



# Dual-skinned polyamide/poly(vinylidene fluoride)/cellulose acetate membranes with embedded woven



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## ARTICLE INFO

### Article history:

Received 23 April 2016

Received in revised form

13 August 2016

Accepted 25 August 2016

Available online 26 August 2016

### Keywords:

Dual-skinned membrane

Multilayer membrane

Forward osmosis

Fouling resistance

## ABSTRACT

We propose multilayer membranes including (i) a thin selective polyamide (PA) layer prepared via interfacial polymerization, (ii) a poly(vinylidene fluoride) (PVDF) asymmetric porous support with high adhesion to the PA layer and high mechanical strength, (iii) a strong woven fabric, and (iv) fouling resistant porous cellulose acetate (CA) layer. The PA layer rejects solutes of the draw solution. The PVDF/woven fabric/CA (PVDF/CA) integrated layer performs as a mechanical support with unique properties for forward osmosis (FO) applications. It consists of a modified PVDF top layer suitable for the deposition of a PA layer and a highly hydrophilic bottom layer (CA) with a tunable pore size to minimize foulant deposition and intrusion onto and into the support. The experimental results using bovine serum albumin (BSA) as a model foulant show that the presence of the CA layer at the bottom of the FO membrane (PA/PVDF/CA) reduces 75% fouling propensity compared to the simple FO membrane made of PVDF, woven fabric and PA (PA/PVDF). Fouling tests with 2000 ppm oily feed faced the bottom of the FO membranes further indicate the superiority of the PA/PVDF/CA membrane compared to the PA/PVDF membrane. Moreover, the bottom CA layer can be adjusted with a flexible range of pore size, varied from sub-micron to sub-nanometer depending on the feed composition. The newly developed multilayer FO membrane has comparable performance to the state-of-the-art membrane with added tailored fouling resistance for specific wastewater feeds.

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## 1. Introduction

The success of separation processes such as microfiltration (MF) [1], ultrafiltration (UF) [2–4], nanofiltration [5–7], reverse osmosis (RO) [8,9] highly depends on the chemistry of the applied membranes and strict morphology control. Membranes for these processes are mostly asymmetric. The optimal performance is hardly obtained with a single material. In most cases membranes consist of multilayers of different materials with a combination of hydrophobicity, chemical and mechanical stability and porosity gradient. A variety of commercial asymmetric membranes are available and well established in different applications, with decades of optimization. Previously available membranes developed for reverse osmosis were the starting choice for emerging applications for wastewater treatment and water reuse, such as forward osmosis (FO) and pressure retarded osmosis (PRO). However this

and other emerging processes have different driving forces and operation conditions than pressure driven processes. It is expected that more optimization would be required to guarantee the full potential of the technology. Optimization could be achieved by the development of new synthesized materials or the combination of commercially available polymers in an innovative construction, tailoring pore size, hydrophilic-hydrophobic balance, adhesion between layers and embedding of mechanical supports [10–15]. In this form water permeance, selectivity, fouling and mechanical resistance could be tuned. We demonstrate here a multilayer membrane constituted by polyamide/poly(vinylidene fluoride)/cellulose acetate (PA/PVDF/CA), which was specifically tailored to optimize all membrane properties required for forward and pressure retarded osmosis. We combine the use of embedded woven with strong mechanical strength and the concept of dual skin membrane in the same membrane to target maximal performance and fouling resistance. Each of these strategies has been used before separately, but not all together in a membrane with multi-material layers. Challenges are (i) how to provide acceptable adhesion between layers of different compositions, and (ii) how to

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co-cast different solutions to form the final membrane, mastering pore morphology control in each layer. By succeeding, we can profit from the best advantages of each of the composing polymeric material, which are known to contribute in different ways to membrane properties:

**Selectivity.** Polyamide (PA), prepared by interfacial polymerization is regularly used as dense selective skin for reverse osmosis membranes, because it is possible to obtain with extremely thin thickness and high salt rejection [16–18]. This secures selectivity without compromising water permeance. PA is chosen as top selective layer in this work.

**Mechanical strength.** Polyester or polypropylene woven is used to strengthen the mechanical stability of a membrane. The integration is done as a bottom layer for UF or an embedded grid in FO membranes [17,19]. The most known case is the commercial HTI cellulose triacetate (CTA). In this work a woven is used embedded in the interface between the CA and PVDF layer. The additional challenge in this step, when using layers of different composition, in comparison to embedding in a pure CTA membrane, is how to avoid delamination.

**Pore tuning and adhesion.** CA has been successfully used as membrane material for decades, with low cost, high hydrophilicity and good processability. It has advantages to reduce fouling too and was chosen as the bottom layer of the membrane in this work as described below. The drawbacks and reasons for not choosing a fully integral asymmetric CA membrane are the following. Although CA membrane coated with a thin PA layer would be good FO membrane, the formation of PA layer onto the hydrophilic CA support is not trivial because of their easy delamination from each other and weak mechanical properties [18,20]. Therefore, a PVDF layer was designed in this study to enhance even more mechanical strength and to strongly link the PA layer and the CA layers. Although CA and PVDF have different properties, such as large differences of hydrophilicity, the miscibility of the two polymer solutions and their similar precipitation rates when immersed in water lead to the good adhesion between CA and PVDF layers. While PVDF is stronger than CA and has a better adhesion with PA, having a full PVDF substrate (without the CA layer) would not be the best choice, since the fouling resistance would not be satisfactory as discussed below.

