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Effects of polyaniline nanoparticles in polyethersulfone ultrafiltration membranes: Fouling behaviours by different types of foulant

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ABSTRACT

Polyethersulfone (PES) was modified by blending it with polyaniline (PANI) nanoparticles to improve the membrane performance. Three types of membranes: PES (controlled sample), PES-PANI self-synthesised, and PES-PANI (commercial), were evaluated by direct interaction with BSA, humic acid, silica nanoparticles, *Escherichia coli* and *Bacillus* bacteria. The surface hydrophilicity of the modified PES membranes was enhanced by the addition of PANI nanoparticles and showed improved fouling resistance and a high flux recovery ratio as well as improvement in BSA and humic acid rejection even with higher pore sizes. The modified membrane also showed less attack from the bacteria, demonstrating improved biofouling activity.

1. Introduction

Membrane separation technology has emerged as a competitive technology for separations and purifications in many areas. Membrane technology has many advantages due to the flexibility and performance reliability of the membrane systems and the increasing demand of a technology that is cost competitiveness and environmental friendly. Ultrafiltration is an important membrane separation processes and has become a leading separation tool for various industrial applications due to its unique separation capability and low energy consumption. The ultrafiltration application areas include food and chemical processing, waste water treatment, pharmaceutical, and biotechnology [1]. Polyethersulfone (PES) is a frequently chosen polymer for the preparation of ultrafiltration membranes and displays excellent membrane-forming properties, such as good thermal resistance, chemical inertness, and strong mechanical properties [2]. Nevertheless, PES typically has a hydrophobic surface that leads to severe membrane fouling, causing the deterioration of membrane performance and decreased membrane life [3].

Due to these problems, several studies have been conducted in order to enhance PES membrane structure and performance. These studies primarily focused on hydrophilic modification of the membrane surfaces, since this method can lead to membranes with low fouling behaviour and higher flux. Some of the modifications reported were UV-initiated graft polymerisation [4], plasma graft [5], and blending with hydrophilic polymeric materials [6]. Blending with hydrophilic polymeric materials is an effective technique since the membranes formed after the modification possess a different structure and properties from the unmodified membrane. The polymeric additives in a casting solution act as pore-forming agents and could suppress macrovoid formation, with the hydrophilisation effect on the membrane clearly observable [7]. Some of the polymeric additives used by researchers are polysulphoxideamide [8], polyethylene glycol (PEG) [9], poly(vinyl butyral) (PVB) [10], and polyvinylpyrrolidone (PVP) [11].

In this study, polyaniline (PANI) nanoparticles were used as a hydrophilic polymeric material for blending with PES matrix membranes. PANI is one of the conducting polymer groups, and it has major applications in chemistry, physics, material science, and engineering [12]. PANI's special characteristics, such as its ease of synthesis, environmental stability [13], simple doping/dedoping chemistry, relatively low cost [14], and solubility in highly aprotic solvents like N-methyl-2-pyrrolidone (NMP) [15], have attracted considerable research into this conducting polymer. PANI already has some application in membrane technology, including use for gas separation [16], pervaporation [17], and semi-conductor [18]. In this present work, PANI nanoparticles were used to improve the hydrophilic properties and permeability of the substrate membrane. PANI's properties, such as high surface energy and high hydrophilicity, were used to obtain superhydrophilic membrane

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surfaces [19]. During membrane formation, PANI nanoparticles were blended with the PES matrix polymer in order to form a membrane with new properties. In addition, this new polymer matrix was shown to be protected against degradation because of the ability of PANI to act as a radical scavenger [20].

Our previous research indicated that PANI can exist stably in the PES polymer matrix and enhance the membrane performance without diminishing the advantageous properties of PES [21]. The optimal parameters of the blending membrane have also been determined by the response surface method (RSM) approach [22]. In this study, three types of membranes were prepared by phase inversion induced by immersion precipitation using the composition obtained from the RSM method reported previously [22]. The membranes were unmodified PES membranes (controlled) and PES membranes modified with self-synthesised PANI and commercially available PANI nanoparticles. The controlled membrane was prepared using the PES membrane material without any modification, while PES-PANI (produced) and PES-PANI (commercial) membranes were prepared by blending the PES solution with PANI solution before proceeding to the casting process. Then, these membranes were tested with four different types of foulants in order to study the membrane fouling behaviour. The purpose of this work was to investigate the fouling reduction effect of blended membranes during the filtration process. This study was mainly focused on the reduction of the fouling effect of PES/PANI-modified membranes compared to the controlled membranes, and the difference between self-synthesised PANI and commercially available PANI on membrane performance.

