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# Fabrication of novel poly(phenylene ether ether sulfone) based nanocomposite membrane modified by $Fe_2NiO_4$ nanoparticles and ethanol as organic modifier

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## HIGHLIGHTS

- The effect of EtOH and $Fe_2NiO_4$ particles as additives in membrane matrix was studied.
- Membrane containing 5 wt.% EtOH showed high rejection and suitable flux.
- Water flux increased from 2 to 14.78 ($L/m^2$ h) by use of 0.02 wt.% NPs and 5 wt.% EtOH.
- The salt rejection was improved for the modified membrane from 49.5 to 94%.

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## ABSTRACT

In this research, poly(phenylene ether ether sulfone) based nanofiltration membranes were prepared by solution casting technique/phase inversion method. The effects of ethanol and $Fe_2NiO_4$ nanoparticles and as organic modifier and inorganic filler additive on membranes physico-chemical properties were studied. Scanning electron microscopy (SEM) and scanning optical microscopy (SOM) analysis, porosity and water content measurements, tensile strength, water flux and salt rejection tests were carried out for the membrane characterization. SEM images showed that utilizing ethanol in polymeric solution led to increase of macro-voids in the membrane matrix. Also images showed that using nanoparticle in casting solution led to increase of the void length. Images showed uniform particle distribution for the composite membranes. Moreover, obtained results exhibited more amount of water content and porosity for the modified membranes compared to virgin type. Results showed that utilizing 0.02 wt.% $Fe_2NiO_4$ nanoparticles and 5 wt.% ethanol in the membrane matrix led to increase of water flux from 2 to 14.45 ($L/m^2$ h) and salt rejection from 49.5 to 93% respectively. Mechanical strength of membrane was decreased obviously by the use of ethanol in casting solution. Mechanical strength was improved initially by the use of 0.01 wt.% NPs in the membrane matrix and then decreased.



## 1. Introduction

Nowadays, membranes play an important role in various kinds of separation processes and also daily human's life [1]. Nanofiltration (NF) is a membrane separation process which has been sized between ultrafiltration (UF) and reverse osmosis (RO). In addition to the sieving mechanism in this process, rejection is also influenced by the charge of membrane pores and surface which makes it suitable for ionic separation due to electrostatic repulsion [2].

The reported researches demonstrated high water flux and suitable salt rejection for the NF membranes in multivalent ionic solution. At the present time, NF is used for the process such as sulfate and nitrate removal [3–7], removal of pesticides [6,8], xenobiotic removal [1], and separation of heavy metals [9–11].

Different polymers such as polysulfone (PS), polyethersulfone (PES), cellulose acetate (CA), polyimide (PI), polyvinylidene fluoride (PVDF), polyamide (PA), polyetherimide (PEI) and poly(phenylene ether ether sulfone) (PEES) [1,8,12–19] have been utilized as polymer based binder in membrane preparation. A few research was found by our literature survey to fabrication of NF membrane by using poly(phenylene ether ether sulfone) (PEES). The PEES is a polymer with good mechanical, chemical and thermal stability which make it suitable for membrane fabrication [19,20]. The PEES is also a hydrophobic polymer.

Various methods such as polymer blending, surface modifications, using different additives/fillers and many more techniques have been used in NF membrane modification [21–28].

Surface modification of PEES with Chitosan has been reported by Shenvi and his co-worker. In this study, Chitosan was used as an active

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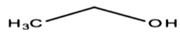
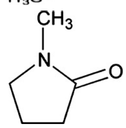
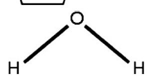
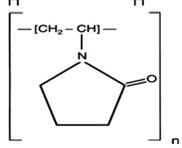
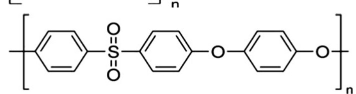
**Table 1**
Chemical structure and physico-chemical properties of used materials.

| Solute/solvent/non-solvent/polymers | Chemical structure | Density (g/mL) | Solubility parameters ($(Cal/cm^3)^{0.5}$) |
|---|---|---|---|
| Ethanol |  | 0.789 | 11.75 [51] |
| N-methyl-2-pyrrolidone (NMP) |  | 1.030 | 11.54 [51] |
| Water |  | 1.000 | 9.40 [50] |
| Polyvinylpyrrolidone |  | – | – |
| Poly(1,4-phenylene ether-ether-sulfone) (PEES) |  | – | – |

layer in order to enhance the PEES hydrophilicity. It was concluded that modified membranes showed fairly good rejection towards inorganic salts even at lower operating pressure [19].

