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Asymmetric polyelectrolyte multilayer membranes with ultrathin separation layers for highly efficient micropollutant removal

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ABSTRACT

New membrane materials are urgently needed to address the increasing concentrations of harmful organic micropollutants (e.g. pharmaceuticals, pesticides and plasticizers) in our surface and drinking water. Currently, the densest available membranes can remove micropollutants sufficiently, but only at very low permeabilities and by producing a highly saline, difficult to treat waste stream. We improve permeability 5–10 fold by producing an asymmetric polyelectrolyte multilayer (PEM) on a porous membrane, with a separation layer thickness of only 4 nm. This is achieved by first coating an open multilayer to prevent defects, and subsequently a thin and dense multilayer. This novel membrane shows a very high (98%) retention toward a mix of common micropollutants. Moreover, it only retains 10–15% of NaCl, preventing the formation of a saline waste stream. A detailed literature study shows that the asymmetric PEM membrane, with this unique combination of properties, significantly outperforms commercial membranes for micropollutant removal applications.

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1. Introduction

The emergence of small organic molecules (100–1000 Da) from medicines, pesticides and plasticizers (micropollutants) in wastewater and surface water is a significant challenge that demands for new and specially designed membrane materials [1–3]. Growing welfare and world-population lead to increasing micropollutant concentrations in surface waters and drinking water sources, threatening both the aquatic environment and drinking water quality.

Current technologies are unable to efficiently remove these micropollutants from wastewater and surface water streams. Adsorption, for example, is not sufficient to remove micropollutants for more than 90% [4]. Membrane technologies are more promising, as many commercial reverse osmosis (RO) membranes do remove >90% of micropollutants, but operating these membranes is very energy-consuming because of their low water permeabilities ($1\text{--}2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for modern RO membranes) [5]. Commercial nanofiltration (NF) membranes are more open, but with increasing permeability comes lower retentions, especially toward small and uncharged micropollutants such as bisphenol A [6,7]. The effectiveness of currently available membranes is there-

fore limited. Moreover, RO and tight NF membranes were designed for desalination and can only remove micropollutants together with ions [8]. This can lead to a product stream where salts need to be re-added to make the water suitable for agriculture or human consumption. Even more problematic is the creation of highly saline micropollutant waste streams, that are complex and expensive to treat [9,10].

Polyelectrolyte multilayers (PEMs) are promising materials to help solve this problem. PE Ms can be coated on surfaces, including porous membrane supports, under mild and aqueous conditions by alternately exposing the substrate to polycation and polyanion solutions. During each of these steps, electrostatic interactions lead to the formation of a thin (0.5–5 nm) polyelectrolyte layer on top of the previous, oppositely charged layer [11–13]. Previous research shows that such multilayers show a high stability when used as dense separation layers on a charged membrane support, being resistant against repetitive backwashing [14]. The strength of coating a PEM as a separation layer is that the properties of the PEM can be finely tuned, for example by the number of layers and the salt concentration and pH during the coating process [13,15]. Additionally, a large variety of polyelectrolytes can be used to determine the properties of the layer [15,16]. Hence, PEM based membranes can be optimized toward specific applications including desalination [17] and ion separation [18]. Moreover, PEM coatings can be easily applied on hollow fiber membranes, that have significant advan-

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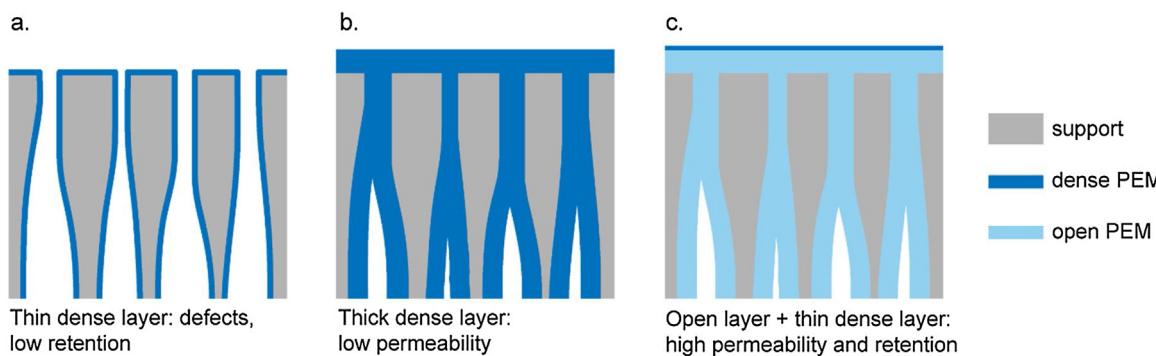