**Fouling.** This is an important issue in practically all membrane-based water treatment processes. The effect on separation performance is strongly dependent on the membrane orientation during operation. This is clearly seen in FO/PRO. In PRO mode, where the active layer faces the draw solution, fouling may occur on and inside the porous support, facing the feed. In addition, the feed concentration may become higher inside the porous support than in the feed (outside the membrane). This phenomenon is referred to as concentrative internal concentration polarization (ICP). In the FO mode, where the active skin faces the feed solution, fouling may occur on the dense selective layer and the draw solution is diluted inside the porous layer by the permeated water that creates a dilutive ICP. Extensive research has confirmed that the PRO mode induces a higher water flux than the FO mode due to the less severe ICP [21,22]. However, membranes operated under the PRO mode have larger fouling propensity because foulants from the feed solution can easily intrude the porous support (internal fouling) that reduces flow channels and enhances ICP [23,24]. As a result, flux drops significantly over time and fouling is more difficult to be removed under the PRO mode than the FO mode. Today, most practical FO applications are operated under the FO mode.

Different approaches have been conducted to eliminate fouling and its impact on FO and PRO processes such as changing operation conditions, cleaning methods, embedding nanoparticles [25], changing material choices [26–29] and chemically modifying

membrane surfaces [30]. Most studies focus on developing membranes with a fouling-resistant *selective* layer. FO membranes with fouling-resistant *support* layers are still less developed. Such membranes are urgently needed so that one can use various brine as draw solutions (i.e., seawater reverse osmosis brine) and explore FO/RO integration for higher water production [13,31]. In this work a fouling-resistant support layer is added based on CA. An interesting approach to reduce fouling in FO/PRO membranes was originally proposed by Wang et al. [32], and subsequently explored by other groups in the field. They introduced a *dual-skinned membrane* as shown in Fig. 1. Dual-skinned FO membranes consist of a dense selective skin facing the draw solution and a loose dense skin facing the feed side could prevent the reverse diffusion of draw solutes and at the same time prevent the foulant intrusion into the porous support. The idea is simple and has been demonstrated in a few reports using integral asymmetric membranes prepared by phase inversion [32,33], surface coating using layer-by-layer (LbL) deposition [34,35], interfacial polymerization [36], or combined interfacial polymerization and surface coating [37]. However there is still a need for optimization of the method and this is one of the goals of this work. The disadvantage of using CA phase inversion to provide both the selective skin and the fouling-resistant skin is that the selective skin prepared in this way has relatively low water permeance, compared to thin PA layers prepared by interfacial polymerization. Poor FO performance is then achieved. This is the reason why the PA selective layer was chosen in this work. On the other hand CA is very effective as secondary skin layer to minimize fouling. For this layer CA is more effective and versatile than the other approaches using dense coatings. It is looser than in other cases, addressing better the requirements appointed in previous mathematical dual-skinned FO membrane studies [38]. Compared to other coatings CA gives more flexibility to adjust the pore sizes of the secondary skin, when working with foulants of different size, without unnecessary loss of water permeance.

In summary the membranes proposed in this work profit from the selectivity and high water permeance of PA thin layers, low delamination and mechanical strength provided by the PVDF layer, further stability added by the embedded woven and fouling resistance given by the CA layer.

## 2. Materials

Commercially available poly(vinylidene fluoride) (PVDF, Kynar<sup>®</sup> HSV 900) was supplied by Arkema. Poly(methyl methacrylate) (PMMA,  $M_w \sim 350,000$ ) and cellulose acetate (CA,  $M_n \sim 50,000$ ) were purchased from Sigma-Aldrich. PVDF, PMMA and CA were dried in a vacuum oven at 60 °C overnight prior to use as the membrane materials. Trimesoyl chloride (TMC), m-phenylene diamine (MPD), lithium chloride (LiCl), n-hexane, isopropanol (IPA), N-methyl-2-pyrrolidone (NMP), ethyl acetate, tween-80 and soybean oil were ordered from Sigma-Aldrich. Sodium chloride (NaCl) and acetone were obtained from Merck. Fluorescein isocyanate conjugated bovine serum albumin (BSA-FITC) was acquired from Invitrogen. Polyester woven fabric sheet (WS0050) was supplied by Industrial Netting. The woven has a nominal hole size of 50  $\mu\text{m}$  and a thickness of 60  $\mu\text{m}$ .

## 3. Experimental

### 3.1. Casting of flat-sheet membrane supports

Before casting the PVDF/woven fabric substrate, the woven fabric was attached onto a glass plate by using a waterproof

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