Various organic materials have been employed as additives for membrane modification. It was found that using organic additives such as hydroxyl (–OH) and carboxyl (–COOH) compounds in the membrane matrix caused variation in NF structure and performance [29,30].

Also, the effect of inorganic materials such as nanoparticles into the membrane matrix has been examined widely to improve the physico-chemical properties of membrane [29,31–37].

Magnetic nanoparticles (NPs) such as various types of iron oxide NPs have attracted much attention in biomedical engineering [38], bio-separation technologies [39] and membrane processes in water treatment [35,40] due to the unique features such as superior magnetic, electrical and selective adsorption characteristics.

Nowadays, demands for the adsorptive/magnetic mixed matrix membranes are increased for the removal of specific metal ions such as lead compounds from waste solutions, treating effluents [35,37,40,41].

In this research, poly(phenylene ether ether sulfone) (PEES) based nanofiltration (NF) membranes were prepared by solution casting technique/phase inversion method. The effects of $Fe_2NiO_4$ nanoparticles and ethanol as inorganic filler additive and organic modifier on physico-chemical properties of membranes were studied respectively. PEES is a polymer with excellent chemical/thermal stability, good mechanical properties and low cost. Iron–nickel oxide nanoparticles also are new class of advanced materials with very interesting features and capacity such as superior magnetic, electrical and selective adsorption characteristics [41–43]. Polyvinylpyrrolidone (PVP) was also used as pore-former in membrane fabrication [44].

**Table 2**
Composition of casting solution used in membrane preparation.

| Membrane | Polymer (wt.%) | | NMP/ethanol (organic modifier) (82 wt.%) | | $Fe_2NiO_4$ NPs (inorganic modifier) (wt./wt.%) |
|---|---|---|---|---|---|
| | PEES (wt.%) | PVP (wt.%) | NMP | Ethanol | |
| M1 | 17 | 1 | 100 | 0 | 0.00 |
| M2 | 17 | 1 | 97 | 3 | 0.00 |
| M3 | 17 | 1 | 95 | 5 | 0.00 |
| M4 | 17 | 1 | 93 | 7 | 0.00 |
| M5 | 17 | 1 | 95 | 5 | 0.01 |
| M6 | 17 | 1 | 95 | 5 | 0.02 |
| M7 | 17 | 1 | 95 | 5 | 0.05 |
| M8 | 17 | 1 | 95 | 5 | 0.10 |

Scanning electron microscopy (SEM) and scanning optical microscopy (SOM) analysis, porosity and water content measurements, tensile strength, water flux and salt rejection tests were carried out for the membranes' characterization.

## 2. Materials and methods

### *2.1. Feed*

An aqueous solution containing $MgSO_4$ with concentration of 2 g/L was used in membrane characterization. All experiments were carried out at pH = 7.

## 3. Materials

Poly(1,4-phenylene ether-ether-sulfone) supplied by Sigma-Aldrich Company (US) was used as membrane based binder. N-methyl-2-pyrrolidone (NMP) (Merck Inc., Germany), deionized water and PVP (Merck Inc., Germany) were used as solvent, non-solvent and pore-former in membrane fabrication, respectively. Ethanol (Merck Inc., Germany) was also applied as organic additive in

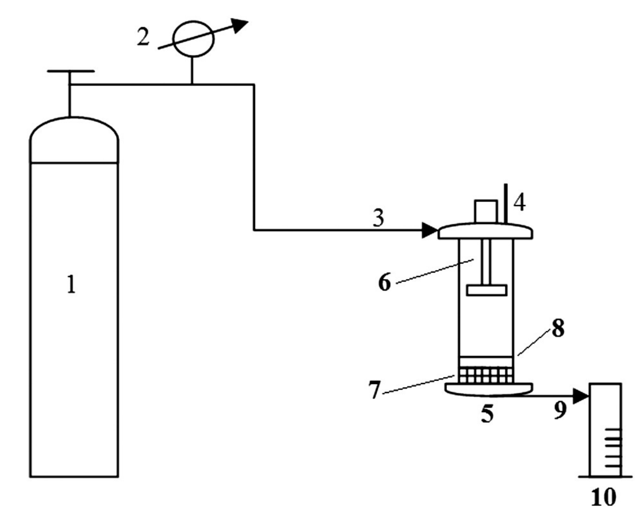



**Fig. 1.** Dead-end filtration set-up: 1—nitrogen gas, 2—pressure gage, 3—nitrogen entrance, 4—feed entrance, 5—filtration cell, 6—agitator, 7—support, 8—membrane, 9—permeate, 10—collector.