Fig. 1. Concept of asymmetric PEM membranes. a: Coating a thin dense layer on a porous support will lead to defects; b: if the support pores are filled with a dense PEM with good separation properties, water needs to travel a long pathway through the PEM and the water permeability will be low; c: if the support pores are filled with an open PEM, and a thin layer of dense PEM with the desired separation properties is coated on top, a combination between a high selectivity and permeability can be achieved.

tages over other membrane geometries such as reduced fouling, which eliminates the need for pretreatment [19].

Their largest advantage, however, is their potential to form very thin separation layers. Since the early days of membrane usage, the active separation layers of membranes have become thinner and thinner to increase permeability and thus decrease energy demand. One of the most important breakthroughs in this regard was the introduction of membranes with an asymmetric pore distribution [20,21], consisting of a thin active separation layer with a small pore size and a supporting layer with a larger pore size to provide mechanical stability without unnecessarily reducing water permeability.

Unfortunately, when coating a few nanometer thin PEM on a porous support, it will not completely close the pores (Fig. 1a). A much thicker layer is required to produce a defect-free membrane. Moreover, once the pores are filled, the effective thickness of the PEM layer is much higher than the coated thickness because permeating water has to travel a long pathway through the filled pores (Fig. 1b). As a consequence, the potential of PEMs to form ultra-thin separation layers cannot be fully exploited and the pure water permeability of PEM based membranes is still relatively low.

Here we introduce a unique approach that improves separation properties by taking membranes to the next level of asymmetry. To maintain high water permeability, we close the support pores with a relatively open, permeable PEM, and subsequently coat a thin, dense PEM on top of the first layer to generate high selectivity (Fig. 1c). We will demonstrate that this approach allows us to make membranes with separation layers as thin as 4 nm.

2. Results and discussion

An essential part in the design of an asymmetric PEM coating is the choice of polyelectrolytes. From previous studies we know that poly(acrylic acid)/poly(allylamine hydrochloride) layers (PAA/PAH), coated at pH 6 and terminated with a PAA layer, form dense PEMs with 60–80% retention of both charged and neutral micropollutants [22]. However, these retentions were achieved at the low water permeability of $1.8 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, in line with expectations (Fig. 1b). PEM membranes prepared with other polyelectrolytes can have much higher permeabilities. For example, membranes based on poly(styrene sulfonate) (PSS)/PAH, terminated with PSS, have a permeability of $13\text{--}16 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ after pore closure (Supplementary Fig. S1). Moreover, PSS and PAH form very stable multilayers with a low polyelectrolyte mobility [23]. A good micropollutant removal membrane requires the permeability and stability of PSS/PAH layers, but the selectivity of PAA/PAH layers.

Producing asymmetric PEM membranes with a PSS/PAH bottom layer and a thin PAA/PAH top layer is therefore a promising option

to fully benefit from the high stability and permeability of the first polyelectrolyte pair and the selective properties of the latter.

Indeed, we find that building such layers on model surfaces is a straightforward process (Supplementary Fig. S2). To demonstrate the potential of such asymmetric layers, five types of hollow fiber membranes were prepared, each with 10.5 bilayers in total. This includes two control membrane types that are coated completely with either PSS/PAH or PAA/PAH ($[\text{PSS}/\text{PAH}]_{10.5}$ and $[\text{PAA}/\text{PAH}]_{10.5}$), and three asymmetric membrane types $[\text{PSS}/\text{PAH}]_{8.5}+[\text{PAA}/\text{PAH}]_2$, $[\text{PSS}/\text{PAH}]_{7.5}+[\text{PAA}/\text{PAH}]_3$ and $[\text{PSS}/\text{PAH}]_{6.5}+[\text{PAA}/\text{PAH}]_4$. All membranes are terminated with the polyanion, because we previously found that PAA-terminated PAA/PAH layers show higher micropollutant retentions than PAH-terminated ones [22].

