



# Preparation, characterization and performance of ZnCl<sub>2</sub> incorporated polysulfone (PSF)/polyethylene glycol (PEG) blend low pressure nanofiltration membranes



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## HIGHLIGHTS

- Polysulfone based NF membranes were cast using PEG 200 and ZnCl<sub>2</sub> as additives.
- Molecular weight cut off of NF membrane was less than 180.
- Membranes were having negative zeta potential.
- About 40% NaCl rejection was obtained at pH 2 and 11 at 690 kPa.
- Rejections of chrysoidine R, crystal violet and congo red were above 95%.

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## ABSTRACT

Simultaneous use of organic (PEG 200), and inorganic (ZnCl<sub>2</sub>) additives to polysulfone for casting of nanofiltration (NF) membrane was reported in this work. Dimethylformamide (DMF) was used as the solvent. The membranes were characterized in terms of surface morphology, permeability, porosity, contact angle, molecular weight cut off and zeta potential. The resultant NF membranes were tested with monovalent and divalent electrolytes sucrose, glucose and three dyes in the range of molecular weight from 263 to 697. Both NF membranes showed rejection of salts, NaCl: 40–43% and Na<sub>2</sub>SO<sub>4</sub>: 52–54%, at 690 kPa and pH 11. The corresponding permeate flux were 20 to 22 l/m<sup>2</sup>·h. Among the dyes crystal violet and congo red are rejected more than 98% and chrysoidine more than 95% over the transmembrane pressure range of 276 to 690 kPa. Electrostatic interaction was found to play a determinant role in rejection of salts, whereas, size exclusion was the major mechanism for rejection of dyes.

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## 1. Introduction

With technological advancement, membrane technology is steadily growing in various industries due to competitive energy prices and environmental concerns. Although a number of pressure driven solvent separations had been explored till date, nanofiltration (NF) is relatively a younger technology. The use of polysulfone (PSF) as a material for the synthesis of ultrafiltration (UF) and NF membrane is widespread because of its good thermal, chemical and mechanical stability. Phase inversion method developed in the early sixties, highlights the most

versatile, economically feasible and reproducible mechanisms for the fabrication of polymeric asymmetric membranes. These membranes possess a skin-layer at the top followed by a porous sub layer. Thin skin layer enables high permeability and selectivity. Limitation of PSF and polyether sulfone (PES) over other polymers is their high hydrophobicity that causes severe membrane fouling. When feed is charged to the membrane module, hydrophilic surface shows better performance against fouling. Surface hydrophilicity can be augmented by different modification routes including graft polymerization, plasma treatment, and physical pre-adsorption of hydrophilic components to the membrane surface [1–5]. Another simple and inexpensive approach for the bulk modification is the incorporation of hydrophilic additives in polymer solution itself. Additives affect the structure and state of the casting solution, altering the physical, morphological and permeation characteristics of asymmetric membranes. The use of different organic additives, like, polyethylene glycol (PEG) [6–8], polyvinylpyrrolidone (PVP) [9–11], acids [12], acetone [13], and alcohols [14,15] has been reported. Kim and Lee [16] found that smaller molecular weight of PEG

*Abbreviations:* PASB, poly[(4-aminophenyl) sulfonyl] butane diamide; mPASB, methylated poly[(4-aminophenyl) sulfonyl] butane diamide; PEI, polyetherimide; PVP, polyvinylpyrrolidone; PES, polyether sulfone; PVDF, polyvinylidene difluoride; PI, polyimide; PA, polyamide; DMF, N,N-dimethylformamide; SPES, sulfonated polyethersulfone; PP, polypropylene; TFC, thin film composite; CS, chitosan; PPES, poly(1,4-phenylene ether ether sulfone); GO, graphene oxide.

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200 and 400 can be used as a pore reducing hydrophilic additive rather than a pore forming one using polyetherimide (PEI) as base polymer.

Nanofiltration membranes recently have gained their importance in the field of drinking water, industrial water and waste water treatment [17,18]. Charge in NF membranes is one of the major factors for the separation of monovalent and divalent ions or organic solutes in the feed solution. Size exclusion and electrostatic interactions are two basic phenomena by which separation occurs in NF membranes [19–21]. Isloor and co-workers have done extensive work in fabrication and characterization of PSF based NF membranes using different functional additives like poly isobutylene-alt-maleic anhydride, poly[(4-aminophenyl) sulfonyl] butane diamide (PASB), and methylated poly[(4-aminophenyl) sulfonyl] butane diamide (mPASB) [22–25]. PSF was better to prepare chlorine resistant membranes. Moreover, it was soluble in most of the organic solvents [26].

The use of inorganic salts in the polymeric solution was also reported to be a promising and effective method to prepare membranes with enhanced performance. These solutes changed the solvent properties as well as interaction between the macromolecular chains [27]. Reasonable literature is available to observe the effects of inorganic salts as additives to various casting solution of PSF, PES, polyvinylidene difluoride (PVDF) and polyimide [28–37]. These are summarized in Table 1. This literature survey highlights the following points: (i) membrane pores were reduced using zinc chloride as additive in the absence of any organic additive [28–30] and the resultant membrane was still in UF range, except in one case, where NF membrane was resulted [30]; (ii) addition of lithium compounds [31–35] and potassium perchlorate [36] led to the increase in pore size of the membranes, all being in UF range.

