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# From ultrafiltration to nanofiltration: Hydrazine cross-linked polyacrylonitrile hollow fiber membranes for organic solvent nanofiltration

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ABSTRACT

Ultrafiltration-level polyacrylonitrile (PAN) hollow fiber membranes were molecularly engineered via chemical cross-linking to obtain membranes suitable for use in organic solvent nanofiltration (OSN). By adjusting the dope composition and spinning conditions, hollow fibers possessing a desirable sponge-like cross-section with minimal macrovoids were obtained. Hydrazine monohydrate was used as the cross-linker and the effects of cross-linking time on the membrane's separation performance were investigated. X-ray photoelectron spectroscopy was used to elucidate the possible reactions and indicated the successful cross-linking of the PAN hollow fiber membranes. The cross-linked nanofiltration-level hollow fibers were subjected to OSN tests using ethanol and dyes as model feed solutions. With this simple and effective modification, the PAN hollow fiber membranes were able to achieve a pure ethanol permeance of 2.32 L $m^{-2}$ $h^{-1}$ $bar^{-1}$ and an impressive Remazol Brilliant Blue R ($M_w$ 626.54 g $mol^{-1}$) rejection of more than 99.9%. Given the ease of fabrication and modification, these PAN hollow fibers represent a significant step forward in the use of hollow fiber membranes for OSN, particularly in larger-scale operations.

## 1. Introduction

From aqueous systems to gases, man-made membranes have played increasingly vital roles in sectors ranging from healthcare to water production and significant research dedicated towards understanding their nature and improving their performance have been conducted [1,2]. However, it was only near the beginning of the twenty-first century that membrane technology truly expanded into the area of organic solvent nanofiltration [3–6]. OSN is a membrane-based process capable of retaining solutes up to a size of 2 nm [7] with a molecular weight cut-off of 200–1000 g $mol^{-1}$ [3,5] in a variety of organic solvents. As with other more established membrane technologies, OSN possesses the advantages of being a continuous process that requires lower energy consumption during operation while having mild operating temperatures [3,4,6]. Given these characteristics, OSN is thus particularly suited for use in the pharmaceuticals and fine chemicals industries where significant amounts of organic solvents are used and products are possibly thermally unstable.

Despite the obvious advantages of OSN, there are not many commercially available OSN membranes to date [3,4] with challenges abound ranging from membrane swelling and leaching to low solvent permeances. More importantly, most OSN research is dedicated towards the fabrication of flat sheet membranes while OSN membranes in the configuration of hollow fibers remain scarce. Compared to flat sheet membranes, hollow fibers have the advantages of possessing a larger surface area per unit membrane volume and a self-supporting structure that does not require additional backing materials [8,9]. Furthermore, many OSN membranes of both commercial and lab-based origins make use of an additional selective layer to achieve the desired separation. This ranges from the use of thin film composite membranes involving interfacial polymerization [10–13] to coating of an additional material atop a supporting substrate [14,15] and even spinning of dual layer hollow fiber membranes [16,17]. Although these methods undoubtedly represent viable means to modify a membrane's properties, care must be taken that all layers of such composite membranes are solvent-resistant. Alternatively, the different layers should swell to the same extent in various solvents to prevent delamination. Hence, designing a hollow fiber OSN membrane without the need of additional backing materials or layers represents a most simple and elegant strategy. Furthermore, such simple designs favour scaling up.

Amongst various polymer types available for membrane fabrication, polyimides (PIs), polybenzimidazole (PBI) and PAN seem to be the most commonly used for OSN [3,4,18]. While these polymers are deemed as excellent solvent-resistant materials, PIs and PBI are often associated

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**Table 1**
Spinning conditions for fabricating PAN hollow fiber membranes.[a]

| Dope solution | A | B | C |
|---|---|---|---|
| Dope composition (wt%) | PAN/PVP K30/DMSO: 15.0/2.5/82.5 | PAN/PVP K30/DMSO: 15.0/4.0/81.0 | PAN/PVP K30/DMSO: 17.0/4.0/79.0 |
| Bore fluid (wt%) | DMSO/DI Water: 95/5 | DMSO/DI Water: 95/5 | DMSO/DI Water: 95/5 |
| Dope flow rate (mL/min) | 5.0 | 5.0 | 4.0 |
| Bore fluid flow rate (mL/min) | 2.5 | 1.5 | 1.5 |
| Take-up speed (m/min) | 7.39 (free-fall), 11.10, 14.81 | 8.76 (free-fall), 13.16, 17.56 | 6.01 (free-fall), 9.04, 12.06 |

[a] Other parameters: Spinneret dimension (OD/ID, mm) – 1.5/0.8. Air gap – 2 cm.

with the formation of nanofiltration-level integrally-skinned asymmetric membranes while PAN is used as an ultrafiltration support for composite OSN membranes [19]. Given the relatively lower price of PAN and its inherent solvent resistance [20], it would be desirable if nanofiltration-level membranes could be fabricated from it directly. Hence, we aim to fabricate a PAN hollow fiber membrane that can be cross-linked to give improved solvent resistance and nanofiltration properties without resorting to additional complicated measures such as interfacial polymerization or coating. To do so, we first prepared an ultrafiltration-level PAN hollow fiber membrane possessing minimal macrovoids and a sponge-like morphology for superior mechanical strength. This was achieved by adjusting the dope composition and spinning conditions. Subsequently, drawing inspiration from literature [10,21–23], hydrazine monohydrate was used as the cross-linker for its simplicity, easy availability and low price. Reaction conditions were then varied to obtain the desired nanofiltration-level hollow fiber membrane. Lastly, the hollow fibers were made into modules for performance tests using various feeds as proof of their functionality. This work may provide useful insights to designing novel cost-effective OSN hollow fiber membranes based on PAN.

