



Precise tuning of salt retention of backwashable polyelectrolyte multilayer hollow fiber nanofiltration membranes



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ABSTRACT

We report a new dynamic Layer-by-Layer (LbL) fabrication method to molecularly engineer the layer build-up within the lumen of hollow fiber membrane involving constant flux permeation rather than the conventional static adsorption method. During the constant flux coating, the polyelectrolyte concentration at the membrane surface rises continuously due to its rejection causing a convective adsorption process of the polyelectrolyte onto the membrane. The retained polyelectrolyte amount correlates with the flux and retention properties of the resulting polyelectrolyte multilayer membranes irrespective of time span or flux level used for the convection step. This fabrication method enables the synthesis of new desalination membranes with unprecedented precision on ion transport properties. Furthermore the resulting hollow fiber nanofiltration membrane is stable towards backwashing. The method can be applied to already existing membrane modules as a finishing step or as an in-operando inline regeneration or repair step.

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1. Introduction

Layer-by-Layer (LbL) assemblies comprise cationic and anionic polyelectrolytes (PE) adsorbed in a sequential manner into ultrathin films as shown in Fig. 1 [1,2]. The adsorbed single layers are in the range of a few nanometers: the overall thickness and the structure can be precisely engineered by layer number, ionic strength, pH, and coating method [3–7]. Due to the ionic nature, LbL films assembled onto porous support membranes show selective transport of monovalent over bivalent ions: through the number of layers, their macromolecular nature, and their charge, polyelectrolyte multilayer membranes can be tailored to have designed properties for water softening application as nanofiltration membranes [8–14]. The generally used method for LbL film assembly is based on adsorption from a liquid phase by dipping, spraying or spin-coating [15,14,16].

De Grooth et al. [17] demonstrated that polyelectrolyte multilayer based on polydiallyldimethylammonium chloride (PDADMAC) and polystyrene sulfonated (PSS), the same system used in the present study, is stable towards NaOCl. The Kentish group reports an LbL based membrane with sulfonated polysulfone

(SPSf)/polyallylamine hydrochloride (PAH) and PSS/PAH layer crosslinked with glutaraldehyde (GA) [18]. The crosslinked membranes show, in comparison to a standard polyamide based reverse osmosis membrane, a much better stability towards NaOCl with comparable performance in terms of flux and retention. Hence, LbL based membranes are also relevant because of their potential chemical stability during disinfection treatment.

Frequently, the studies on LbL functionalized membranes are performed on flat membrane geometries [19–26]. As hollow fiber membranes allow higher packing densities, one would like to modify existing industrial ultrafiltration modules to make them more selective and operable with backwashing operation for instance. As early as 2001, Frank et al. [27] report the preparation and use of new capillary nanofiltration membranes prepared by interfacial polymerization. The product has been sold during the last 10 years, however it has some disadvantages. The retention behavior is difficult to tune and the preparation process involves a non-aqueous solvent. The resulting polyamide selective skin layer is sensitive to hypochlorite treatment. A synthetic concept free of organic solvents resulting in tunable properties with backwash and hypochlorite resistance is highly desirable. The synthetic concept should be scalable for large scale production. A first step towards a LbL based hollow fiber nanofiltration membrane was published during the submission of this contribution [28], however the essential concept of backwashing is yet not addressed there.

Very recently, some new developments have emerged: the group of Vankelecom recently demonstrated that the number of

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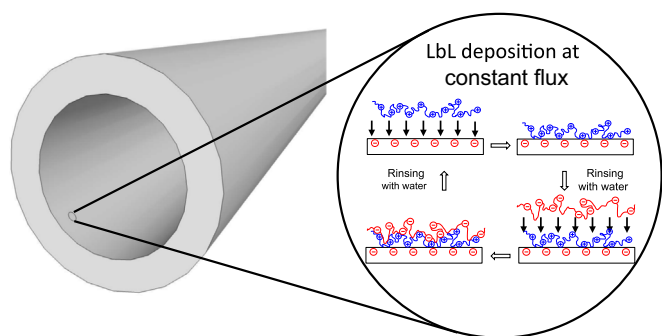


Fig. 1. Scheme of alternating assembly of polycations and polyanions in the lumen of a negatively charged membrane.

polyelectrolyte bilayers can be reduced to just a few to obtain already a defect-free layer making a potential upscaling feasible. In particular, the question on how quickly a membrane can be made has been addressed [29] in order to reduce the number of processing steps from 20 to 80 down to 6.

