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Regenerable polymer/ceramic hybrid nanofiltration membrane based on polyelectrolyte assembly by layer-by-layer technique



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ABSTRACT

A new regenerable nanofiltration membrane based on LbL film assembly of PDADMAC/PSS on a ceramic support is presented. Using a constant flux coating method the large pores of the ceramic support with a diameter of about 100 nm could be covered and closed with only 3 bilayers. The performance of the presented membrane is comparable to today's nanofiltration membranes. Remarkably, the stability is superior as the membranes withstand backwashing as well as low and high pH. The intrinsic contradiction of a stable but also regenerable membrane is addressed as well. The LbL film is deconstructed using high concentrated salt solution, ionic surfactants, and hypochlorite in succession. After deconstruction the film is rebuilt resulting in exactly the same properties as observed before film deconstruction. Due to the ability of regeneration the more stable but also more expensive ceramic support can be reused. The regeneration was conducted within the membrane housing demonstrating its practical viability for membrane assembly and regeneration within modules being potentially on-site in a membrane plant.

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1. Introduction

One of the world's greatest challenges in the coming decades will be adequate water supply, even in regions considered "water-rich" [1]. Water treatment research focuses on not only salt retention but also on the separation of micropollutants such as pesticides, hormones, pharmaceuticals or endocrine disrupting compounds. An alternative for conventional water treatment methods is nanofiltration which successfully retains most of the micropollutants, thus preventing their accumulation during the production of drinking or produced water [2–7]. Today's membranes are mostly thin-film composites made from polyamides assembled on a porous support by interfacial polymerization. However, the membranes suffer from limited chemical stability, as the polyamides are not stable in the presence of hypochlorite

commonly used for membrane cleaning. Furthermore, these membranes are mostly produced in flat sheet geometry and packed into spiral-wound modules. Such modules are (a) often not backwashable, which is an additional desired strategy to mitigate membrane fouling, and (b) the packing density is lower than in hollow fiber membrane modules.

Better mechanical, chemical, and thermal resistance can be expected for ceramic membranes. Ceramic micro- and ultrafiltration membranes are successfully established, for instance, in waste water treatment [8,9], drinking water production [10,11], produced-water treatment [12,13], and skim milk production [14]. The situation is different for nanofiltration membranes. Although recent developments report nanofiltration membranes with a molecular weight cut-off (MWCO) below 500 Da, with possible use at harsh chemical conditions – i.e. high and low pH or organic solvents [15,16] – the membranes are not established in the market yet. Preparing them defect-free is still difficult and cumbersome, and they are too expensive to be competitive to polymeric nanofiltration membranes: their production is time- and material-intensive due to many successive production steps.

Recently, a layer-by-layer (LbL) assembly from polyelectrolytes

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from aqueous solution [17] on a more open, but affordable, ceramic support [18–20] suggested to be a viable alternative to the all-ceramic NF membranes. LbL films are generally a few nanometers thick and are made of alternating positively and negatively charged polyelectrolytes adsorbed on a surface. The thickness and thus the properties of the LbL films are tailored by various parameters: polyelectrolyte type, its molecular weight and concentration, the ionic strength and pH of the coating solution, the adsorption time, coating method, and number of layers [21–28]. In case of a dynamic coating process – i.e. with convective transport of the polyelectrolyte perpendicular to the permeable support surface – the layer properties are defined by the amount of polyelectrolyte transported by the convective flow to the surface ($m_{PE}^* = J t c_{PE}$, with m_{PE}^* : the mass of polyelectrolyte transported to the surface, J : the flux, t : the coating time, and c_{PE} : the polyelectrolyte concentration within the coating solution [29]).

LbL films on various porous support membranes have been proven to be adequate for fabricating nanofiltration membranes [27,30–34]. Depending on the chosen polyelectrolytes and the coating parameters, even reverse osmosis properties can be realized [35]. Polyelectrolyte films, assembled from PDADMAC and PSS, also exhibit chemical stability in the presence of hypochlorite as well as low and high pH [36,37]. Hence, they fulfill the prerequisites of a stable nanofiltration membrane. Besides chemical stability, back-washability is highly desired to ensure fouling mitigation and better cleaning. The concept of a backwashable hollow fiber nanofiltration membrane was already addressed by Frank et al. [38] in 2001. The membrane was fabricated by interfacial polymerization. However, the retention behavior was difficult to tune and the production involved non-aqueous solvents. De Grooth et al. [36] demonstrated a backwashable hollow fiber nanofiltration based on LbL technology and proved that the backwash is only non-destructive if the support membrane exhibits sufficient negatively charged groups at the membrane surface.

