant value. The higher flux reached from the CA compared to the PC membrane with the PS particles, can be explained as the membrane abrasion mechanism was much more significant, and higher repulsion might have occurred as CA is more negatively charged. The higher degree of membrane abrasion let bigger particles to pass through, but also more water. On the glass microfiber filter, we found the smallest number of particles compared to the other membranes, but the filter did catch the biggest particles in comparison to the other membranes. The PS particles had an average diameter of 75.51 μ m, varying in the range of 10–300 μ m.

3.3.3. PTFE membrane

No increase in the TMP was recorded for the PTFE membrane after 10 min in the presence of 100 mg/L of either PA or PS particles. However, the flux decreased from 7.30 ± 1.67 L·s⁻¹·m⁻² without MP particles to 3.17 ± 0.72 L·s⁻¹·m⁻² for PA and 1.61 ± 0.34 L·s⁻¹·m⁻² for PS. PTFE is also a derivative of plastic and was chosen for its hydrophobicity; thus, it was expected to interact more with polyamide and other hydrophobic surfaces. However, at higher TMP, the removal gives similar results for both types of MPs showing that TMP is the main parameter. The sizes of these particles, on the glass microfiber filter, were 21.72 μ m (7–90 μ m) and 29.49 μ m (8–220 μ m) for PA and PS, respectively with similar unremoved number of particles/L.

4. Conclusions

This study showed the results of the evaluation of commercial microfiltration membranes suitable for the development of a low-cost technology effective on MPs removal. The main conclusions of the work are:

- Despite having a nominal pore size smaller than the MPs size range, a complete removal is not achieved in any system. Although high mass removal efficiencies were reached with all membranes for both types of MPs (above 94% for all cases), variable performances were observed as a result of differences on the MPs-membrane interaction, membrane hardness, MPs shape irregularity and breaking down of the particles.
- Microplastics in the range of 20–300 μ m are detected passing through the membranes pores nominally smaller (5 μ m). The most likely explanation is based on the existence of membrane abrasion induced by the sharp-cornered particles and low membrane hardness value. On the other hand, the filtrate present MPs particles with a smaller size than the feed stream. The reason is that MPs broke down into particles smaller than 20 μ m due to the mechanical stress associated to the filtration TMP (1.6 bar for PTFE membrane and around 1 bar for PC and CA membranes). Therefore, the choice of the membrane properties needs to compromise the risk of producing a higher amount of nanoplastics (NPs) or allowing the passage of bigger MPs particles.

- For comparable overall mass removal efficiencies, the optimal membrane is that operating with the lower TMP, and therefore the lower pumping costs. PTFE, due to its hydrophobicity, requires a high working pressure, negatively affecting the pumping costs. PC and CA membranes have similar behaviour during PA filtration. However, during PS filtration, CA allowed higher water flux.

Summarising, CA seems to be optimal membrane material for implementing a domestic household device in terms of a balance between water flux, transmembrane pressure and MPs mass removal efficiency.

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.

Acknowledgements

The authors acknowledge the financial support of the European Union's Horizon 2020 research and innovation programme in the frame of REWATERGY, Sustainable Reactor Engineering for Applications on the Water-Energy Nexus, MSCA-ITN-EID Project N. 812574.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cscee.2020.100075>.

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