Of the five different membrane types, we determined pure water permeability and molecular weight cutoff, MWCO (Fig. 2a). The permeability of the $[\text{PSS}/\text{PAH}]_{10.5}$ membranes is $15.2 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, while for $[\text{PAA}/\text{PAH}]_{10.5}$ it is only $1.4 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, showing the clear difference in permeability between a dense and a more open PEM coating. The asymmetric membranes have significantly higher permeabilities than the $[\text{PAA}/\text{PAH}]_{10.5}$ membranes, up to $12.8 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for the $[\text{PSS}/\text{PAH}]_{8.5}+[\text{PAA}/\text{PAH}]_2$ membranes. While the permeability keeps on decreasing with an increasing number of PAA/PAH layers, the 90% MWCO plateaus around 240 Da for the asymmetric membranes. These results already demonstrate the promise of these asymmetric membranes, showing that we can decrease the MWCO by coating PAA/PAH on top of PSS/PAH layers, while retaining a permeability close to the much more open PAH/PSS multilayer. Surprisingly we found a very high 90% MWCO for the 10.5 bilayer PAA/PAH membranes. For a better comparison, Supplementary Fig. S3 shows the full sieving curves of our membranes, where we can see that the $[\text{PAA}/\text{PAH}]_{10.5}$ membranes actually perform better than the others in the low molecular weight range. The poor 90% MWCO performance of these membranes indicates that they suffer from small defects; we elaborate on this in S3.

Although the obtained MWCO results give a good indication that our asymmetric membranes could retain micropollutants, it is critical to prove this by measuring real micropollutant retentions. For this purpose we use a micropollutant mix with 8 micropollutants, containing positively charged, negatively charged and neutral organic molecules, with size varying from 216 to 624 Da. Among them are several pharmaceuticals (atenolol, sulfamethoxazole, naproxen and bezafibrate), a pesticide (atrazine) and a plasticizer (bisphenol A). Structures, molecular weight and pK_a values of the micropollutants can be found in Supplementary Table S4.

The micropollutant retentions show a clear optimum for the asymmetric membranes (Fig. 2b), which is in line with the MWCO

