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A comparison between blending and surface deposition methods for the preparation of iron oxide/polysulfone nanocomposite membranes

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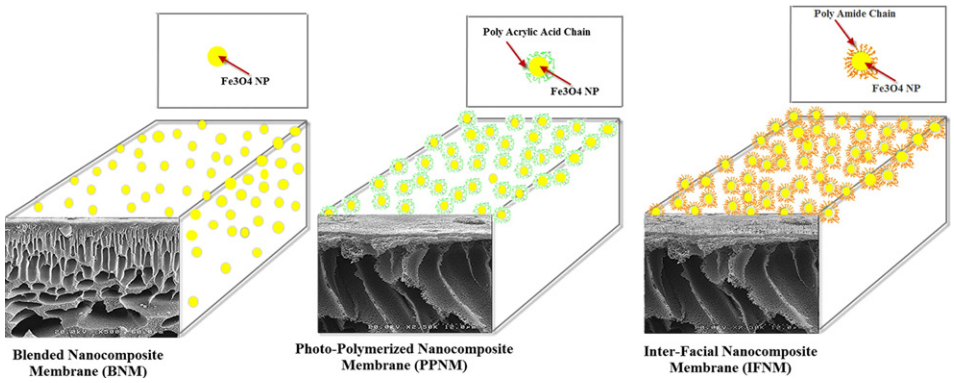
HIGHLIGHTS

- Three types of nanocomposite membranes containing Fe_3O_4 nanoparticles were prepared.
- Polysulfone/Fe_3O_4 nanocomposite membranes were prepared by blending method.
- Polyacrylic acid/Fe_3O_4/polysulfone membranes were prepared by photopolymerization.
- Polyamide/Fe_3O_4/polysulfone membranes were prepared by interfacial polymerization.
- Structural and functional properties of all nanocomposite membranes were compared.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study is to investigate the effect of the presence and impregnation of iron oxide nanoparticles with the polysulfone membrane matrix. The nanoparticles were synthesized via co-precipitation method and were added to the membrane structure through blending with the polymeric matrix (Blended Nanocomposite Membranes (BNM)), deposition by photopolymerization (PhotoPolymerized Nanocomposite Membranes (PPNM)) and deposition by interfacial polymerization (Interfacially Polymerized Nanocomposite Membranes (IPNM)). FTIR analysis proved the presence of nanoparticles in all of the three types of membranes. According to AFM images, nanoparticles enhance the membrane roughness. On the account of SEM images obtained from the membrane surface, nanocomposite membranes have a more uniform surface compared to neat polymeric membranes. In addition, the cross-sectional SEM images of the membrane revealed that the blending method provides the opportunity of controlling the membrane morphology by means of nanoparticles. Contact angle analysis confirmed the development of nanocomposite membrane hydrophilicity versus neat polymeric membranes. The filtration experiments including permeation flux, dye rejection, and molecular weight cut off were done to compare all of the nanocomposite membranes. The results indicated that the blending method can improve the membrane structural properties and the deposition method can improve their separation yield.

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1. Introduction

Separation processes are among the most important and applicable processes in many industries such as chemical [1], food, and pharmaceutical [2] industries. Membrane separation processes have found great applications due to possessing the following advantages: producing no by-product, low process temperature, relatively low cost, and high efficiency [3]. In recent years, there have been many pieces of research conducted on improving the membrane performance and membrane processes [4,5]. Increasing the separation yield [4] and the membrane flux [5] has been the target of many of these investigations. Typically, those methods that develop the membrane flux decrease the membrane separation percentage. At the same time, those methods which enhance the separation yield reduce the membrane flux [6]. Therefore, it is desirable to develop methods that could increase both membrane separation percentage and membrane flux, simultaneously [7]. Nanocomposite membranes are a new group of membrane materials that have the benefits of polymeric membranes and nanostructure materials at the same time [8–10]. Various nanoparticles have been used in the structure of polymeric membranes. The aim of adding some of these particles to the membrane structure is to improve the membrane flux [11,12] and some other to develop the separation yield compared to raw membranes [13]. Nanoparticles donate their intrinsic properties to the nanocomposite membrane and can improve the membrane functional properties. TiO_2 [14], Ag [15] and ZnO [16] nanoparticles have an antibacterial property, ZrO_2 [17] and Fe [18] have catalytic properties, SiO_2 [19] nanoparticles have a nature of electrical conductivity, and Fe_3O_4 [20] nanoparticles donate a magnetic property to the nanocomposite membrane.

