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Influence of chitosan coating on the separation performance, morphology and anti-fouling properties of the polyamide nanofiltration membranes

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ABSTRACT

Chitosan was coated into polyamide membranes by in situ reaction of amine and hydroxyl groups of chitosan and un-reacted of acylchloride of polyamide active layer. Effect of chitosan concentration and coagulation time on the membrane chemical structure, morphology, separation performances and anti-fouling properties were characterized by FT-IR, SEM, AFM, cross-flow membrane module device and cetyltrimethylammonium bromide experiment. Water flux of the polyamide membranes enhanced from 32.9 to 59.6 L/m^2 h and anti-fouling results proved that excellent fouling resistance. Thus, chitosan as a secondary modifier has special potential to improve the performance of polyamide membranes.

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Introduction

One of the major challenges facing to widespread application of NF technique is membrane fouling which resulted in reduction advantages such as production capacity, low operation pressure, high permeate water flux and selectivity, and higher operation costs [1,2]. Fouling is a process where foulants in feed solution deposit onto membrane surface in a way that causes water flux and quality decline and leads to the lower selectivity. Membrane fouling is often caused by irreversible deposition of organic compounds in the feed solution on the hydrophobic membrane surface [3–5].

Several parameters are reported to affect the membrane fouling such as: charge, roughness, and hydrophilicity of membrane surface [6]. So, pretreatment of polluted feed solution and surface modification of membrane surface to lower charge and roughness and enhancement of hydrophilicity properties is a potential procedure to improving anti-fouling membranes. Several strategies exist to hydrophilic modification of membrane surface including: new interfacial polymerization monomers [7], improvement of interfacial polymerization process [8], surface adsorption

[9,10], surface coating [11,12], hydrophilization treatment [13], radical grafting [14,15], chemical coupling [16,17], plasma polymerization or plasma-induced polymerization [18], initiated chemical vapor deposition [19] and incorporation of nanoparticles into the membrane structure [20,21]. But, most of these methods need to special instruments or conditions which limit their application. Interfacial polymerization is the most commonly followed technique for preparing TFC membrane because having a many benefit such as: high selectivity, high water flux, wide pH tolerance, and high mechanical properties [22]. In this technique, the PA active top layer is produced on the asymmetric membrane by reacting two monomers, each dissolved in a two immiscible solvent. Polymerization reactions take place at or near the interfacial boundary of two immiscible aqueous and organic solutions [23]. PA active layer having numerous active functional groups provides the possibility of secondary surface modification via chemical coupling reaction or coating process. The conventional PA membrane surface have un-reacted acylchloride, free carboxylic acid and amine groups making them prone to new modifications [18,24].

Chitosan is a cationic polysaccharide usually obtained by alkaline N-deacetylation of chitin polymer and routinely applied in membrane preparation for its high hydrophilicity and environmental benignancy properties [25]. Some suitable features of modified membranes such as charge density, high hydrophilicity,

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mechanical and chemical stabilities, antibacterial, non toxicity and non allergic, antiviral, high radiation resistance, the capability for the immunological protection against pathogens, biodegradability and biocompatibility are the main reasons of chitosan using as a PA membrane modifier [26]. Two hydroxyl and one amine functional groups existing in the monomer unit of chitosan chains and its solubility in weak acidic aqueous solutions provide wide possibilities to synthesis of new membranes with different properties [27]. Chitosan is deposited onto the PA membrane by mechanisms: (1) electrostatic forces [28], (2) reaction between acylchloride and chitosan amine groups [27], and (3) reaction between hydroxyl groups and acylchloride [29].

The main aim of current study is to investigate the role of secondary chitosan modification after the interfacial polymerization leading to prepare a high performance PA NF membrane. PA NF membrane was prepared by interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMC) in presence of triethylamine (TEA) and then modified using chitosan solution with different concentration and coagulation time. The morphological, topological and chemical characteristics of the resulting membranes were studied by SEM, AFM, and FT-IR, respectively. Performance of PA NF membranes was determined by filtration of aqueous feed solutions containing NaCl, Na$_2$SO$_4$, and CaCl$_2$. The relationship between salt rejection, water flux, and chitosan amount was discussed. Anti-fouling properties of membrane were investigated using flux measurement of 1500 ppm CTAB feed solution during time and then calculating reversible resistances (R_r) and irreversible resistances (R_{ir}). In current study, we introduced a novel and simple method to PA NF membrane surface modification.