An issue rarely considered is the regeneration of membranes: it may be considered as a sustainable concept that could potentially minimize polymer consumption. In case of a ceramic support with an LbL film as separation skin, only the LbL film may be regenerated. Thus, regeneration would potentially compensate for the initially costly ceramic membrane support as the more expensive ceramic support but also more stable support could be reused. The life span of such a ceramic support is about 10 to 15 years and thus two to five times longer as compared to polymeric membranes. The regeneration would be executed as soon as (a) the LbL film is damaged or (b) the overall performance of the membrane falls below a certain threshold. By removing the LbL film, potential irreversible fouling would be removed as well, as it is attached to the polymeric LbL assembly [39]. On flat non-porous surfaces, the deconstruction was shown by the use of a highly concentrated salt solution [40,41] and ionic surfactants (CTAB and SDS) [42–44]. Ahmadiannamini et al. [45] proposed a route for disassembling PE films for polymeric flat sheet membranes: in case of weak PEs, low or high pH followed by Triton X-100 (non-ionic surfactant) should be applied, whereas strong PEs are removed just by Triton X-100. Ilyas et al. [46] demonstrated the effective removal of weak PEs by a trigger consisting of low pH (pH 3) and high ionic strength (3 M NaNO₃) from dense ultrafiltration membranes; however, the presented membrane was not pH-stable. In general, understanding of such destruction process is shallow requiring more systematic research.

In the present study we demonstrate a regenerable nanofiltration membrane based on polyelectrolyte assembly on a commercially available multi-channel ceramic support. We were faced with the following fundamental as well as applied questions:

1. Is it possible to cover and close a 100 nm pore with a LbL system at a reasonable number of coating steps?
2. Is it possible to perform the LbL membrane build up in a monolithic module?
3. Does the LbL film show mechanical and chemical properties which are equal or superior to today's nanofiltration in terms of backwashing and pH-resistance?
4. Is it possible to deconstruct such layers while they were specifically made to be chemically and mechanically stable?
5. Is it possible to identify construction and deconstruction systems that resolve this intrinsic contradiction to regenerate the membranes inside the module by complete deconstruction of the used LbL film and subsequent rebuild of a new native LbL film?

2. Material and methods

2.1. Materials

The support membrane monoliths employed in the present study are shown in Fig. 1. They are produced by Metawater (Japan) and were provided by RWB Water Services B.V. (Netherlands). The ceramic support is made from alumina with a nominal pore size of 100 nm. The untreated support shows a pure water permeability of about 1100 LMH/bar. The monolith comprises 55 channels, each 2.5 mm diameter and a length of 9.25 cm resulting in a support membrane surface is 0.04 m². Due to its material the support membrane can withstand harsh chemical conditions, such as low and high pH, oxidizing agents such as hypochlorite or organic solvents. The polycation, polydiallyldimethylammonium chloride (PDADMAC) and the polyanion, poly(sodium 4-styrene sulfonate) (PSS) were purchased from Sigma Aldrich, PDADMAC with a molecular weight of 400–500 kDa and PSS with a molecular weight of 1000 kDa. 1 g/l of the polyelectrolyte together with a certain amount of NaCl were diluted in ultra pure water.

2.2. Coating

Before the coating was performed the support membranes were pretreated over night with a 1500 ppm sodium hypochlorite (NaOCl) solution. The NaOCl cleaned and activated the surface for a better attachment of the first layer leading to an increased coating reproducibility. Our previously developed dynamic coating procedure was applied for the ceramic monolith support membrane following the details described in [29]. The geometry of the membrane module goes along with a certain large dead volume on the feed and retentate side. To avoid polyelectrolyte complex



Fig. 1. Ceramic membrane monolith comprising 55 feed channels.

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