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Polyelectrolyte-modified polyethersulfone ultrafiltration membranes for wastewater treatment applications

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ABSTRACT

This work reports on the use of the layer-by-layer (LbL) technique to modify the surface of polyethersulfone hollow fibre (HF) ultrafiltration membranes for wastewater treatment. The polyelectrolytes employed are poly (ethylenimine), poly (diallyldimethylammonium chloride) and poly (styrene sulfonate) to obtain up to three layers. Sludge supernatant was used as feed for filtrations and the throughput across the polyelectrolyte-modified membrane was characterized by permeability measurement and the composition of the discharged permeates. Furthermore, the molecular weight cut off (MWCO) of the modified membranes was determined. To evaluate real separation performance of polyelectrolyte-modified membranes the total organic carbon (TOC) removal and the change in ultraviolet absorbance (UVA_{254}) at 254 nm as a function of the number of deposited layers were determined for the sludge supernatant. Between 30% and 50% TOC rejection was observed for modified membranes as compared to only 15% for virgin membranes.

Keywords: Polyelectrolytes; Layer-by-layer; Ultrafiltration membrane

1. Introduction

Polyethersulfone is one of the materials being used to manufacture membranes employed for wastewater treatment in membrane bioreactors (MBRs). MBRs have many edges over the conventional activated sludge treatment, such as smaller footprint, a higher mixed liquor suspended solids concentration etc. However, membrane fouling is a major drawback of MBRs. To minimize fouling, much effort has been made to either optimize the module aeration systems, the backwashing duration, often combined with chemical cleaning, or to improve the crossflow velocities in side stream modules [1, 2]. Besides this, membrane modification is another option to improve filtration performance. Currently, more attention is being given to plasma treatment, which is with its rich spectrum of options, one of the most widely used methods to modify membranes. Tyszler et al. [3] performed corona treatment and plasma treatment followed by graftings on hollow fibre (HF) membranes. They found out that plasma treatment seemed to be a suitable modification method. However, long-term experiments showed [3] stronger permeability decline with modified membranes as compared to unmodified ones.

An alternative method to modify and tune the surface of membranes with desired properties is through the layer-by-layer (LbL) assembly of polyelectrolytes on the membrane [4]. The LbL technique consists of the sequential adsorption of polyanions and polycations on any charged surface, irrespective of shape and size. The thickness and roughness, hence porosity and permeability, of the assembled layers can be finely tuned by various parameters such as the type of polyelectrolytes used and the dipping conditions employed: salts concentration, type of salts, pH and ionic strength. It has been shown that the last layer adsorbed can have a significant influence on the overall properties of the assembled layers [5]. There has not been much work done on LbL of

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Table 1
Characteristics of the PES membrane employed.

Membrane material	Abbrev.	Isoel. point	Unmod. membr. permeability [L/(m^2.h.bar)]	Contact angle [°] (adv./rec.)
Polyethersulfone	PES	2.1	1056	65/11

polyelectrolytes on membranes [6–11]. The advantage of the LbL technique over plasma treatment for surface modification lies in its simplicity and mild condition as compared to graft polymerization.

This contribution focuses on the use of polyelectrolyte-coated membranes for wastewater treatment. For this purpose, polyethersulfone HF ultrafiltration membranes have been chosen. The polyelectrolytes employed are poly (ethylenimine), poly (diallyldimethyl-ammonium chloride) and poly (styrene sulfonate) to obtain up to three layers using the LbL technique. Sludge supernatant was used as feed for filtrations and the throughput across the polyelectrolyte-modified membrane was characterized by permeability measurement and the composition of the discharged permeates. Furthermore, the molecular weight cut off (MWCO) of the modified membranes was determined.

2. Material and methods

The coating experiments were carried out with polyethersulfone HF ultrafiltration membranes. Characteristics of the membrane type are summarized in Table 1.