Experimental

PAN fibers from textile wastes of Sepehr manufacturing company in Kashan city were used as polymer for membranes preparation. Chitosan polymer (medium molecular weight) purchased from Sigma–Aldrich Company. N,N-dimethylformamide (DMF) as PAN solvent, trimesoyl chloride (TMC) as active monomer in organic phase, piperazine (PIP) as active monomers in aqueous phase, triethylamine (TEA), n-hexane, cetyltrimethylammonium bromide (CTAB), sodium hydroxide and hydrochloride acid were obtained from Merck Chemicals (Germany), and used without further purification.

Preparation of the membrane

Preparation of PAN support membrane
PAN casting solution was prepared by dissolving PAN (16%, w/w) in DMF solvent through stirring (500 rpm) for 24 h at 70 °C. After preparation of homogeneous casting solution, doping solution was held at the ambient temperature for 1 h to remove the air bubbles. The solutions were cast uniformly onto a glass substrate by a hand-casting knife with a knife gap set at 250 μm and immediately immersed in a coagulating water bath with 25 ± 1 °C temperature for at least 24 h until most of the solvent replaced with water and formed support frame completely.

Fabrication of PA membrane
The active skin layer of PA membrane was prepared by conventional interfacial polymerization method on the microporous PAN supporting membrane. First, the support layer was dipped into an aqueous diamine solution containing 2% (w/w) PIP and 0.6% (w/w) TEA. Using a soft rubber roller excess solution was drained from the dip coated support membrane surface until no liquid of amine solution remained. Subsequently, the PAN support membrane was clamped between two teflon frames with a 2 cm

high and 5 cm × 10 cm inner cavity. Then, the organic solution of TMC (0.1, 0.2 and 0.3%, w/v) in n-hexane was poured into the frame where the conventional interfacial polymerization reaction occurred for 60 s. Concentration of TMC monomer were optimized to obtain the most suitable one for the formation the PA active top layer on the support substrate. These membranes were thoroughly washed and stored in de-ionized water before evaluation studies at 4 ± 1 °C.

Modification of PA membrane surface with chitosan
Reached PA membranes modified by chitosan polymer solution using different concentrations (0.1, 0.2 and 0.3%, w/w) coagulation times (10, 20, 30, and 40 min). As a simple method, PA membrane immediately immersed in the chitosan solution and after modification was stored in de-ionized water for use at 4 ± 1 °C temperature.

Performance testing

PA membranes performances were evaluated by measurement of water flux, salt rejection of NaCl, Na$_2$SO$_4$ and CaCl$_2$ with total concentration of 1000 ppm using cross-flow filtration system (Fig. 1). The performances of the provided membranes were analyzed using a batch cross-flow system with the effective membrane surface area of 21 cm^2, and each membrane before experiment was subjected to pre-treatment pressure at 4 bar for 1 h. The permeation tests were carried out under 3 bar pressure, 5 L/min flow rate, and ambient temperature (25 ± 1 °C). The water flux (J, L/m^2 h) of the membrane was determined by direct measurement of membrane permeate volume which was calculated by the following equation:

$$J = \frac{V}{At} \qquad (1)$$

where V (Lit) is the volume of permeated water, A (m^2) is the effective membrane area and t (hour) is the filtration time. The solute concentration of permeation was measured by conductometer and calibration curve. The membrane rejection (R) was calculated by using the following equation:

$$(2) \quad R\,(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

In which C_p and C_f (mg/L) are permeate and feed solution concentration, respectively. To minimize water flux and salt concentration measurement error, all experiments carried out three times and the average value was reported.

Characterization of membranes

Fourier Transform Infrared Spectroscopy (FT-IR) (Nicolet MagnaIR 550) was used to investigate the chemical structure of the PA NF membranes in the region of 400–4000 cm^{-1}. The membrane samples were dried in vacuum oven before analysis. For FT-IR analysis of membrane samples, irtran crystal at 45 °C angle of incidence was employed. Membrane morphology characterization
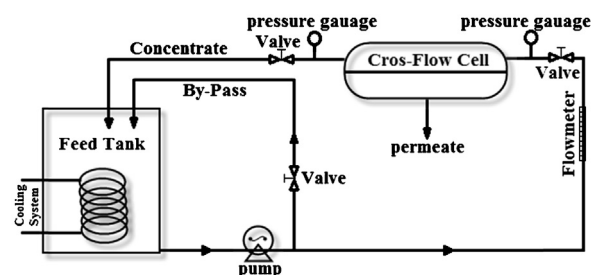

Fig. 1. Cross-flow filtration diagram.