Enhancing the performance and antifouling properties of nanoporous PES membranes using microwave-assisted grafting of chitosan

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HIGHLIGHTS
• New thin layers from chitosan were coated on PES membranes.
• Acrylamide and microwave irradiation were employed to fabricate the thin layers.
• Effects of irradiation powers, irradiation times as well as acrylamide concentrations were investigated.
• Irradiation power and irradiation time increase the separation properties of thin layers.
• Results showed that low concentration of acrylamide was suitable for preparation of thin layers.

ABSTRACT
In this work, we have tried to improve the surface and antifouling properties of polyethersulfone (PES) membranes coated by a thin layer of chitosan. Acrylamide (AAm) as a grafting agent and microwave-assisted grafting as a physical procedure were employed to grafting of the chitosan thin layer without using any chemical initiator. Different acrylamide concentrations (1.8, 3 and 4.2 wt.%), irradiation times (0, 10, 30 and 60 s) as well as irradiation powers (180, 360 and 520 W) were employed. The modified membranes showed an outstanding antifouling property for bovine serum albumin (BSA) in some conditions of preparation. The separation properties of the thin film composite membranes for ion solutions (NaCl, Na2SO4 and MgCl2) increased and changed. Water contact angle measurement, ATR-IR apparatus, SEM, AFM and membrane filtration set-up were used for supporting the results. We used Taguchi designs to analyze many factors with few runs.

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1. Introduction

The membrane process has been used in many applications such as wastewater treatment, industrial water production, water softening, and in the separation of compounds having different molecular weights. A thin film composite (TFC) membrane is obtained by forming an ultra-thin layer on a porous support. Nowadays, several processes
Chitosan is a unique basic polysaccharide and partially deacetylated polymer of glucosamine obtained after alkaline deacetylation of chitin [3]. It is the second most abundant biopolymer on earth after cellulose, widely distributed in crustacean shells and cell walls of fungus [4]. Chitosan is used for waste water treatments due to its pseudo natural cationic properties [5,6]. However, chitosan has few drawbacks such as acidic solubility, low thermal and mechanical stability. To change the chitosan properties, physical and chemical modification procedures have been improved. Furthermore, both hydroxy and amino groups in chitosan are appropriate sites for reaction with desirable chemical materials such as vinyl monomers [7–10]. Modification of chitosan can introduce desired properties and enlarge the field of the applications.

Microwave irradiation using the commercial household microwave oven has received increasing interest in organic synthesis due to the remarkable enhancement of the rates of some organic reactions over conventional reaction [11–13]. Microwave energy can be directly and uniformly absorbed throughout the entire volume of an object, causing it to heat up evenly and rapidly [14]. The microwave irradiation has been successfully used in the synthesis of the super absorbent resin of starch–sodium acrylate graft and the water-absorbent rate of the resin synthesized is much higher than that of the resin by traditional polymerization [15]. It has been also used in the synthesis of chitosan–graft-poly(acrylonitrile) without any radical initiator in a very short time of 1.5 min [16]. In this work, the microwave apparatus was utilized to study the reaction of acrylamide with chitosan for preparing of PES-modified chitosan thin film. Comprehensive literature review showed that no outstanding researches in this field were already performed. Structural analysis as well as the membrane performance was examined to investigate the effects of the modification process on the morphology, rejection capability and antifouling properties of obtained thin layers.

## 2. Experimental

### 2.1. Materials and apparatus

Polyvinylpyrrolidone (PVP, 25,000 g/mol), dimethylformamide (DMF), polyethylene glycol 600 (PEG), ACRYLAMIDE (AAM), Acetic acid (HAC) and acetic acid from Merck were used. Polyethersulfone (PES Ultrason E600P with MW = 58,000 g/mol) was supplied by BASF Company (Germany). MgCl2, Na2SO4 and NaCl salts (from Merck) were held at the ambient temperature for around 4 h to remove the air bubbles. Afterwards, the dope solution was cast on the non-woven polyester (with 150 μm thickness) at 150 μm height using a film applicator at room temperature and in 30% humidity without evaporation. After coating, the membrane was immersed into a distilled water bath for at least 24 h to guarantee complete phase separation.

### 2.2. PES support preparation

The PES support was prepared by dissolving 18 wt.% of PES in DMF with 10 wt.% of PVP, 3 wt.% of acrylic acid and 5 wt.% of PEG 600 as additives by stirring for 4 h at 50 °C. The stirring was carried out at 300 rpm. After formation of a homogeneous solution, the dope solution was held at the ambient temperature for around 4 h to remove the air bubbles. Afterwards, the dope solution was cast on the non-woven polyester (with 150 μm thickness) at 150 μm height using a film applicator at room temperature and in 30% humidity without evaporation.

### 2.3. Fabrication of chitosan thin film membranes

The PES support membrane was clamped between two Teflon frames that were 0.7 cm high and inner cavity 7.5 × 20 cm². The PES-modified chitosan membranes were prepared as follows:

Three grams of chitosan was dispersed in 1000 g of 3% HAC solution at room temperature. The temperature was raised up to 60 °C to completion the chitosan dissolving. Therefore, obtained solution were poured on the top of the PES support membrane and allowed to get wet for 60 min at the ambient temperature. The surface was rolled by a soft roller to eliminate any little bubbles during the drying procedure. After draining off the excess solution, the second solution (aqueous phase) of AAm with different concentrations (1.8, 3, and 5 wt.%) was poured into the holders. The membranes immediately were exposed to the different irradiation power for different times. After 60 min, the excess solution was poured off and the membrane was exposed to the hot air for 5 min at 70 °C. Before preparing for filtration, all prepared thin layers were immersed in pure water for 24 h for removing unattached reagents. Table 1 shows the composition of obtained thin layer membranes. In this study we used Taguchi designs (orthogonal arrays), which allows to analyze many factors with few run.

### 2.4. Characterization of membranes

The surface of membranes was examined by using a scanning electron microscope-Philips model (SEM). Chemical alteration of the membranes was investigated using an Equinox 55 Bruker FT-IR spectrometer from Germany with an attenuated total reflection (ATR) attachment. The atomic force microscopy (AFM, non contact mode) was used to analyze the surface morphology and roughness of the membranes. The AFM apparatus was a DualScope™ scanning probe-optical microscope (DME model C-21, Denmark). The static contact angles were measured using a contact angle measuring instrument (G10, KRUSS, Germany). The ion rejections were investigated by measuring the permeate conductivity using a conductivity meter (Hanna 8733 Model, Italy).

### 2.5. Membrane performance evaluation

The performance of prepared membranes was analyzed by using a batch cross flow system (Fig. 1). The membrane surface area in the filtration cell was 22 cm². The flux of each membrane was determined at 10 min intervals under 0.8 MPa. The experiments were carried out at 25 °C. The cross flow velocity was approximately 0.6 m/s for all tests. The permeation rate and salt rejection were determined for all membranes using different ion solutions (NaCl, Na2SO4 and MgCl2) in

### Table 1

<table>
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<tr>
<th>Name</th>
<th>Concentration of CS (wt.%)</th>
<th>Irradiation power (W)</th>
<th>Concentration of AAm (wt.%)</th>
<th>Irradiation time (s)</th>
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