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# Multifunctional polyelectrolyte multilayers as nanofiltration membranes and as sacrificial layers for easy membrane cleaning

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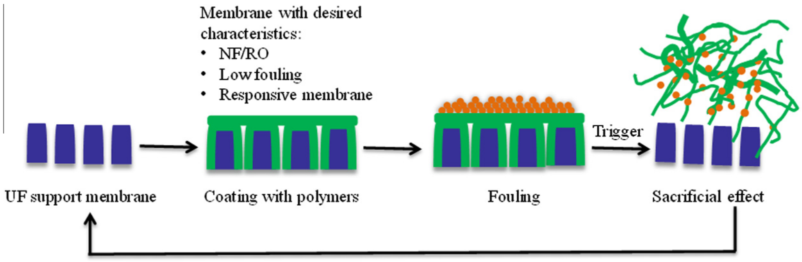
## GRAPHICAL ABSTRACT



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## ABSTRACT

This manuscript investigates the modification of an ultra-filtration (UF) membrane support with polyelectrolyte multilayers (PEMs) consisting of the weak polyelectrolytes poly(allyl amine) hydrochloride (PAH) and poly(acrylic acid) (PAA). These prepared polyelectrolyte multilayer membranes have a dual function: They act as nanofiltration (NF) membranes and as sacrificial layers to allow easy cleaning of the membranes. In order to optimize the conditions for PEM coating and removal, adsorption and desorption of these layers on a model surface (silica) was first studied via optical reflectometry. Subsequently, a charged UF membrane support was coated with a PEM and after each deposited layer, a clear increase in membrane resistance against pure water permeation and a switch of the zeta potential were observed. Moreover these polyelectrolyte multilayer membranes, exhibited rejection of solutes in a range typical for NF membranes. Monovalent ions (NaCl) were hardly rejected (<24%), while rejections of >60% were observed for a neutral organic molecule sulfamethoxazole (SMX) and for the divalent ion $SO_3^{2-}$. The rejection mechanism of these membranes seems to be dominated by size-exclusion. To investigate the role of these PEMs as sacrificial layers for the cleaning of fouled membranes, the prepared polyelectrolyte multilayers were fouled with silica nano particles. Subsequent removal of the coating using a rinse and a low pressure backwash with pH 3, 3 M $NaNO_3$ allowed for a drop in membrane resistance from $1.7 \cdot 10^{14}\ m^{-1}$ (fouled membrane) to $9.9 \cdot 10^{12}\ m^{-1}$ (clean membrane), which is nearly equal to that of the pristine membrane ($9.7 \cdot 10^{12}\ m^{-1}$). Recoating of the support membrane with the same PEMs resulted in a resistance equal to the resistance of the original polyelectrolyte multilayer membrane. Interestingly, less layers were needed to obtain complete foulant removal from the membrane surface, than was the case for the model surface. The possibility for backwashing allows for an even more successful use of the sacrificial layer approach in membrane technology than on model surfaces. Moreover, these PEMs can be used to provide a dual function, as NF membranes and as a Sacrificial coating to allow easy membrane cleaning.

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## 1. Introduction

Fouling of surfaces and interfaces is a well-known and often studied problem in colloid and interface science. Irrespective of the anti-fouling strategies employed, all surfaces will eventually become fouled under adverse conditions [1]. Fouling is an especially crucial issue in membrane technology [2]. Separation processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are used widely for numerous commercial applications in various fields such as water and wastewater treatment, desalination, the food industry, biotechnology and others [3]. However, fouling is an inherent problem for all of these membrane processes, causing fluxes to decline and thus leading to a decrease in productivity and/or an increase in energy demand. While the removal of foulants can be performed using various cleaning techniques, cleaning is often found to be incomplete (irreversible fouling) and cleaning can damage the membrane itself. In both cases, the membrane will need to be replaced, which increases the operational cost of the process. Over the years much research has been devoted to develop methods to make the cleaning easier, such as the use of surfactants [4], superhydrophobic coatings with self-cleaning properties [5], nanobubbles [1] and antifouling layers such as polymer brushes [6]. A very different approach to cleaning was proposed a few years ago and was denoted as the “sacrificial layer” approach [7,8]. This sacrificial layer approach involves the precoating of a surface with a nanometer thick polymer layer that upon fouling can be desorbed/sacrificed from the surface along with any attached foulants. Sacrificing the layer is based on a simple trigger i.e. a change in pH, salt concentration or by the addition of a surfactant. The cleaned surface can subsequently be recoated with a new polymer layer to use it again. As this polymer layer inhibits the contact between foulant and the interface, the success of the approach should be independent of the type of foulant. Additionally when polymers are coated on an interface, it results in a change in the surface properties of the interface. The sacrificial layer coating could thus have additional benefits such as antifouling or anti adhesive properties. We strongly believe that the sacrificial layer approach is also ideally suited for membrane applications. Especially as for membranes, the sacrificial layer coating could not only be used for easy cleaning, but could even function as the active separation layer. A schematic representation of this concept on membranes is illustrated in Fig. 1.