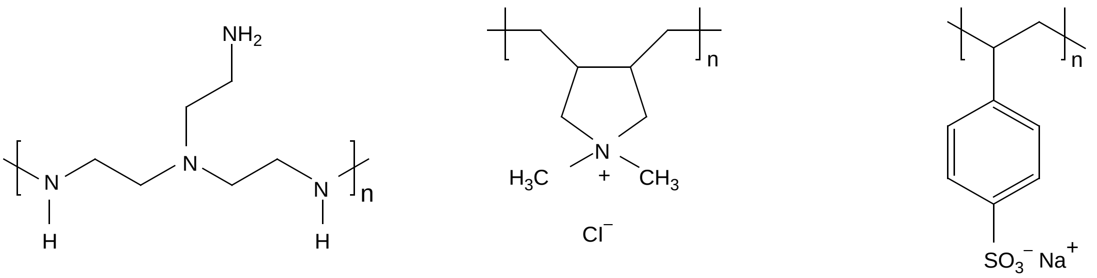
Clean water permeability was measured with deionised water in a cross-flow mode set-up. Prior to the experiment PES membranes were soaked in deionised water for 24 h to remove the conservation substance. Filtration was carried out at a trans-membrane pressure of 0.2 bar and the cross-flow velocity was set to 0.1 m/s.

To determine the molecular weight cut-off (MWCO) a dextran solution (dextran dxtb2000 supplied by Polymer Standards Service; MW = 1 520 000 g/mol; w (feed) = 1 g/L; w (NaN_3) = 0.5 g/L) was filtrated in cross-flow mode. During these tests, the cross-flow velocity was also set to 0.1 m/s and the trans-membrane pressure to 0.2 bar. The chemical composition of the feed and the permeate solution was analysed by the size exclusion chromatography (SEC) carried out with a High Performance Liquid Chromatography system (Agilent Technologies, Series 1100; Software WINGPC Unity, Polymer Standards Service). A representative MWCO was estimated by calculating the average out of two cut-off measurements.

The same method was also applied to characterize the molecular mass distribution of soluble compounds in the sludge supernatant and permeate.

2.1. Polyelectrolytes and coating procedure

The characteristics of polyelectrolytes employed (purchased from Sigma-Aldrich) in this study are summarized in Fig. 1. Solutions of the polyelectrolyte were prepared from 0.02 M (based on repeat units of the monomer) in water for PEI and in 0.5 M NaCl for PDADMAC and PSS respectively. PES membranes are negatively charged (cf. IP in Table 1), therefore the first layer adsorbed is a polycation. PEI and PDADMAC were chosen as polycations due to their high-surface charge density to promote anchoring of the first layer to the PES membrane. In this work, PES membranes have been modified with a single layer (PEI or PDADMAC respectively), two layers (PEI/PSS and PDADMAC/PSS) and three layers (PEI/PSS/PDADMAC and PDADMAC/PSS/PEI) of polyelectrolytes. Briefly, the PES membrane is dipped into a polyelectrolyte solution



Branched Polyethylenimine
PEI, (Mw = 750000 g/mol)

Poly (diallyldimethylammonium chloride)
PDADMAC, (MW = 100000–200000 g/mol

Poly(sodium 4-styrene sulfonate)
PSS, (Mw = 70000 g/mol)

Fig. 1. Selected polyelectrolytes in this study: PEI and PDADMAC are polycations and PSS is a polyanion.