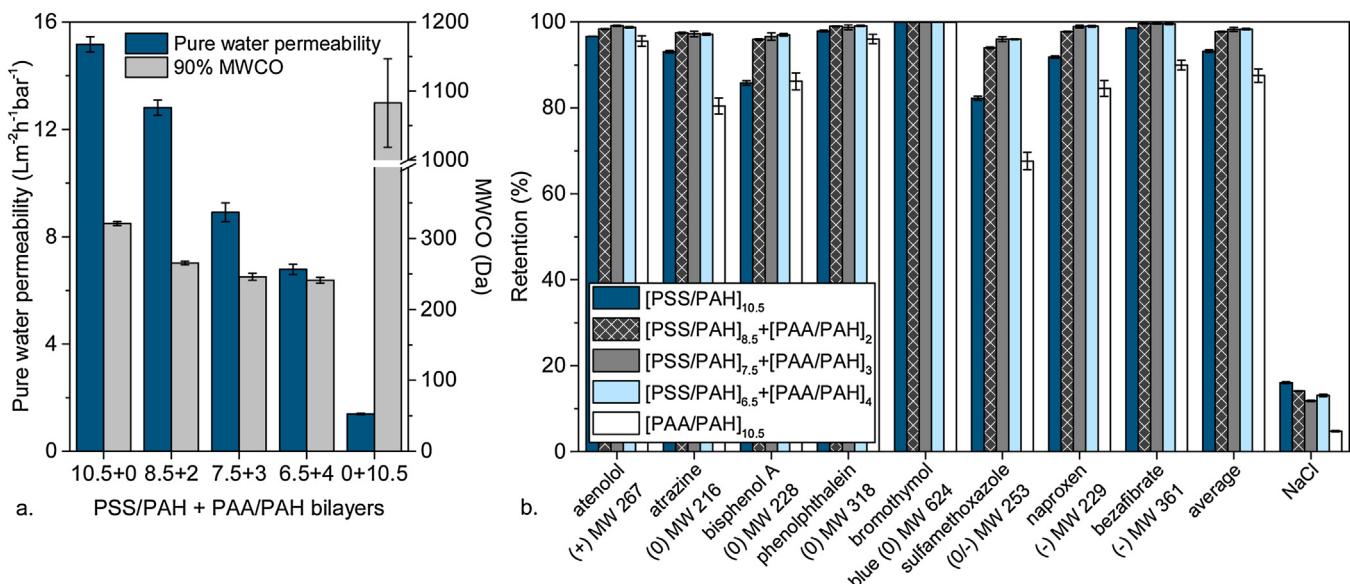


Fig. 2. Performance of the asymmetric and control membranes. a: Pure water permeability and molecular weight cutoff; b: micropollutant and NaCl retention. Error bars: standard error; n = 4.

results. Moreover, all micropollutant retentions are above 90% for the asymmetric membranes, showing that the asymmetric concept provides an excellent selectivity for water over micropollutants. The dense PAA/PAH top layers reject the micropollutants more effectively than PSS/PAH, but as the PAA/PAH top layer is very thin the water permeability remains high. The asymmetric membranes are even shown to be more selective than a symmetric dense PAA/PAH layer. We expect that the stable PAH/PSS bottom layer helps to prevent defects that would otherwise lower the selectivity. Moreover, in nanofiltration a higher water flux tends to lead to a higher solute retention according to the solution-diffusion model [24], which also explains the optimum in micropollutant retention for the asymmetric membranes.

The differences in retention between the micropollutants seem to be largely dependent on micropollutant size. Bromothymol blue, the largest molecule in the mix, is not detected in any of the permeates. The other large micropollutants bezafibrate, phenolphthalein and atenolol are retained well by the asymmetric membranes without a clear charge dependency. The smallest micropollutants (atrazine, bisphenol A, sulfamethoxazole and naproxen) are retained slightly less. Differences in retention between those do not correlate to size or charge, but could be explained according to the solution-diffusion model by differences in affinity for the PEM.

The low sodium chloride retentions of the asymmetric membranes, only 11–14%, demonstrate even more clearly that size exclusion is the predominant separation mechanism. Sodium chloride ions, with a diameter of 0.2 nm for both Na^+ and Cl^- [25], are much smaller than the micropollutants that typically have dimensions around 1 nm [26] and are therefore retained less. If a charge based exclusion mechanism would be dominant, no large difference would be expected between the retention of sodium chloride ions and other monovalent species such as the charged micropollutants. Interestingly, the lack of charge exclusion shows that our membranes contain a very low net charge, even though their separation layers consist of polyelectrolytes.

The average micropollutant retentions of all the asymmetric membranes are around 98%. In this region of high retentions, a small change in retention requires a very large improvement in membrane selectivity. From standard PAH/PSS membranes (93% retention) to the asymmetric membranes we observe a 3.5 fold increase in membrane selectivity. Specifically with the

[PSS/PAH]_{8.5}+[PAA/PAH]₂ membranes, we can therefore produce water with 3.5 times less micropollutants at only slightly lower fluxes compared with our PSS/PAH control membrane. The asymmetric coating approach clearly leads to much higher selectivities, with just a small reduction in flux. Because of this combination of high selectivity and permeability, we expect that the asymmetric membranes have very thin separation layers. Indeed, by ellipsometry we estimated the 2, 3 and 4 bilayer PAA/PAH separation layers to be only 4, 9 and 16 nm in thickness, respectively, in their hydrated state (Supplementary file S5). The [PSS/PAH]_{8.5}+[PAA/PAH]₂ layers were also visualized by field emission scanning electron microscopy (Supplementary Fig. S6), where the total thickness of the dry PEM was found to be around 30 nm, in line with the ellipsometry results.