The effect of nanoparticles on the structure and thereby on the function of membranes depends on how nanoparticles are added to the membrane, regardless of the type of nanoparticles [9]. Although the majority of nanocomposite membranes are synthesized based on adding nanoparticles to the membrane matrix [21,22], in recent years deposition of nanoparticles on the membrane surface has been extensively used to make nanocomposite membranes [23,24]. Rahimpour et al. performed a comparison between the efficiency of blending and immersion deposition methods in terms of membrane performance improvement [25]. The results indicated that deposition method has a more effective role in improving the membrane performance. However, sustainability of the deposited layer is less than that of trapped nanoparticles in the polymer matrix. In addition to the immersion method, there have been other methods used to modify the surface of polymeric membranes such as interfacial polymerization [26,27] and UV-assisted photopolymerization [28–31]. These methods provide higher surface layer sustainability by creating stronger chemical bonds compared with the immersion method. UV-assisted photopolymerization has been done on polymeric surfaces that are sensitive to irradiation such as polysulfone [29,30]. In this process, vinyl monomers are used to create a thin layer on the membrane surface [31]. Our previous research demonstrated that it can be an appropriate method to stabilize Al_2O_3 nanoparticles [28]. Interfacial polymerization is another useful and effective method to create a thin layer on membrane surface and has been used to deposit different nanoparticles such as TiO_2 [26,27], Al_2O_3 [32] and zeolite [33,34] on polymeric membrane surfaces.

In recent years, Fe_3O_4 nanoparticles have drawn great attention to the field of nanocomposite membranes due to possessing both magnetic and hydrophilic properties, [20,35–38]. Huang et al. 2006 compared the performance of magnetized and non-magnetized membranes in ultrafiltration of a pig blood solution. Their research showed that the magnetized membrane had a higher blood protein recovery, flux, and relative flux compared to the corresponding non-magnetized membrane.

In the present study, Fe_3O_4 nanoparticles were used as a nanostructure modifier to enhance the membrane performance. The deposition of Fe_3O_4 nanoparticles on polymeric membrane surfaces has not been studied so far and nanocomposite structures containing Fe_3O_4 nanoparticles have been synthesized solely by the blending method [20,35–38]. Blended nanocomposite membranes were formed through impregnating nanoparticles with the polymeric solution. In addition, nanoparticles were stabilized on the membrane surface by photopolymerization and interfacial polymerization methods. The performance of the synthesized thin film nanocomposite membranes was compared with nanocomposite membranes synthesized via blending method. The effect of the presence of nanoparticles was investigated on surface and structural properties, and thereafter, on the filtration performance of each of these three classes of nanocomposite membranes.

2. Materials and methods

2.1. Materials

The materials used in this research, including those used in the synthesis of membrane and nanoparticles, modification of membrane surface and membrane analysis are summarized in the following table (Table 1).

2.2. Preparation of the nanocomposite membrane

In this study, synthesized nanocomposite membranes were compared in terms of surface properties, structure, and filtration performance. The synthesis of nanocomposite membranes was performed via three different methods: 1) blending nanoparticles with polymeric matrix (BNM), 2) deposition of nanoparticles on a pre-fabricated polymeric membrane through photopolymerization method (PPNM) and 3) the interfacial polymerization method (IPNM). For all nanocomposite fabrication methods, Fe_3O_4 nanoparticles were synthesized via same methods (co-precipitation) and impregnated to membrane structure via: blending with casting solution (for BNM), dispersion in acrylic acid monomer solution (for PPNM) and dispersion in trimesoyl chloride solution (for IPNM). The details of the synthesis method are described in following sections.

2.2.1. Preparation of the nanocomposite membrane via blending method

Iron oxide nanoparticles were synthesized through the co-precipitation method and utilizing bi- and trivalent iron salts $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ as precursors and ammonium hydroxide as a reducer under intermittent agitation in the presence of nitrogen gas. Having settled in the reactor, nanoparticles were separated by a

Table 1
The specifications of utilized materials in this research.

Chemical	Properties	Supplier	Purification
Polysulfone	MW: 7500 Da	Across Organics	
N-methylpyrrolidone		Merck	
Polyethylene glycol	MW: 2000, 3000, 4000, 6000, 10,000, 20,000 Da	Merck	
$FeCl_2 \cdot 4H_2O$		Merck	
$FeCl_3 \cdot 6H_2O$		Merck	
NH_3		Merck	
Acrylic acid		Merck	
Deionized water			One distillation
Piperazine		Merck	
HCl		Merck	
Trimesoyl chloride		Merck	
n-Hexane		Merck	
$BaCl_2$		Merck	
KI		Merck	
I_2		Merck	
Disperse dye (yellow 4GNL)		Rang Alvan Sabet	