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Recent developments in thin film (nano)composite membranes for solvent resistant nanofiltration

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By separating organic mixtures at a molecular level, solvent resistant nanofiltration is offering a sustainable and reliable solution to many separation challenges in modern process industry. As solvent permeance is usually inversely proportional to the thickness of the selective layer, so-called thin film composite membranes offer great potential. They consist of a thin polymeric top-layer on a support which is generally prepared from another type of polymer. Excellent combinations of retention and permeance have been achieved by the most recent developments in this field. The incorporation of fillers, for example metal organic frameworks, in the top-layers has the potential to even further enhance the membrane performances. These solvent resistant nanofiltration membranes in general are expected to play an important role in the future industrial separation of solutes from organic streams.

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Introduction

Solvent resistant nanofiltration (SRNF) (or its synonyms organic solvent nanofiltration and organophilic nanofiltration) is a pressure driven technique to realize membrane separations up to a molecular level in solvent streams. Small solvent molecules will permeate through the membrane, while solutes (with a typical molecular weight in most applications between 200 and 1000 Da) will be retained (Figure 1) [1]. It is a relatively young technology that broke through around the beginning of this century and gained a lot of interest since [2]. According to a recent extensive sustainability assessment, SRNF has a huge potential in becoming the best available technology (BAT) among the separation techniques in organic media [3]. Compared to competing technologies, like for example preparative chromatography, distillation, extraction or crystallization, it is generally more energy efficient, mostly does not create extra waste streams and allows for mild operating conditions [3]. SRNF can also very well complement these conventional separation techniques into more efficient hybrid processes. In industry, SRNF may be applied in many solvent-intensive processes, some of them with a large economic impact, such as edible oil refining and degumming, catalyst recovery, solvent recycling in the pharmaceutical industry, solvent dewaxing, polymer fractionation and athermal solvent exchanges.

An exhaustive review on molecular separations with SRNF was published very recently [4]. It discusses membrane materials (including thin film (nano)composites) and membrane characterization, transport models and process design as well as applications, thus largely updating the very first review in this field published in 2008 [1], while another recent review focuses on the role of SRNF in the pharmaceutical industry [5].

Polymeric membranes are considered to be the most interesting material for SRNF applications. Advantages are the large variety of available polymers, their relatively low price and the ease of fabrication and upscaling of polymeric membranes. An important limitation of polymeric membranes however, is their limited thermal and chemical stability. Interactions between organic solvents and the membrane can cause these membranes to swell extensively (or ultimately even dissolve) resulting in loss of selectivity. The current limited commercial availability of robust membranes with good performance is probably one of the main reasons for the delayed breakthrough of SRNF in industry, together with the general reluctance of the chemical industry to implement new technologies. Reports on successfully implemented SRNF separations at large (or at least pilot) scale could surely help to lower the barrier. Moreover, the transport mechanism through SRNF membranes is much less straightforward than for example aqueous applications. The wide variety of solvents that constitute the feed will all interact in a very different way with the membrane material. This renders a membrane excellent in one solvent and useless in another, even to retain the same solute. Membrane stability in a wide range of organic solvents, combined with excellent and reproducible performances on the long term are thus the main challenge for the further expansion of SRNF.