The estimated 4 nm thickness of the [PAA/PAH]₂ top layer is incredibly thin, given that common commercial separation layer thicknesses are 0.1–1 μm [24]. Via some procedures it is possible to obtain more homogeneous and thinner layers via interfacial polymerization, down to 25 nm [27] or even 8 nm [28]. To our knowledge, however, our 4 nm separation layer is the thinnest separation layer reported so far by using scalable technology. Besides being readily scalable, asymmetric PEM coating also provides a very easy and environmentally friendly way to produce these extremely thin, defect-free separation layers. Moreover, the asymmetric multilayers are physically stable as incubating them in an acidic salt bath hardly influences permeability and MWCO (Supplementary Fig. S7). This demonstrates the potential of asymmetric PEMs for large-scale applications.

To validate the outstanding properties of our asymmetric membranes, in particular the [PSS/PAH]_{8.5}+[PAA/PAH]₂ membranes, we compared the performance of our membranes with the performance of commercially available reverse osmosis and nanofiltration membranes as described in literature. A detailed overview can be found in supplementary Table S8. In Fig. 3a, permeability and micropollutant retention are plotted against each other for our asymmetric PEM membranes (dark symbols), symmetric PEM membranes (grey symbols) and commercially available membranes (white symbols). Where the asymmetric PEM membranes have a consistently high retention for all micropollutants, the commercial membranes tend to work well for only some of the investigated micropollutants, while showing low retention for oth-

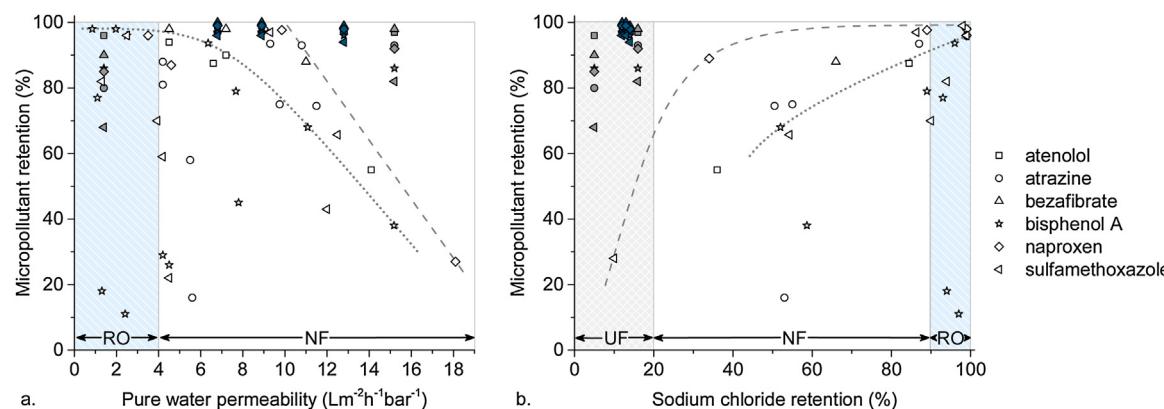


Fig. 3. Asymmetric and symmetric PEM membranes in comparison with commercial nanofiltration and reverse osmosis membranes. a: Permeability versus micropollutant retention; b: sodium chloride retention versus micropollutant retention. White symbols: commercial membranes; grey symbols: symmetric PEM membranes in this study; dark symbols: asymmetric membranes in this study. Dashed lines: best single results obtained with commercial membranes; dotted lines: best single results obtained with commercial membranes for bisphenol A. If for a single micropollutant different data were obtained in literature with the same commercial membrane, results were averaged. Detailed information can be found in Supplementary Table S8.

ers. The dashed lines show the upper limit for single micropollutant results obtained with commercial membranes. The retentions of our $[\text{PSS}/\text{PAH}]_{8.5}+[\text{PAA}/\text{PAH}]_2$ membranes are above these lines for all micropollutants, which shows that their average performance is even better than the best results for commercial membranes. Dotted lines show the upper limit for bisphenol A as obtained with commercial membranes. Bisphenol A is the most difficult micropollutant to retain, as for the commercial membranes, only the RO membranes retain it for more than 95%. The high retention of our membranes toward all micropollutants, including bisphenol A, thus demonstrates that our asymmetric membranes have a micropollutant retention comparable with or better than the best RO membranes. At the same time they have a pure water permeability in the range typical for NF membranes.