The present work employs simultaneous use of organic (PEG 200) as well as inorganic ( $ZnCl_2$ ) additives (both are well known pore constrictors) [16,28–30] to PSF/DMF system in order to get NF membrane. In the first step, concentration of PEG 200 was selected to obtain highly selective dense UF membrane. In the next step, the effect of  $ZnCl_2$  was investigated in PSF-PEG/DMF system to arrive at NF membrane. The membranes were characterized in terms of permeability, molecular weight cut off (MWCO), morphological study, contact angle and surface zeta potential. Performance of NF membrane was tested in terms of rejection of monovalent and divalent salts, glucose, sucrose and various dyes.

Thus, the novelty of this work is that it is the first attempt to use simultaneous inorganic ( $ZnCl_2$ ) and organic (PEG 200) additives on PSF/DMF system to get NF membrane.

## 2. Experimental

### 2.1. Materials

PSF with an average molecular weight of 22,400 Da was procured from M/s, Solvay Chemicals, Mumbai, India and was used as the base polymer. Solvent N,N-dimethylformamide (DMF) was purchased from M/s, Merck (India) Ltd., Mumbai, India. Polyethyleneglycol (PEG) of average molecular weight 200 Da, 400 Da, 600 Da, 4 kDa, 20 kDa and 35 kDa were supplied by M/s, S. R. Ltd., Mumbai, India. Dextran (average molecular weight: 70 kDa) and polyethylene glycol of average molecular weight 100 and 200 kDa were procured from M/s, Sigma Chemicals and M/s, Aldrich Chemicals, USA, respectively. These neutral solutes were used to evaluate molecular weight cut-off (MWCO), of the cast membranes. The dyes chrysoidine R, MW: 262.74, and congo red, MW: 696.65, were supplied by M/s, Loba Chemie Pvt Ltd., Mumbai, India. Crystal violet, MW: 407.5, was procured from M/s, Sisco Research Laboratory, Mumbai, India. Distilled water was used as the non-solvent in the coagulation bath. All chemicals were of analytical grade and used without further purification.

### 2.2. Determination of coagulation value

Thermodynamic stability of polymeric solution can be explained in terms of its coagulation value [28]. Coagulation value is defined as

weight in grams of 1:1 wt.% non solvent/solvent mixture needed to initiate a visual turbidity in 10 g of polymeric solution, which persists for 24 h at 25 °C.

### 2.3. Membrane preparation

Flat sheet PSF membranes were prepared by phase inversion method and the steps involved in the membrane fabrication were as follows. Fixed amount of PEG was added to a premixed 18% PSF in DMF dissolved at 60 °C. The solution was magnetically stirred for at least 12 h to ensure complete dissolution of the polymer. During the whole process of stirring, the lid of the container was kept closed to prevent the loss of solvent due to evaporation. The prepared solutions were kept for at least 24 h without stirring at room temperature to remove air bubbles. In the first step of casting of membranes, non-woven polyester fabric of thickness  $118 \pm 22.8 \mu\text{m}$  (product number TNW006013, supplied by M/s, Hollytex Inc., New York, USA) was attached to a clean glass plate using adhesive tape. The casting solution was drawn down the fabric using a doctor's blade with an adjustable thickness fixed at 200  $\mu\text{m}$  and was immediately immersed in a precipitation bath containing distilled water at room temperature to initiate the non-solvent induced phase separation. The membrane was kept in the precipitation bath for 10 min and then, it was transferred to another container having fresh distilled water for 24 h to remove the excess solvent. After that, the membrane was ready to be tested. In order to see the effect of  $ZnCl_2$  on the casting solution, another set of asymmetric membranes were cast by following all the above steps using  $ZnCl_2$ , in the concentration range of 0 to 2 wt.%. Concentration of PEG of molecular weight 200 Da was varied up to 10 wt.%. Casting of the membranes was done at room temperature ( $25 \pm 2^\circ\text{C}$ ). Viscosity of the polymer solution was measured using a rheometer (model: Physica MCR 301, supplied by M/S, Anton Parr, Austria).

### 2.4. Characterization of membranes

The following characterizations were carried out for the prepared membranes.

#### 2.4.1. Porosity ( $\epsilon$ ) and contact angle (CA)

Membrane porosity plays an important role in its performance. Membrane porosity was measured by the mass loss of wet membrane after its drying. The membrane, soaked with distilled water was weighed after mopping superficial water with filter paper. Then, the wet membrane was placed in an air-circulating oven at 60 °C for 24 h and then further dried in vacuum oven before measuring the dry weight until a constant mass was obtained. From the two weights (wet sample weight,  $w_0$  and dry sample weight,  $w_1$ ), the porosity of the membranes was calculated using the following equation [7].

$$\epsilon = \frac{w_0 - w_1}{\rho_w A l} \times 100\% \quad (1)$$

where,  $\epsilon$  is the membrane porosity,  $A$  is the membrane surface area,  $l$  is the membrane thickness and  $\rho_w$  is water density. In order to minimize the experimental errors, the membrane porosity of each sample was measured three times and the average values were reported. The contact angle was measured by a Goniometer (supplied by Labline instrument, Mumbai, India, manufactured by Rame-Hart instrument Co., New Jersey, USA; model number: 200-F4) using sessile drop method. The contact angle was measured at six different locations of the membrane and the average value was reported.

#### 2.4.2. Membrane permeability

Measurement of pure water permeability was carried out in a batch filtration cell [7]. Effective area of the membrane in the module was 34  $\text{cm}^2$ . First, the cell was filled with 500 ml of distilled water and

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