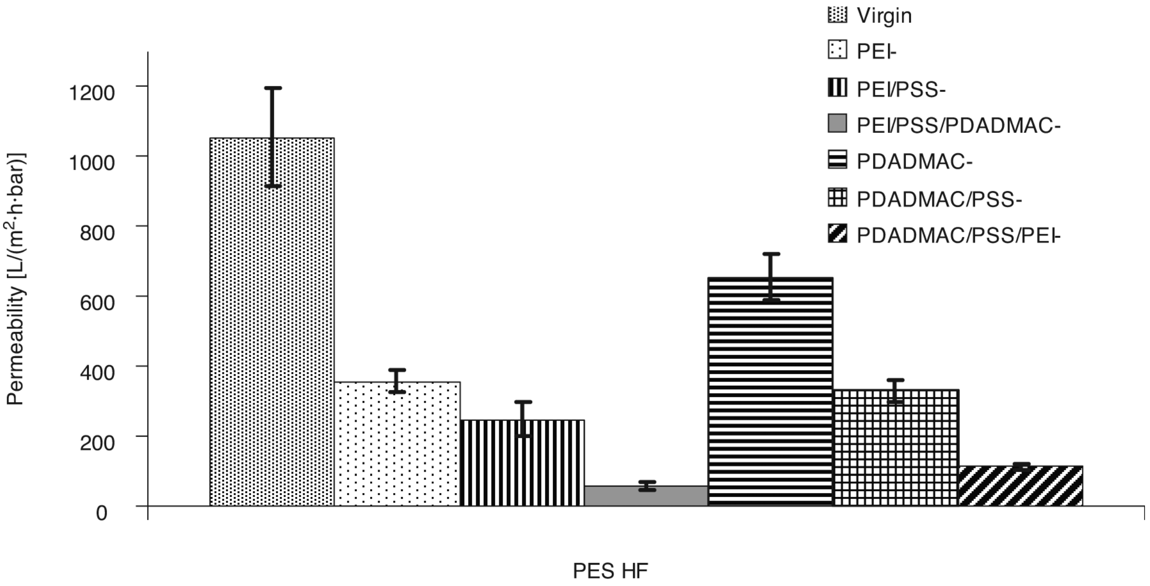


Fig. 2. Permeability at T = 20°C of virgin and 3h-coated membranes with 1, 2 and 3 layers.

for 3 h at room temperature (20°C), washed three times with deionised water to remove any loosely bound polyelectrolyte before immersion in the next polyelectrolyte solution. This cycle is repeated until the desired number of layers is achieved. Coating experiments with different numbers of layers where performed with pieces obtained from one single fibre in order to assure comparable starting conditions.

3. Results and discussion

Figure 2 shows the clean water permeability of unmodified and polyelectrolyte-modified membranes with different number of layers.

The permeability (adjusted to T = 20°C) decreases substantially upon deposition of the first layer from 1056 L/(m^2.h.bar) (for the unmodified membrane) to 357 L/(m^2.h.bar) for PEI and to 655 L/(m^2.h.bar) for

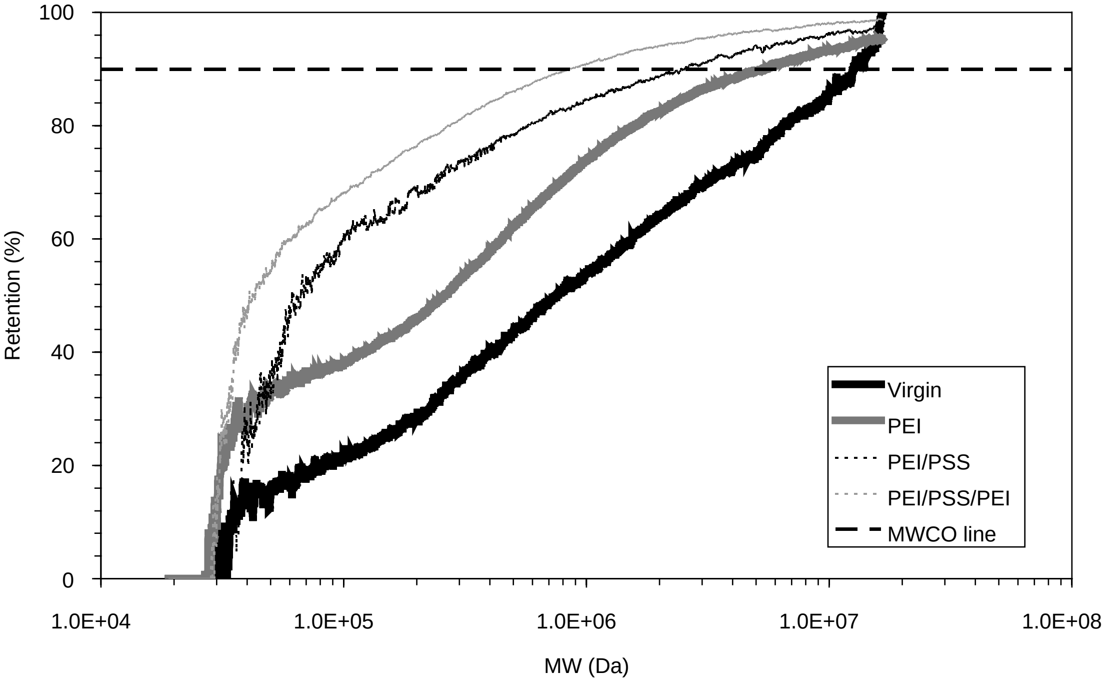


Fig. 3. Molecular weight composition of dextran solutions in the feed and permeates.

