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# Stability and permeation behavior of a porous membrane modified by polyelectrolyte networks enabled by electro-deposition and cross-linking for water purification

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## ABSTRACT

A novel nanofiltration (NF) membrane is developed via polyethyleneimine (PEI) deposition on a hydrolyzed polyacrylonitrile (PAN) substrate enhanced by an electric field and chemical cross-linking to achieve improved desalting properties. Compared to the PEI static-deposition process, dramatic increase in salt rejection and substantial reductions of deposition time and PEI concentration are achieved for the membranes prepared by electro-deposition. What's more, the resulting membrane exhibited both stable flux and salt rejection in filtrating seawater for a relatively long term due to a significant membrane stability attributed to the electro-deposition. Desalting properties in terms of salt rejection and flux were found to be strongly affected by both hydrolysis and electro-deposition conditions. Under the optimal fabricating conditions, the resulting NF membrane exhibited a high flux of 24 L/m<sup>2</sup>h, excellent MgCl<sub>2</sub> rejection of ~92% and low NaCl rejection of ~39% when filtrating 2000 mg/L salt solution at 0.5 MPa. Under filtration of raw seawater at 1.8 MPa, the resulting membrane exhibited a high flux of 30.2 L/m<sup>2</sup>h and a significant improvement in seawater softening efficiency compared to various commercial NF membranes, which is attributed to its excellent separation efficiency between divalent and univalent ions. The current investigation demonstrated that polyelectrolyte NF membranes fabricated by electro-deposition and cross-linking led to excellent separation performance and satisfactory stability and durability that can be used in seawater softening for a relatively long time.

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## 1. Introduction

Water is the most essential component of life. However, water scarcity has become a serious issue in many parts of the world today. Among various water purification techniques, nanofiltration (NF) and reverse osmosis (RO) have gained popularity for drinking water production because of their excellent effectiveness in removing low molecular weight impurities such as small organic compounds and ions [1–4]. NF process is preferable compared to RO process due to its low energy consumption and higher permeate flux, which encouraged the application of NF membranes for several commercial purposes, such as wastewater reclamation, water softening, desalination, dye purification and so forth [5–7].

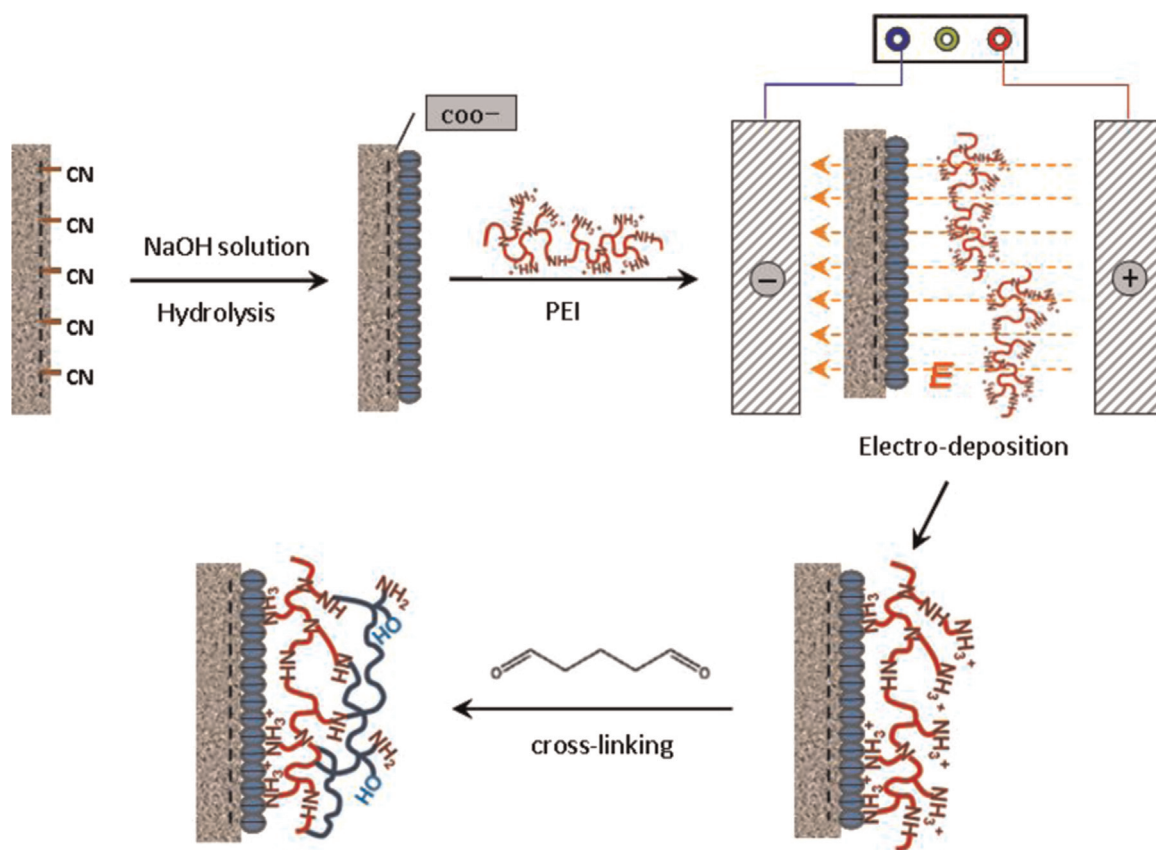
Development of NF membranes has been greatly improved with the deposition of polyelectrolytes onto the existing