Here we report a systematic and rigorous description of a new constant flux LbL fabrication process in the lumen of a polymeric hollow fiber membrane as we first disclosed at ICOM2014. The method is applicable for single and multiple bilayer polyelectrolyte films supported on the lumen side of hollow fiber membranes based on controlled convective transport of polyelectrolytes towards the surface of the membrane. The evidence reported below proves that the amount of polyelectrolyte transported to the membrane surface determines the membrane properties such as permeability and retention for bivalent ions. Controlling the flux rather than the pressure, as it is found elsewhere [21,24–26,30], enables the precise tailoring and engineering of the properties of the resulting membranes. The methods applied in the former mentioned studies and the method that is presented here have in common, that dynamic adsorption, i.e. a convective flow of polyelectrolyte towards the membrane surface, is involved. However, this study is the very first one that performs the convective adsorption at constant flux. Also static, i.e. without convective flux, and constant pressure coatings were applied for a comparison between the conventional coating method and the new suggested method at constant flux conditions.

The essential finding of the work described below is that the amount of rejected polyelectrolyte mass inside the hollow fiber correlates strongly with the permeance and the retention of resulting membranes. Additionally, the LbL-modified hollow fiber nanofiltration membranes are shown to be stable towards backwashing.

2. Material and methods

The support membrane employed is a polyethersulfone-based ultrafiltration membrane provided by Pentair X-Flow (Netherlands).

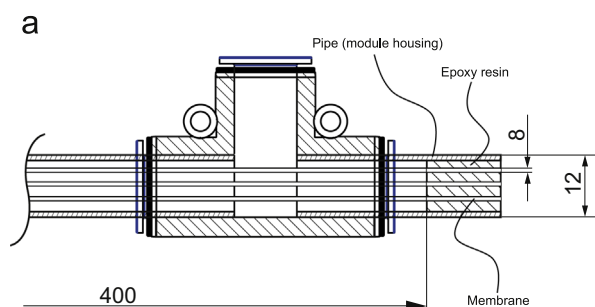


Fig. 2. Membrane module with 10 PES membranes. (a) Technical drawing of membrane module and (b) 3D drawing of membrane module.

Ten of those fibers were potted with a two component epoxy resin into a module housing (PA tube with 9 mm inner diameter and 12 mm outer diameter). Each fiber has a length of 40 cm and an inner diameter of 0.8 mm resulting in a total membrane area of about 0.01 m² per module (Fig. 2). The membranes have a pure water permeability of about 120 LMH/bar and a separation skin with pores of about 10 nm on the lumen side: the separation skin is negatively charged. Hence, the first applied polyelectrolyte is a polycation, in this case polydiallyldimethylammonium chloride (PDADMAC) with a molecular weight of 350 kDa. The applied polyanion is polystyrene sulfonate (PSS) with a molecular weight of 1000 kDa. For the convective coatings 1 g/l of each polyelectrolyte together with 0.5 mol/l NaCl was dissolved in water to obtain the polyelectrolyte solution. The polyelectrolyte concentration for the static coating was varied while the salt concentration was kept constant at 0.5 mol/l.

As the membrane pores are significantly smaller than the size of the polyelectrolyte, the latter is rejected and accumulates in front of the membrane surface. After rinsing the coated lumen and convectively transporting the oppositely charge polyelectrolyte towards the surface by dead-end filtration, a bilayer of cationic and anionic polyelectrolyte emerges. The exact procedure of preparing the bilayer is important and needs to be performed with care:

1. The lumen of the water wetted membrane is flushed at 3.5 l/h for 3 min with the first polyelectrolyte. The flow rate and time was optimized to ensure that the lumen is completely filled with the polyelectrolyte solution. However, this step must not be too long since as soon as the first polyelectrolytes enter the lumen of the membrane the diffusive adsorption (static) starts.
2. Adsorption step of polyelectrolyte:
 - (a) In the case of diffusive coating (static) the polyelectrolyte solution remained for 10 min within the lumen of hollow fiber membrane.
 - (b) In the case of convective adsorption a constant flux – variable pressure – dead-end permeation with convection of the polyelectrolytes to the surface of the membrane for a defined time at a defined flux was applied.
 - (c) In the case of constant pressure – variable flux – adsorption the feed side of the membrane was connected to a constant pressure reservoir filled with the polyelectrolyte solution while the permeate flow rate was measured with a flow meter. The coating time was adjusted to pass a defined permeate volume.
3. Rinsing of the lumen of the hollow fiber membrane with deionized water to remove the excess polyelectrolyte at 8.5 l/h for 20 min. During this period the polyelectrolyte present inside the lumen and loosely bound to the surface of the membrane will be removed. The conductivity of the deionized water used for this step and the next step was frequently measured and was always between 1 and 2 μS/cm.
4. Permeation with deionized water to determine the pure water

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