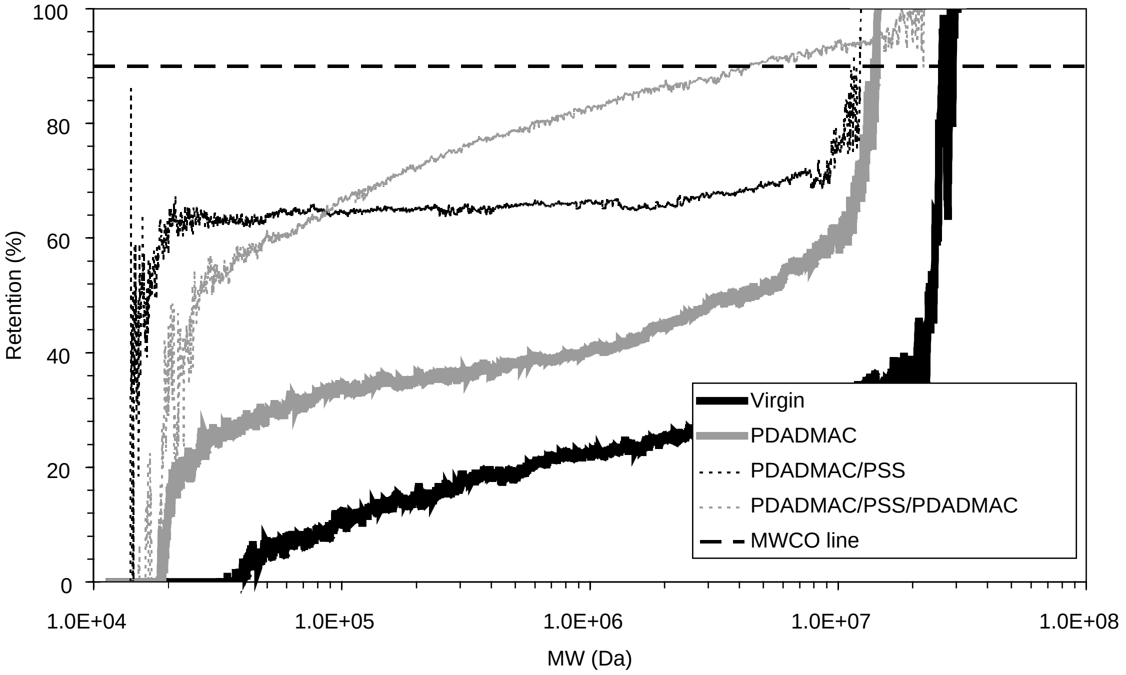


Fig. 4. Molecular weight composition of dextran solutions in the feed and permeates discharged through unmodified and PDADMAC-, PDADMAC/PSS- and PDADMAC/PSS/PDADMAC-coated PES membranes.

PDADMAC. Upon adsorption of a second (PSS), the permeability decreases further to 248 L/(m^2.h.bar) for two layers PEI/PSS and to 329 L/(m^2.h.bar) for PDAMDAC/PSS. Upon adsorption of PDADMAC to produce PEI/PSS/PDADMAC, the permeability drops down to 57 L/(m^2.h.bar). For the three-layer system PDADMAC/PSS/PEI, the permeability is slightly higher compared to PEI/PSS/PDADMAC, 112 L/(m^2.h.bar). It is clear that the more polyelectrolyte adsorbed on the PES membrane the lower is the permeability. However the significant decrease in permeability upon the deposition of the first layer is quite unexpected. This could be attributed to the fact that the coating does not only take place on the surface of the membrane but also within the pores of the membrane, causing an additional resistance to the permeation of water by pore blockage. It is noteworthy that the size of the polyelectrolytes used is smaller than the pore diameter of the membrane.

