



# Fabrication of a high-flux sulfonated polyamide nanofiltration membrane: Experimental and dissipative particle dynamics studies



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## ABSTRACT

Novel high-flux thin film composite (TFC) nanofiltration (NF) membranes were fabricated via interfacial polymerization (IP) on a polysulfone substrate using 2,2'-benzidinedisulfonic acid (BDSA) as the amine monomer in aqueous solution. The intrinsic resistance of the resulting membranes ( $R_m$ ) was found to be as low as  $2.37 \times 10^{13} \text{ m}^{-1}$ , indicating a considerably low tolerance against hydraulic resistance. The optimized membrane TFC-1.0 showed excellent rejection towards different inorganic electrolyte solutions in the following order:  $\text{Na}_2\text{SO}_4 > \text{NaCl} > \text{MgCl}_2 > \text{CuSO}_4 > \text{MgSO}_4$ , indicating the negatively charged nature of the membrane. Surface properties were evaluated by field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and contact angle measurements, and the results indicated a smooth and moderately hydrophobic surface. Using dissipative particle dynamics (DPD), the coarse-grained model molecules at the mesoscale level were used to establish an oil-water interface model with regard to the current IP process. The orientation of BDSA monomers was studied and it was found that most of the sulfonic acid groups were facing towards the aqueous solution, while the outer faces were covered by the nanoaggregates of the rigid polymer backbones. This finding is consistent with the observed experimental results and provides a reasonable explanation for the surface properties. The NF membrane has a high water permeability of  $16.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  and high rejection ability for inorganic salts and organic solutes. These results confirm the suitability of this membrane for various applications, such as desalination and dye removal from wastewater.

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## 1. Introduction

Nanofiltration (NF) is a relatively new pressure-driven membrane separation technology with efficiency in between that of ultrafiltration and reverse osmosis. NF was first introduced during the late 1980s, and generally exhibits the favorable separation characteristics of high permeation flux and retention of multivalent salts and organics with molecular weight greater than 200 Da [1–8]. Due to its low pressure operation, mild working conditions and adaptability to different applications, the NF process has been gradually adopted in several research areas including water softening, organic pollutants recovery and heavy metal removal [9–13].

Most of the present day commercially available NF membranes are derived from cross-linked aromatic polyamides (PA) through interfacial polymerization (IP) between acyl chlorides and various

water-soluble reactants [14–17]. The key merit for this process is that the individual characteristics of the active thin layer could be separately optimized to achieve a better separation performance. It is generally considered that the polymeric structure at the surface directly determines the separation performance in terms of water permeability and solute rejection [18–22]. Therefore, the IP process has been extensively studied in recent years, particularly in evaluating new functional precursors.

For instance, Jiang et al. prepared TFC membranes using diethylenetriamine, triethylenetetramine, tetraethylenepentamine and piperazine as the small molecular monomers. Their results showed that the higher the solubility of the amine-monomers in the organic solvent, the greater would be the pore density and permeability of the resulting membrane [23]. Wang and his team also investigated a polyelectrolyte, *i.e.*, branched polyethyleneimine as the starting material. The resulting membranes were positively charged when placed in neutral water, and thus rather strongly rejected  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions [24].

However, to date, most of the NF related studies are focused on the separation performance of the membrane, *i.e.*, the permeate

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flux and rejection properties. Due to the increasing usage of membrane technology in water treatment processes, it is important to improve our understanding of synthetic membranes and separation mechanisms. One convenient method to achieve this objective is to employ computational techniques [25–30]. For instance, Lo et al. used a quantum mechanical simulation to calculate the global/local reactivity of piperazine (PIP) and *m*-phenylenediamine (MPD) molecules towards trimesoyl chloride (TMC) based on density functional theory (DFT). It was found that the reaction between MPD and TMC for the preparation of TFC membrane was more favorable than the reaction between PIP and TMC. The reason for this is possibly the greater number of unreacted carboxylic groups left, resulting in a more charged surface, in turn leading to better selectivity of bivalent salt rejection for the latter [27]. More recently, the properties of a hydrated amorphous PA membrane-foulant system were investigated using molecular dynamics (MD) simulations by Leng et al. [28]. The authors found that the carboxylate groups in both the PA surface and alginate exhibit strong binding with metal ions, and the predominantly existing bidentate configuration leads to the surface fouling. A more interesting method has been reported by Roux's group, in which only TMC and MPD monomers were initially mixed in a box, followed by a polymerization process based on heuristic distance criterion obtained from MD simulations [29]. The atomic density in the model membrane was found to be close to the reference value and the water permeability agreed well with the experiment data, suggesting the reliability of their method. In general, while there are increasing number of reports on the simulations, most of these studies focus on the method improvements or describing the structures based on some commercially available membranes. There is limited information regarding the newly-designed membranes. Furthermore, whether the simulation is performed on the atomic or molecular level, the fundamental aim is to reveal the interactions between the functional groups, particles or water molecules, in order to understand the molecular movement on and through the membranes. In other words, these simulation methods are intended to provide us with a deeper understanding of the phenomena in membrane-based water treatment processes. However, the major drawback is that simulation is a time consuming process, especially when the system contains ten thousand atoms or more. Due to the inherent length and time scale of the simulation process, it would be difficult to monitor the molecular diffusion and self-assembly behaviors during the membrane forming process.

