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Long term physical and chemical stability of polyelectrolyte multilayer membranes

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ABSTRACT

This work presents a detailed investigation into the long term stability of polyelectrolyte multilayer (PEM) modified membranes, a key factor for the application of these membranes in water purification processes. Although PEM modified membranes have been frequently investigated, their long term stability, critical for application, has not been considered up till now. We focus on both the physical stability of the multilayer on different membranes as well as on the chemical degradation of two different multilayers in the presence of sodium hypochlorite. Two different polymeric ultrafiltration membranes are modified to become dense nanofiltration membranes by applying a thin (PEM) coating on the membrane via the Layer-by-Layer technique. During sequential backwash cycles, no performance loss is observed for PEM modified membranes based on sulfonated poly(ether sulfone) (SPES). On the other hand, PEM modified membranes based on the non-ionic poly(ether sulfone) (PES) show a gradual increase in permeability and loss in retention after each backwash cycle. We demonstrate that a PEM on an ultrafiltration membrane that bears ionic charges has superior adhesion to the substrate, ensuring long term stability. In addition, the chemical stability of two different multilayers is assessed by means of the resistance against sodium hypochlorite degradation. An important factor in the chemical stability is the type of polycation. Membranes coated with multilayers based on the primary polycation poly(allylamine) hydrochloride (PAH) show a loss in performance after 24,000 ppm hours NaOCl (pH 8). Membranes coated with multilayers based on the quaternary polycation poly(diallyldimethylammonium) chloride (PDADMAC) are stable for more than 100,000 ppm hours NaOCl (pH 8), which is an excellent stability, comparable to that of commercial PES ultra- and microfiltration membranes.

1. Introduction

A versatile method for membrane modification is the coating of membranes with different polyelectrolytes [1]. By alternatingly exposing the membrane to positively and negatively charged polyelectrolytes, thin polyelectrolyte multilayers (PEMs) are formed on the membrane. This so-called Layer-by-Layer (LbL) technique, introduced by Decher et al. in the early nineties [2], offers excellent control and flexibility of the properties of these PEMs in the nanoscale range [3,4]. This has led to a wide variety of possible applications of PEMs, including the modification of membranes to improve many aspects of their performance. Membranes have for instance been modified with PEMs to make membranes low fouling [5,6], responsive [7], but also to produce new nanofiltration [8–11], bipolar [12], ion selective [13], and solvent resistant membranes [14].

Until now, most of the research on PEM modified membranes has been focused on the effect on membrane performance. However, studies on the long term performance and stability of the PEM membranes under process conditions are lacking. In many filtration processes the membranes are exposed to solutes that eventually will cause fouling on the membrane. This is especially the case for aqueous applications, such as water or beverage filtration, where the process will have to cope with (bio) fouling and scaling [15,16]. As a result, the membranes need to be cleaned periodically. Different industrially applied cleaning strategies can be utilized. Physical cleaning – by means of a backwash, a forward flush and/or air sparing – introduces high shear loads in order to remove loosely bound foulants. Chemical cleaning, e.g., pH changes or oxidation, is used to remove fouling that is bound stronger to the membrane surface. Because of the necessity of the cleaning steps, we reason that for a successful breakthrough in the application of PEM modified membranes, long term stability of the multilayers on the membrane, especially when exposed to different cleaning conditions, is paramount.

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Recently, Ng et al. showed that PEM modified PES membranes have a permeability increase after a backwash of approximately 30% to 170% and noted the contribution of the lack of surface charge on the PES support towards this instability [17]. These results were only for a single backwash and to our knowledge, lifetime studies that assess the long term stability of the PEMs on membranes under various cleaning conditions have not been performed. However, it is known that the polyelectrolyte complexes themselves are stable for months [18,19]. The effect of different operation conditions on the stability of PEMs has been investigated for coated capillaries used in chromatography. Nehmé et al. showed that silica capillaries modified with poly(diallyldimethylammonium) chloride (PDADMAC)/poly(sodium 4-styrenesulfonate) (PSS) multilayer coatings, were stable over a wide pH range (2.5–9.3) [20]. However, PEMs are known to reorder themselves under certain conditions, such as temperature, ionic strength and stress [21–23]. Especially the latter could be of influence for the long term stability of PEM membranes since high shear forces are applied during backwashing.

In addition to backwashing, membranes are often cleaned by means of an oxidative step (e.g. with sodium hypochlorite or hydrogen peroxide). The oxidative cleaning is applied to remove irreversible organic- and bio-fouling. The ability to withstand this chemical degradation (typically expressed as a product of the hypochlorite concentration and exposure time (ppm-hours)), is a major factor in determining the membrane lifetime. The stability of PEMs against such chemical treatment has been investigated only for a few occasions. Botero-Cadavid et al. investigated the degradation of poly(allylamine) hydrochloride (PAH)/poly(acrylic acid) (PAA) modified optical sensors by H_2O_2, and showed that over time the PEMs were degraded by the peroxide. Sato et al. showed that the degradation rate of multilayers from phenylboronic acid-bearing poly(allylamine) hydrochloride (PBA – PAH) and poly(vinyl alcohol) (PVA) was dependent on the H_2O_2 concentration. The degradation of different polycations by sodium hypochlorite was investigated by Gregurec et al. [24], who showed that the stability is determined by the degree of alkylation of the amines.