The adsorption of polyelectrolyte brings about evident changes of separation performance which has been characterized by MWCO. A series of rejection curves of dextran solutions using modified membranes wherein the first layer is either PEI or PDADMAC is shown in Fig. 3 and in Fig. 4, respectively. The corresponding results on the MWCO are additionally summarized in table 2. Comparing the same number of layers, the MWCOs of PEI-modified PES membranes are notable higher than those of PDADMAC-modified ones.

Comparing the dextran rejection curves from Figs. 3 and 4, it can be seen that the PEI-based first layer modified membranes feature sharper separations of dextran compared to those with PDADMAC as a first layer. This observation can be explained by the molecular structure of the polyelectrolyte. PEI is a highly branched high molecular weight polyelectrolyte known for its anchoring ability on surfaces. Deposited PEI layer gives rise to

Table 2
MWCO of unmodified and coated membranes.

	Unmodified	PEI-modified	PEI/PSS-modified	PEI/PSS/PEI-modified
MWCO [Da]	1.26×10^7	2.85×10^6	8.45×10^5	4.65×10^5
	Unmodified	PDADMAC-modified	PDADMAC/PSS-modified	PDADMAC/PSS/PDADMAC-modified
MWCO [Da]	2.82×10^7	1.87×10^7	1.76×10^7	3.73×10^6

Table 3
Removal of TOC and change of UVA_{254} value by unmodified and coated membranes.

	TOC [mg/L]		TOC retention [%]	UVA_{254} [1/m]	
	Feed	Permeate		Feed	Permeate
Unmodified	11.3	9.5	15.9	19.73	18.21
PDADMAC-	11.1	7.7	30.5	18.76	13.15
PEI-	11.2	7.5	33.0	17.95	9.03
PEI/PSS-	10.3	5.1	50.5	17.23	11.93
PDADMAC/PSS-	10.2	5.9	42.2	17.39	12.21