membrane surface. In comparison to other important membrane fabrication methods, polyelectrolyte deposition has more advantages over blending and grafting for the following reasons [8–10]: (1) polyelectrolyte-deposited membranes are not changed in terms of their structural properties and mechanical strengths; (2) the charges imposed by the polyelectrolytes can be effectively used in salt rejection, and the resulting thin layers of polyelectrolytes can also provide high water permeability and reduce flux deterioration; (3) membranes modified by polyelectrolyte can be easily tailored to suit various applications, and the depositing process can be applied to existing membranes or existing installed membrane system using static or dynamic coating methods; (4) less (or no) expensive equipment is required; and (5) the depositing process has mostly been performed under ambient conditions (no specific temperature or pressure) with a shortened chemical reaction time. Therefore, due to the fact that the process offers a cheap, easy, no-damage solution to membrane modification, the polyelectrolyte deposition onto the membrane surface has become more and more popular to improve membrane performance.

Amongst the various polyelectrolyte deposition methods, layer-

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**Fig. 1.** Schematic of the assembly and cross-linking of PEI film on the hydrolyzed PAN substrate. The layering of polymers represents the number of preparation steps but is likely not present in the film structure.

by-layer (LBL) self-assembly has been successfully performed by several researches [11,12] and considered as one of the most common key practices for polyelectrolyte-modified membranes [13]. However, the major challenges with the polyelectrolyte-modified membrane prepared via LBL self-assembly involve a considerably large number of depositions (as many as 60–90) and its poor stability in high ionic strength conditions [20]. Therefore, a robust and single polyelectrolyte layer buildup onto porous substrate is needed to produce a membrane with the desired property and performance [14], such as the significant simplification of operating procedure, the sufficient low mass transfer resistance and the durability in a real application.

In an attempt to resolve the aforementioned issues, two remedial approaches were used, involving chemical cross-linking [15–17] and dynamic deposition [18]. Cross-linking method can not only lead to surface densification [19] but also efficiently improve the stability of polyelectrolyte-modified membranes in high ionic strength conditions and chlorine treatment [20]. Dynamic deposition which was proposed in 1997 implies a process where the polyelectrolyte solution is forced to move on/through the support membrane, such as cross-flow system [21] and vacuum-filtration system [22]. Obviously, dynamic deposition process offers a time-saving, layer number-reducing solution compared to static self-assembly process. Up to now, rare study on a NF membrane prepared via single polyelectrolyte deposition on a microporous substrate with high stability has been reported and the integrated approach of dynamic deposition and cross-linking is an effective solution.

In this work, we explore the novel integrated approach of dynamic deposition and chemical cross-linking to fabricate a NF membrane from a porous polyacrylonitrile (PAN) substrate, and to understand the permeation behavior of the resulting membrane in NF application and its stability in seawater. A electric field was

adopted to enhance the electrostatic attractive force between positively charged polyelectrolyte and negatively charged substrate, which can also improve the regularity of LBL structural order and thus the membrane performance [23]. Polyethyleneimine (PEI) was used as the polyelectrolyte because of its suitable charge density and electrolyte strength for LBL self-assembly [15,24]. Due to a large number of primary and secondary amino groups on the long carbon chains of PEI molecule, cross-linking can be adopted to form a dense and steady polyelectrolyte layer. Objective of this work was to improve separation performance and the stability in real application such as seawater softening of PEI-deposited membrane. Our method provided a new procedure for the fabrication of a robust polyelectrolyte-modified membrane with a high water purification performance.

## 2. Experimental details

### 2.1. Materials and chemicals

Unless stated otherwise, all solutions and reagents were prepared with analytical grade chemicals and deionized (DI) water. Polyacrylonitrile (PAN) substrate (MWCO  $\approx$  50 kDa) was provided by Lanjing Membrane Co. Ltd. (Shanghai, China). Sodium hydroxide (NaOH, BASF) was used as the alkali solution for the hydrolysis of PAN substrate to enhance its surface charge density and hydrophilicity. PEI (Mw  $\approx$  10,000, 99%, Aladdin) was used as the polyelectrolyte for the formation of the single layer on the PAN substrate. Glutaraldehyde (GA, BASF) was used as cross-linker of PEI molecules. NF performance was determined using magnesium chloride ( $\text{MgCl}_2$ ), magnesium sulfate ( $\text{MgSO}_4$ ) and sodium chloride (NaCl), obtained from BASF Chemical Co. Ltd.

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