In contrast, the degradation of conventional membranes by hypochlorite has been studied intensively. Both reverse osmosis (RO) and nanofiltration membranes based on polyamide thin film composites, show a significant drop in performance after prolonged exposure [25,26], mainly caused by an electrophilic attack by the hypochlorite followed by an Orton rearrangement [27]. Short term exposures have been shown to give small improvements in membrane performance, an effect attributed to an increase in the membrane charge density as a result of amide bound cleavage [28,29]. The degradation of ultra- and microfiltration membranes based on poly(arylene sulfones) has been studied intensively as well, and their main degradation mechanism is attributed to an electrophilic attack of radicals formed by the hypochlorite [30–32]. In general it can be said that the ultra- and microfiltration membranes are more resistant against hypochlorite compared to the thin film composite RO and nanofiltration membranes. Knowledge on how the stability in hypochlorite of polyelectrolyte multilayer membranes compares to conventional membranes and how this can be influenced by the choice of polyelectrolyte is, in our opinion, key to the further development of PEM membranes and critical for the industrial application.

This is the first study that systematically investigates the long term stability of PEM modified polymeric membranes exposed to physical and chemical cleaning conditions. First, the effect of applied shear during repetitive backwashes and forward flushes on the membrane performance is investigated. For this a PEM coating, based on the well-known PDADMAC/PSS pair was applied to both a standard polyethersulfone (PES) ultrafiltration membrane and an ionically charged sulfonated polyethersulfone (SPES) ultrafiltration membrane. Both PEM modified membranes were subsequently exposed to numerous backwashes. In this way we demonstrate the important role of ionic pendant groups on the stability of a PEM on the substrate. In addition to this, the chemical stability against sodium hypochlorite oxidation of PEM modified membranes is investigated. Membranes were modified with different PEMs and exposed to sodium hypochlorite solutions. Over time, the performance of these membranes was measured. We will show that a careful selection of the polyelectrolytes is of key importance with respect to the long term chemical stability of PEM membranes.

2. Experimental

2.1. Materials and chemicals

Poly(diallyldimethylammonium chloride) (PDADMAC, Mw = 150 kDa, 20 wt% in water) was obtained from Kemira (Finland). Polystyrene sulfonic acid (PSS, Mw = 100 kDa, 20 wt% in water) was obtained from Tosoh Organic Chemical Co., Ltd. (Japan). Poly(allylamine) hydrochloride (PAH, Mw = 150 kDA, 40 wt% in water) was obtained from Nittobo Medical Co., Ltd. (Japan). 15 wt% Sodium hypochlorite (NaOCl) solution in water was obtained from Vivochem (The Netherlands). All other chemicals were purchased from Sigma-Aldrich (The Netherlands). All chemicals were used without any further purification steps.

2.2. Membrane materials

Polyelectrolyte multilayers were coated on hollow fibers kindly provided by Pentair X-Flow (The Netherlands). For this, two different ultrafiltration membranes were used. The UFCLE membrane is based on poly(ether sulfone) (PES), and has a molecular weight cut-off (MWCO) of 100 kDa. The HFS membrane is based on PES covered with a separation layer of sulfonated poly(ether sulfone) (SPES), and has a MWCO of 10 kDa. Both membranes are designed for inside-out filtration, having the smallest pores at the inside of the fiber. Scanning electron microscope (SEM) pictures of the membranes are made with a JEOL JSM-5600LV.

For the determination of the zeta-potential of the UFCLE and HFS membrane, single hollow fiber membranes were measured in a cylindrical cell with an electrokinetic analyzer SurPASS (Anton Paar, Graz Austria). The zeta potential is calculated by measuring the streaming current versus the pressure four times in a 5 mM KCl solution at room temperature using the following equation:

$$\zeta = \frac{dI}{dP} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \frac{L_s}{A_s} \qquad (1)$$

where ζ is de zeta potential (V), I is the streaming current (A), P is the pressure (Pa), η is the dynamic viscosity of the electrolyte solution (Pa s), ε is the dielectric constant of the electrolyte, ε_0 is the vacuum permittivity (F m^{-1}) and A_s is the cross section of the streaming channel (m^2).

2.3. Polyelectrolyte chemical stability

The reactivity of hypochlorite in the presence of different polyelectrolytes was measured by means of UV–vis [24]. For this, 25 ml of a 0.4 g l^{-1} hypochlorite solution at pH 8.0 was mixed with either 25 ml of a 0.04 g l^{-1} polyelectrolyte solution or with 25 ml water (for the hypochlorite reference). The pH of the solutions was maintained at a pH of 8.0. Of these solutions, the UV–vis spectra (250–500 nm) were measured every hour for 12 h in a quartz cuvette with a Varian Cary 300 Scan UV–vis Spectrophotometer.