Finally, as shown in Fig. 3b the membranes have a very low sodium chloride retention compared with commercial membranes, in the range of tight ultrafiltration (UF) membranes. The asymmetric PEM coating thus allows us to decouple the usual correlation between permeability, salt retention and micropollutant retention, and improves membrane efficiency beyond the traditional limits. This means that categorization of our new asymmetric PEM based membrane as an NF membrane is not suitable because typically, NF membranes are considered to show average separation properties, in between those of RO and UF membranes. In contrast, our membrane decouples and combines single desirable properties of RO, NF and UF type membranes: high water permeability (NF), high micropollutant retention (RO) and low salt retention (UF). We thus propose that the membrane should be considered the first in a new category, the Chimera membrane, named after the mythical creature that also combined aspects of various different animals into one.

The unique properties of our membranes are further highlighted by their exceptional permselectivity in terms of salt permeation over micropollutant permeation, that is at least one order of magnitude higher than for commercial membranes, as shown in Fig. 4 (calculation methods can be found in Supplementary file S9). Some commercial membranes show a permselectivity below 1, which means that their salt retention is higher than their micropollutant retention, in strong contrast to the high sodium chloride permeation of the asymmetric PEM membranes. Salt permeation is very beneficial as it will prevent the formation of a highly saline waste stream that is typical for standard RO and NF membranes. Moreover, it avoids buildup of a high osmotic pressure over the membrane, that would demand a higher transmembrane pressure to achieve the same water flux.

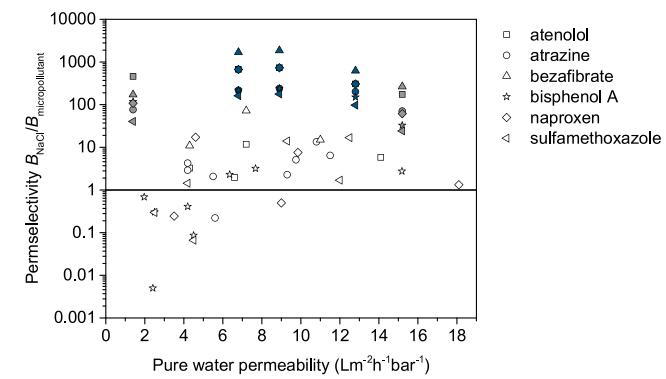


Fig. 4. Pure water permeability versus permselectivity of PEM and commercial membranes. Dark symbols: asymmetric PEM membranes in this study; grey symbols: symmetric PEM membranes in this study; white symbols: commercial membranes. If for a single micropollutant different data were obtained in literature with the same commercial membrane, results were averaged. Calculations are explained in Supplementary file S9.

3. Conclusion

In summary, our new concept of asymmetric PEM membranes allows us to create advanced membrane materials with ultrathin separation layers and a unique combination of desirable separation properties, allowing its classification in a new membrane category: the Chimera membrane. We have successfully applied this new membrane to achieve an outstanding micropollutant retention (98%) and water permeability ($12.8 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), thereby outperforming the selectivity of commercial membranes to a large extent. With asymmetric $\text{PSS}/\text{PAH}+\text{PAA}/\text{PAH}$ coatings we were able to produce selective layers as thin as 4 nm, using a highly scalable membrane fabrication approach. An additional benefit of our PEM membranes is their low salt retention, such that NaCl does not accumulate in the micropollutant waste stream. Clearly, our approach to produce asymmetric PEM membranes is highly beneficial for micropollutant removal processes. These membranes are very suitable for the production of safe drinking water and for micropollutant removal from wastewater, but also for other applications such as the separation of salts and organic compounds in biorefinery. Finally, this work provides fundamentally new membrane design principles for improved selectivities that can be tuned to other important applications, including desalination and ion recovery.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apmt.2019.100471>.

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