To modify the surface of the materials to provide them with the desired properties, a simple and versatile approach is the use of polyelectrolyte layer-by-layer assembly (LbL) [9,10]. This approach involves alternatingly dipping of a substrate in a polycation solution and a polyanion solution, typically with an intermediate rinsing step with solvent to remove loosely bound electrolytes from the surface. This LbL approach allows to prepare polyelectrolyte multilayers (PEMs) of just a few nanometers in thickness on an interface. The possibility to use a wide range of water soluble polyelectrolytes, its easy application, and the ability to apply it on surfaces of any shape and size are the key strengths of this technique. Since its discovery [10], this technique has been proposed for many applications, including drug delivery, solar sensors, lenses, cell engineering, fuel cells, and membrane processes [11]. For membrane processes the PEMs are always coated onto a membrane support, and have been employed for the preparation of both gas [12] and liquid separating membranes [13]. The key strength of the PEM membranes is the large variety of membrane properties that can be achieved by building in a LbL fashion. As such PEM membranes with a wide variety of properties have been produced for use as reverse osmosis membranes [14], nanofiltration membranes [14–18], solvent resistant nanofiltration (SRNF) membranes [19], forward osmosis membranes [20], low fouling membranes [21–26], antiseptic/antibacterial membranes [22,26–28], stimuli responsive membranes [8,29–32] and ion selective membranes [33–36]. Selection of the right combination of polyelectrolytes can also make the membrane sensitive to a certain trigger (such as a change in pH or salt concentration) that leads to a controlled destruction of these PEMs when required [7,37–39]. The above shows that PEMs hold much promise for membrane technology, especially in combination with its use as sacrificial layers. For the polymers to be used as sacrificial layers we need to tune the interaction between the polymers.

The use of one or more polymers bearing weak acid/base functionality affords the possibility of controlling the average charge per repeat unit and thus the extent of interaction between charged polymers [38]. Bruening and co-workers [8] have successfully used a PEMs as both a sacrificial layer and as the separating layer of an NF membrane. However, they chose to use the combination of poly(styrene sulfonate) (PSS) and PAH to create their PEM based NF membranes, a combination of polyelectrolytes that is known to give extremely stable layers. They could only remove or sacrifice

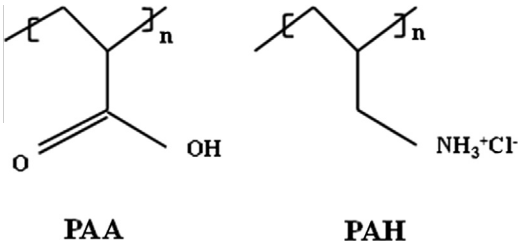

**Fig. 2.** Polyelectrolytes used for this study PAA poly(acrylic acid) and PAH poly(allyl amine) hydrochloride.

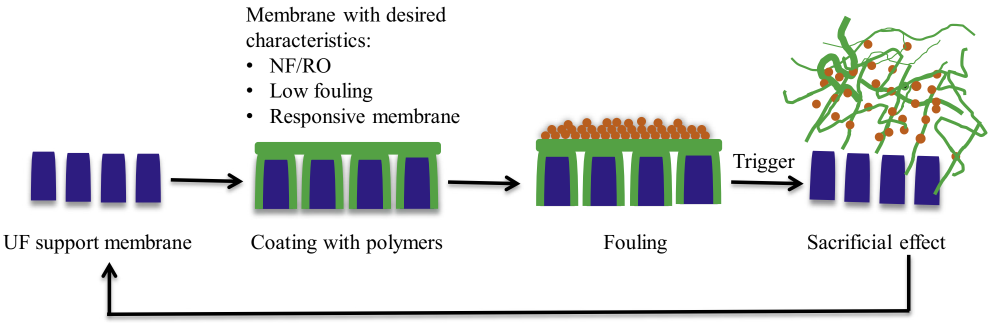

**Fig. 1.** Schematic representation of the application of a thin polymer film onto a UF support membrane and its subsequent use as a “sacrificial layer” to remove fouling. For membranes the sacrificial layer could act double as the effective separating layer to create NF, RO membranes, and/or to create low-fouling and responsive membranes.

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