2. Experimental

2.1. Materials

PANI nanoparticles (commercial; PANI; Aldrich), Aniline (ANI; Aldrich), 37% hydrochloric acid (HCl; R&M Chemicals), ammonium peroxydisulphate ($(NH_4)_2S_2O_8$; APS; R&M Chemicals), 30% ammonium hydroxide (NH_4OH; R&M Chemicals), *Escherichia coli* and *Bacillus cereus* (*E. coli* and *Bacillus*; Microbiology laboratory stock culture), Bovine serum albumin (BSA; ICN Biomedicals), Silica (SiO_2; Aldrich, 70–100 nm), Humic Acid (R&M Chemicals), and Nutrient Agar (Merck) were used as received. Membranes were prepared from PES (Ultrason E1010 NAT; BASF Corporation; Mw = 58,000 g/mol) and the solvent used was 1-methyl-2-pyrrolidone (NMP; Merck). All aqueous solutions were prepared with ultrapure water.

2.2. Membrane fabrication

2.2.1. Synthesis of polyaniline nanoparticles

PANI was synthesised using a chemical oxidative polymerisation method, which involved the oxidation of aniline in an acidic medium. In this method, aniline was dissolved in HCl solution. Then, APS solution, which acts as oxidising agent, was added dropwise to the monomer solution. After the addition was complete, the solution was sonicated in an ultrasonic bath for 20 min in order to avoid agglomeration of the nanoparticles. Then, the reaction mixture was left for 24 h with constant mechanical stirring. After 24 h, the solution had turned completely dark green, indicating the presence of PANI in the form of emeraldine salt. The precipitate was collected, filtered, and washed with distilled water (10× 200 mL) and methanol (10× 200 mL). Next, further treatment was needed for the conversion of the emeraldine salt to emeraldine base.

PANI in emeraldine base form was chosen for this study because of its high solubility in NMP. PANI in emeraldine salt form has poor solubility in most solvents, and this problem restricts its applications, especially in membrane fabrication. The PANI salt obtained using the above procedure was dedoped using a large excess of 1 M ammonium hydroxide to obtain the emeraldine base. The solution was kept overnight under vigorous stirring to ensure complete conversion to the base form. The dark blue precipitate was separated by vacuum filtration. The filter cake collected after the filtration was washed with distilled water (10× 200 mL) and methanol (10× 200 mL) and dried in a vacuum oven at 60 °C for 24 h to obtain dark blue PANI. The final dark blue PANI was ground into powder for future use. On average, approximately 17–20 g of PANI powder was obtained. The characterisation of PANI nanoparticles produced by this method was reported in a previous paper [23]. In order to compare the size of the produced and commercial PANI nanoparticles, their particle size distributions were measured using a Master Sizer 2000 (Malvern Instruments, Malvern, United Kingdom) laser particle analyser, using ethanol as the dispersant.

2.2.2. Preparation of blended membranes

The membranes were prepared by the standard phase inversion method based on the composition suggested by the RSM software. Table 1 shows the casting specifications for each membrane prepared. The membrane produced included PES (controlled membrane), PES-PANI (produced), and PES-PANI (commercial), in which the polymer and nanoparticle weight percentages were based on the total casting solution.

The controlled membrane was prepared by dissolving PES in NMP without PANI nanoparticles. The solution was heated using a water bath and stirred at 80 °C for 5 h to ensure complete dissolution of the polymers. After obtaining a homogeneous solution, the casting solutions were left overnight to allow complete release of bubbles. The blended membranes were prepared by adding PANI solution that was prepared separately from the PES solution. The PANI solution was prepared by dissolving PANI nanoparticles in NMP and stirring for 12 h. The solution was then filtered using a 0.45 μm syringe filter and sonicated in an ultrasonic bath in order to reduce agglomeration. To complete the preparation of PES-PANI blended membranes, the PANI solution was mixed with the PES solution and was mechanically stirred for 8 h and then left overnight to deaerate.

The prepared solutions then were cast on a sterilised glass plate with a Filmographe Doctor Blade 360099003 casting knife with a thickness of 150 μm. The membrane was exposed to the atmosphere based on the evaporation times before immersing the glass plate in a coagulation bath filled with ultrapure water. Once immersed in the coagulation bath, the membranes that formed were peeled off and subsequently immersed in ultrapure water for 24 h to remove residual solvent and pore-forming agent. A detailed characterisation of membranes manufactured using this method has been reported previously [22].

2.3. Membrane characterisation

2.3.1. Fouling studies

The fouling study was conducted by measuring the permeation and rejection properties of the membranes using pure water, BSA (1 g/L), silica (0.05 g/L), and humic acid (0.05 g/L) solutions. The apparatus used consisted of 200 mL dead-end stirred

Table 1
Membrane casting specifications during the membrane fabrication process.

Membranes	Casting specifications		
	PES (wt%)	PANI (wt%)	Evaporation time (min)
Controlled	18.33	0	1.34
PES-PANI (produced)	18.33	0.75	1.34
PES-PANI (commercial)	18.33	0.75	1.34