## 2. Experimental methods

### 2.1. Materials

Polyacrylonitrile (PAN, $M_w$ = 200,000 g mol$^{-1}$) was kindly provided by Dolan GmbH. Dimethylsulfoxide (DMSO, > 99.9%, Sigma-Aldrich) was used as the solvent for preparing the dope and bore fluid while polyvinylpyrrolidone K30 (PVP K30, Sigma-Aldrich) was employed as an additive in the dope solution. Hydrazine monohydrate (reagent grade, 98%, Sigma-Aldrich) was used for the cross-linking of the membranes. Polyethylene glycol and polyethylene oxide of various molecular weights (PEG, $M_w$ = 400 g mol$^{-1}$, 1000 g mol$^{-1}$, 2000 g mol$^{-1}$, 4000 g mol$^{-1}$, 12,000 g mol$^{-1}$ and PEO, $M_w$ = 100,000 g mol$^{-1}$, Sigma-Aldrich) were utilized to determine the molecular weight cut-off (MWCO), mean pore size and pore size distribution of the membranes in deionized (DI) water. Rose Bengal ($M_w$ = 1017.64 g mol$^{-1}$), Brilliant Blue R ($M_w$ = 825.97 g mol$^{-1}$) and Remazol Brilliant Blue R ($M_w$ = 626.54 g mol$^{-1}$) were purchased from Sigma-Aldrich and used to determine the membrane rejections in the organic solvent ethanol (analytical reagent grade, Fisher Scientific). All chemicals were used as received unless otherwise stated.

### 2.2. Fabrication of PAN hollow fiber membranes

The PAN polymer was first dried in a vacuum oven overnight at 50 °C to remove moisture prior to use. To prepare the dope solution, PAN and PVP K30 were dissolved in DMSO and stirred overnight in a 70 °C water bath until a clear solution was obtained. The dope solution was then allowed to stand still and degas for one day. Next, the solution was loaded into a 500 mL ISCO syringe pump heated to 60 °C with a heating jacket and further degassed overnight prior to spinning.

The hollow fibers were spun using a dry-jet wet-spinning technique where the dope solution was fed into the outer annulus of the spinneret while the bore fluid was fed into the inner annulus. The spinneret was wrapped in a heating jacket set at 55 °C to maintain a more consistent temperature after the dope solution was extruded from the pump. Both extruded streams were allowed to pass through a 2.0 cm air gap before entering the coagulation bath of water with a temperature of 6–7 °C. The hollow fibers were then collected on a take-up drum. To observe the effects of take-up speed on morphology and separation performance of the hollow fiber membranes, the hollow fibers were collected under free-fall conditions (i.e., no stretching) as well as approximately 50% and 100% higher take-up speeds compared to the free-fall condition. The latter two conditions were labeled as “50% stretch” and “100% stretch”, respectively. Detailed dope compositions and spinning conditions are summarized in Table 1. After immersing the spun hollow fibers in water for 2 days to remove residual solvents, the membranes were post-treated in two different ways as follows. Firstly, to test the performance of the as-spun hollow fiber membranes, the unmodified fibers were immersed in a 50 wt% aqueous glycerol solution for 2 days and air dried under ambient conditions before being made into membrane modules. The humectant glycerol was meant to prevent the pores from collapsing during drying [24]. To prepare the membrane module, the bundle of fibers were held in place in a male run tee with epoxy. To ensure that the feed can only permeate through the membrane's selective shell surface and be collected after passing through the lumen, one end of the fiber bundle was sealed with epoxy as well. Each module consisted of 6 hollow fibers with an effective length of 15.5 cm and a total effective area of approximately 0.0019 m$^2$. Alternatively, some hollow fibers were freeze-dried for morphological characterizations.

### 2.3. Cross-linking of PAN hollow fiber membranes

Unmodified hollow fiber membranes preserved in water were used for cross-linking. The hollow fibers were first placed in a solvent-exchange bath of ethanol to remove residual water. Subsequently, the fibers were immersed in a 25 v/v% solution of hydrazine monohydrate in ethanol and heated at 70 °C for various lengths of time ranging from 8 to 18 h. The modified hollow fiber membranes were then washed and stored in DI water overnight to remove the excess cross-linker. Next, the cross-linked fibers were immersed in a 50 wt% aqueous glycerol solution for 2 days and air dried under ambient conditions before being made into membrane modules for performance testing. On the other hand, some cross-linked fibers were freeze-dried for morphological characterizations.

### 2.4. Characterizations

The morphologies of hollow fiber membranes were observed using a field emission scanning electron microscope (FESEM, JEOL JSM-6700F). The freeze-dried hollow fibers were immersed in liquid nitrogen and fractured before being coated with a layer of platinum using a JEOL JFC-1300 platinum coater. Surface chemical functionalities of freeze-dried samples were studied using X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS Ultra$^{DLD}$ spectrometer (Kratos Analytical Ltd.) equipped with a monochromatized Al Kα X-ray source (1486.71 eV, 5 mA, 15 kV).