Figure 1

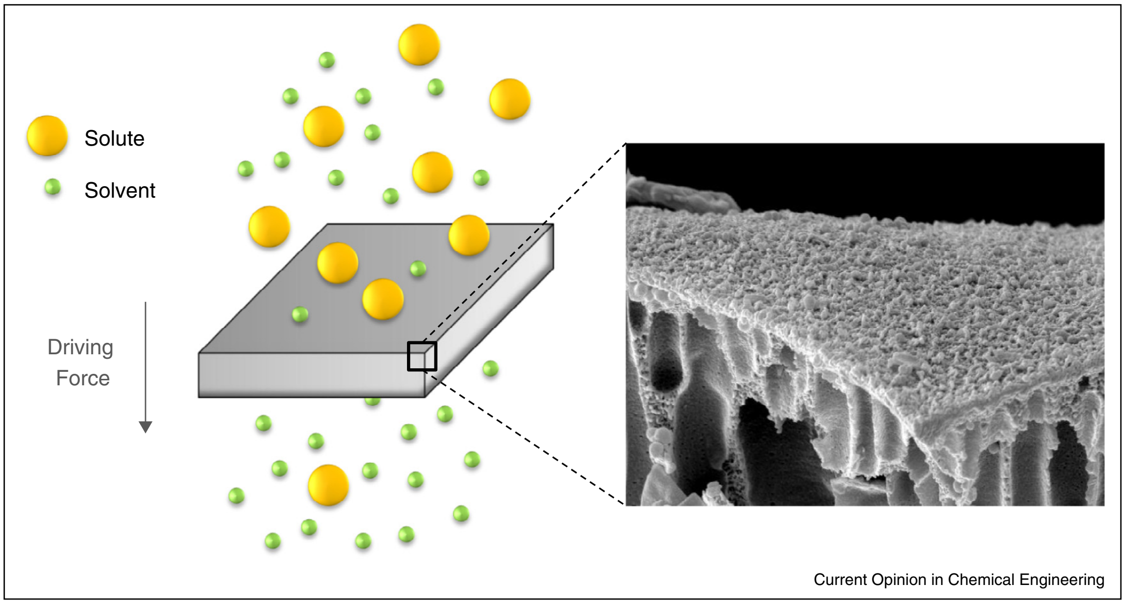


Illustration showing the principle of SRNF, including a SEM image of a thin film composite membrane, consisting of a selective barrier layer on top of a porous support.

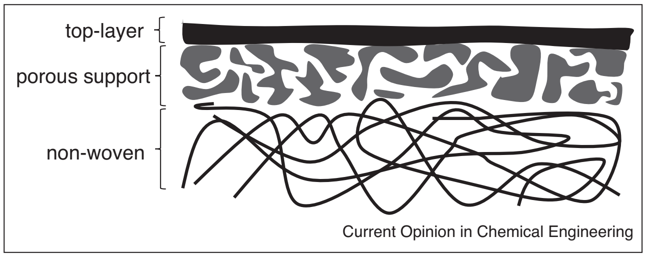
Because of their specific characteristics (i.e. very thin top-layers), thin film composite (TFC) and thin film nano-composite (TFN, containing fillers in the selective layer) membranes can be of great value here, complementing the so-called integrally skinned asymmetric SRNF membranes prepared via phase inversion. Polysulfone [6], polyimide [7,8], polybenzimidazole [9], poly(ether ether ketone) [10] and polyaniline [11] have already proven to be valuable polymers for the preparation of integrally skinned asymmetric SRNF membranes via phase inversion, even more so after introducing crosslinking. Since SRNF is a relatively young technique, many materials are yet to be explored for use in this field. This review focuses on the most important developments in TFC and TFN membranes for SRNF applications over the last 5 years.

TFCs for SRNF: general considerations

TFC membranes consist of a very thin, selective layer on top of a porous ultrafiltration (UF) support. Since support and top-layer are synthesized separately, both layers can be independently optimized to achieve a good membrane performance. In general, a TFC membrane comprises three distinct layers (Figure 2): first, a 'non-woven' fabric, typically made from solvent stable polyester or polypropylene, providing mechanical strength and easy handling of the membrane, second, a porous support layer, allowing for a defect-free top-layer formation, and third, a thin top-layer, which is the actual selective barrier [12].

The support layer of a TFC membrane is typically prepared via phase inversion, which refers to the controlled transformation of a cast polymer solution from a liquid into a solid state [13]. Crosslinking of the polymer is often required to obtain stability in harsh organic solvents, like dimethylformamide (DMF), and can be done thermally, chemically or by means of UV irradiation [14,15]. The same solvent resistant polymers applied in the synthesis of integrally skinned asymmetric membranes are often used to prepare the porous support for TFC membranes. The most common methods to create a selective layer on top of these support layers are interfacial polymerization (IP) and coating where a polymer solution is contacted with them, mostly at labscale via dip or spin coating. Both IP and coating will be discussed in more detail below. Another method for the preparation of TFCs is plasma polymerization. Ultrathin diamond-like carbon nanosheet membranes were prepared by using a plasma enhanced chemical vapor deposition reactor [16]. Permeation experiments revealed

Figure 2



Scheme of a TFC membrane consisting of a non-woven fabric, a porous support layer and a thin, selective top-layer.