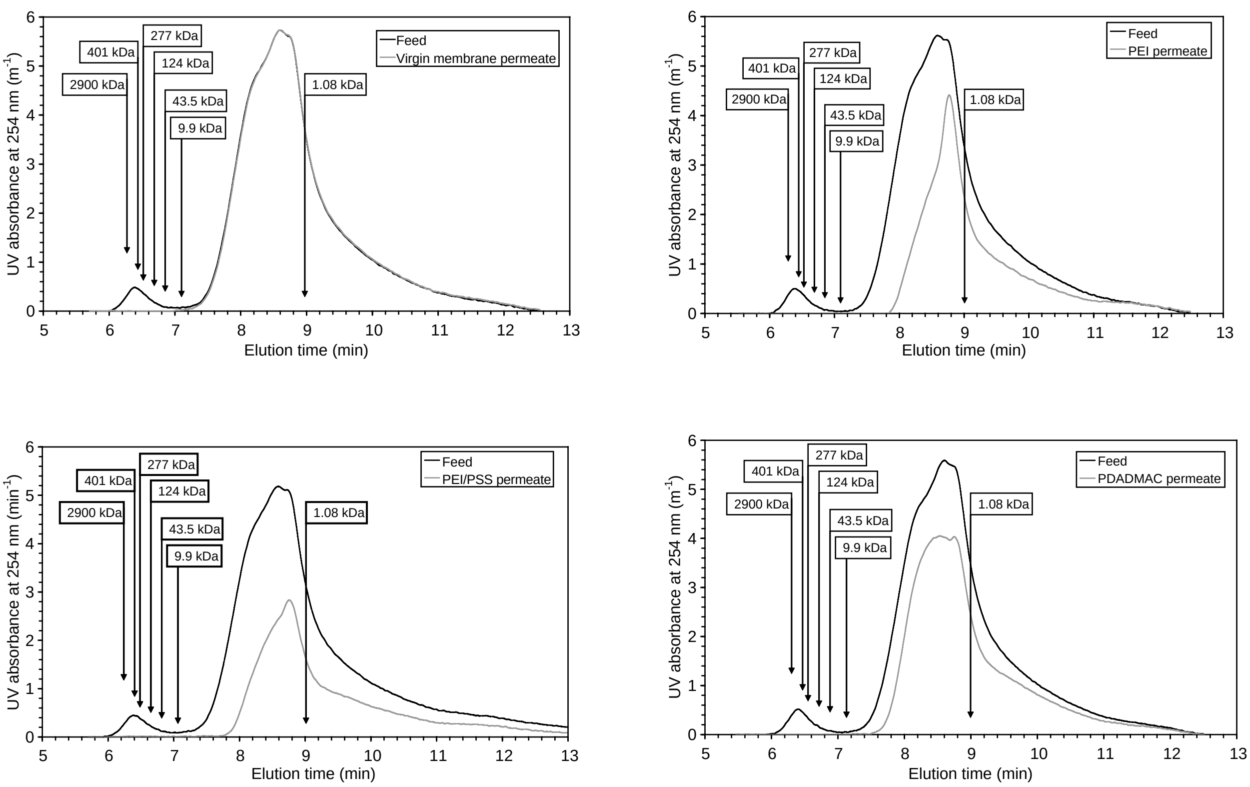


Fig. 5. SEC analyses of permeate and feed for unmodified and coated membranes.

a dense assembled layer resulting not only in lower flux but also in lower values of MWCO.

Though dextran is a standard polysaccharide commonly used in a model solution of foulants, the composition of mixed substances is never matched to real foulants. To evaluate real separation performance of polyelectrolyte-modified membranes in terms of TOC removal and UVA_{254} at 254 nm reduction as a function of the number of deposited layers, sludge supernatant has been used. Sludge supernatant is known to contain foulants which are responsible for a high percentage of irreversible membrane fouling [12, 13]. The characteristics of the feed in terms of TOC and UVA_{254} as well as the TOC removal degree of unmodified and coated membranes are presented in table 3.

As seen from Table 3, the virgin PES membrane is able to remove only 15.9% of TOC from the feed. After deposition of a single (positively charged) and a double layer (negatively charged) the TOC rejection is increased two- and three-fold, respectively. Only from the TOC study it is not clear if this rejection increase is due to the charge of the surface or the thickness (hence interaction between the layers) of the layers.

Figure 5 shows the results of SEC analysis of permeate and feed for unmodified and coated membranes. These results complement the investigation of the organic matter removal. It is clear from Fig. 5 that modified membranes are able to reject smaller substances than unmodified membranes as detected and confirmed by the UV absorbance

Table 4
TOC and UVA_{254} values of permeate for membranes coated at different salt concentrations.

	TOC [mg/L]		TOC retention [%]	UVA_{254} [1/m]	
	Feed	Permeate		Feed	Permeate
Unmodified	9.1	7.4	18.7	21.98	16.24
PDADMAC (0.5 M NaCl)	9.9	6.7	32.3	22.82	13.18
PDADMAC (0.5 M NaBr)	9.9	6.3	36.3	21.9	12.23
PDADMAC (0.5 M Na_2SO_4)	9.7	7.1	26.8	21.64	14.73

study as a function of the elution time and comparing the integral area between feed and permeate curves.

Coating parameters govern the internal structure of the deposited multilayer, thereby determining the thickness, roughness and even porosity of the film, and consequently have a huge influence on the performance of the coated membranes. One of the most crucial parameters is the type of salts [14] used in the polyelectrolyte depositing solution. Preliminary results obtained from a single layer of PDADMAC deposited on the membrane from a 0.5 M NaBr and Na_2SO_4 polyelectrolyte solutions are summarized in Table 4. Single layer obtained from 0.5 M NaBr shows the highest supernatant rejection (36%).

4. Conclusion

The results demonstrate that the coating of PES membranes (without any harsh pretreatment) with polyelectrolyte using the layer-by-layer technique is feasible. The polyelectrolyte-modified membranes feature sharp rejection of dextran molecules at lower MWCO values but also a decline in the permeability. Deposited layers also induced a better separation performance in sludge supernatant filtration characterized by TOC and SEC respectively. Altering of type of ions (salt) in the polyelectrolyte solutions shows an influence on the separation performance of sludge supernatant. The highest rejection, 36% of TOC, was achieved when NaBr salt was used with the polyelectrolyte solution.

Acknowledgements

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