Clearly, there is a definite need to obtain an overall picture of the important aspects such as the structure-property relationship of the monomer, or the polymeric precursors with regard to the IP process. For example, what would be the real geometry of the precursors, what kind of diffusion behavior would they exhibit, and what might be the orientation of the precursors once they came into contact and reacted with the aryl chloride in the organic phase? Only after having understood the answers to these questions, would it be possible to obtain clear structural configurations.

In this work, we used BDSA as a typical water-soluble monomer in the IP process for fabricating the TFC membranes. The unique structure of BDSA based on a hydrophobic phenyl-phenyl backbone and two hydrophilic sulfonic acid groups, could effectively help us explore the diffusion process as well as the final properties of the active sulfonated polyamide (SPA) layer. The TFC membranes were prepared *via* the IP process, for the purpose of desalination. The separation properties of these membranes were then evaluated by determination of the permeate flux and rejection ability for salts and dye solutions. Moreover, the dissipative particle dynamics (DPD) simulation was performed by adopting the concept of an oil-water two-phase interface. The complex interactions among the monomers, organic solutions and aqueous

solutions were neglected and replaced by the repulsion between the motion groups. In this way, the diffusion process of the BDSA molecules and their orientation in the SPA layer were clearly illustrated. Finally, through a combination of the separation properties and DPD results, a new configuration model was proposed in regards to our BDSA/TMC NF membrane system.

## 2. Experimental

### 2.1. Materials

BDSA, Sodium laurylsulfonate (SDS), Triethylamine (TEA), Congo red (MW: 696.68 Da), Methylene blue (MW: 319.86 Da) and Bovine serum albumin (BSA) were purchased from Sinoparm Chemical Reagent Co. Ltd. (China). TMC, ethylene glycol, diethylene glycol, triethylene glycol, and glucose were purchased from J&K Chemical Reagent Co. Ltd. (Beijing, China). Polysulfone (PSf) ultrafiltration membranes (Molecular weight cut-off: 20,000; Water flux:  $120 \text{ L m}^{-2} \text{ h}^{-1}$ , 0.1 MPa) were supplied from Development Center of Water Treatment Technology (Hangzhou, China) and used as a support membrane. Sodium sulfate, Magnesium sulfate, Magnesium chloride hexahydrate, Sodium chloride, Copper(II) sulfate pentahydrate and *n*-hexane were purchased from Nanjing Chemical Reagent Co. Ltd. (Nanjing, China). All other chemicals were obtained from commercial sources and used without further purification. Deionized water was used throughout this study.

### 2.2. Procedure of membrane preparation

The active skin layer of TFC membrane was prepared by conventional interfacial polymerization technology at room temperature about 25 °C. A PSf support membrane was immersed in deionized water overnight, then removed from the water and fixed on a plastic plate. First, the aqueous-phase solution containing a certain amount of BDSA and 0.04% (w/w) of SDS was prepared with pH 10 adjusted by TEA. The organic-phase solution was prepared with a certain amount of TMC in *n*-hexane at room temperature. 100 mL of BDSA solution were poured into the frame and allowed to contact the PSf membrane for 5 min before draining the excess aqueous solution. This residence time allowed BDSA to penetrate into the pores of the porous support. Residual droplets of solution on the top surface of the PSf membrane were removed by rolling a rubber roller across the membrane surface. Afterwards, the frame and gasket were reassembled on top of the PSf membrane, and 100 mL of TMC solution were poured into the frame. After 1 min, the TMC solution was drained off and the membrane surface was rinsed using *n*-hexane (100 mL) to wash away residual reagents. Finally the membrane was dried in air at ambient conditions for 30 s, immersed in a weak acidity aqueous solution for several hours, and saved in deionized water before carrying out for evaluation studies.

### 2.3. Membrane characterization

Surface chemical characterization was performed using X-ray photoelectron spectroscopy (XPS, PHI Quantera II, Japan). Square-shaped coupons with approximate dimensions 1 cm × 1 cm were cut from each of the coated membranes and mounted on the XPS stage. The survey scan was performed in the binding energy range 0–1000 eV with a resolution of 1 eV. High resolution scans of C (1s), N (1s), O (1s) and S (2p) were conducted under similar conditions with 0.05 eV steps, pass energy 20 eV.

Surface morphology and cross-sections were examined using Field Emission Scanning Electron Microscopy (FE-SEM, FEI Quanta

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