



Preparation of high-performance graphene nanoplate incorporated polyether block amide membrane and application for seawater desalination

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ABSTRACT

In this study, a novel graphene nanoplates (GNPs) incorporated polyether block amide (PEBA) membrane was successfully prepared to be used for seawater desalination. Pervaporative desalination performances were performed in a temperature range of 35–65 °C. Effects of GNPs content in PEBA, membrane thickness, and temperature were evaluated in terms of the flux and total salt rejection. The long-term stabilities of the membranes were experimented. Incorporating graphene nanoplate into PEBA matrix enhanced flux and ion rejections simultaneously. Experimental stability of the membrane was improved by GNPs incorporation. Graphene incorporated membranes showed excellent seawater desalination performance with the salt rejection of > 99.89% and flux of > 2.58 kg/m²·h. Based on the flux and rejection results, optimum GNPs contents in PEBA matrix were observed as 2 wt% GNPs and 3 wt% GNPs. Increasing temperatures improved the water flux and did not significantly affect the salt rejection. The highest salt rejection was obtained as 99.94% with a flux of 2.58 kg/m²·h at 35 °C when the 3 wt% GNPs incorporated membrane was used. The nanohybrid membrane preserved 99.8% of its performance during 60 h, while the rejection performance of the pristine membrane decreased to 96.8%.

1. Introduction

Demand for freshwater shows a rapid increase due to the non-stable population, industrialization and urbanization growth. When the impact of climate change and global warming on depleting of the freshwater source are taken into account, it will not be surprising that the water scarcity will cause global problems in a very close future. Water production from the natural water source is one of the best solutions to meet the future's water need. Desalination is a process that produces freshwater from the natural water reservoir by removing hydrated ions, salts, heavy metals, and the other constituents [1–3]. Conventional desalination technologies are classified into two main groups as thermal and membrane-based systems. Owing to the lower energy consumption and fewer equipment requirements, membrane-based technologies such as reverse osmosis (RO) seems to overcome both economic and environmental problems of desalination technologies [4–7]. Besides the well-known and commercialized membrane desalination technologies, relatively new and emerging processes such as membrane distillation (MD) [8,9] and pervaporation (PV) have attracted researcher's interest for deep purification of saline water. Recently, pervaporative desalination has been considered to be a promising and emerging technology depending on its energy-saving process property [10–13].

Pervaporation is a chemical potential driven process. The separation

in PV is directly related to the pressure difference across the membrane. The major difference between PV and RO is the vapor phase presents in the permeate stream of pervaporation. Since a non-porous selective membrane is used in pervaporation, the membrane is able to reject a wide variety of contaminants including heavy metals and hydrated ions having small kinetic diameters. By enabling the rejection of almost all impurities in seawater, > 99.5% salt rejections have been achieved using PV [14–20]. Recent studies have shown that PV is effective to remove many of chemicals including chloride, bromide, and boron where RO cannot purify in a single stage [16]. The main drawback of using pervaporation in commercial scale is insufficient flux obtained during the separation. Since the membrane is the main constituent of pervaporation system, scientific studies have been performed to develop water-selective membranes having excellent separation capability. Organic polymeric membranes are suitable for desalination applications which pose good film forming ability and ease of modification; however, they still suffer from structural problems that lead to a decrease in desalination performance. Although many of inorganic membranes (zeolite, graphene or clay) have been reported in the literature, the higher production cost of inorganic membrane limits the commercial application. Over the past decade, inorganic particle incorporated organic membranes, in other words, mixed matrix, composite or hybrid membranes are gaining attendance based on their

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higher permeability, and long-term thermal-mechanical stability. The major factors that directly affect the separation performance of the membranes are the problems related to the particle dispersing within the membrane, structural defect in the membrane, poor polymer-inorganic interactions, and the surface properties of the particles.

In the most of the reported pervaporative desalination studies, hydrophilic non-porous membranes have been used to enhance water flux and rejection factor simultaneously. Xie and co-workers [18,19], reported two studies by preparing a polyvinyl alcohol/maleic acid/silica (PVA/MA/Si) membranes for the pervaporative desalination of the NaCl-water solution. In the first study, a flux of 11.7 kg/m²·h and rejection of > 99.9% were obtained. Differently from the first study, the influence of membrane thickness was investigated. In the second study, water flux and the rejection were achieved as 6.93 kg/m²·h and 99.5% respectively. An et al. [21] synthesized a clinoptilolite-phosphate membrane and performed pervaporation experiments using different concentrations of NaCl-water solutions. As a result, they obtained a flux of 15 kg/m²·h accompanied with final rejection above 95% at 95 °C. Cho et al. reported a desalination experiment using pervaporation technique by preparing NaA zeolite membrane [15]. They pointed out that they found a rejection of 99.9% with a flux of 1.9 kg/m²·h. Zhu and co-workers [22,23] fabricated MFI zeolite-based membranes and they achieved salt rejection as 80% and 93% in different two studies respectively. Most recently, nano-sized inorganic materials or fillers have also been studied for desalination purposes. Besides them, graphene-based materials are more attractive. Graphene is a two-dimensional carbon-based material. Due to its unique properties, it is used as functional filler in a wide variety of industries from electric industry to automotive. Graphene-based hybrid materials such as nanohybrid polymers provide good mechanical strength, electrical conductivity, and thermal properties. Owing to its precise sieving properties and small thickness, graphene layer restricts the diffusion of the small molecules through its structure [24–26]. Depending on its selective separation capability, it is considered a good candidate to be used for filler within a selective membrane. Graphene and graphene oxide membranes have been used in the many of membrane processes including gas separation, nanofiltration, and reverse osmosis [27–30]. In the earlier literature studies, graphene nanosheet derivative pervaporation membranes were fabricated to enhance both flux and separation factor of the target component [31–33]. Recently, graphene has been used for water desalination [24,26,34–36]. It is reported that the separation performance and lifespan of graphene incorporated polymeric membranes significantly increase due to the anti-microbial properties of graphene [37]. Investigations also show that graphene-based membranes may be more effective to retain salt ions compared to the commercial reverse osmosis membranes [38].

In this study, graphene nanoplates (GNPs) incorporated polyether block amide (PEBA) nanohybrid membranes were fabricated to desalinate seawater. Differently from the literature, a hydrophobic matrix (PEBA) matrix was used and graphene was incorporated to enhance the selective separation capability of the membrane. In the literature, researchers have mostly fabricated mixed matrix membrane by incorporating hydrophilic fillers into a hydrophilic polymer. Hydrophilic polymers may exhibit unstable desalination performance due to the high swelling degree. Therefore, using a hydrophobic polymer as the matrix may improve the stability of the membrane during desalination. According to the author's knowledge, this is the first study on using of graphene nano-plate loaded PEBA membrane for desalination application. Due to the high aspect ratio and high surface area of GNPs, they exhibit good compatibility with polymers [39]. Based on its anti-fouling property, it resists the biological fouling of the membrane in seawater media. To take these advantages of graphene, different amounts of graphene particles were incorporated into PEBA matrix. Regarding GNPs incorporation, it was expected to improve flux, rejection results and long-term stability of the PEBA based membranes.

2. Materials and methods

2.1. Materials

Polyether-block-amide (Pebax 2533) which is a block copolymer contains 80 wt% poly (ethylene oxide) and 20 wt% polyamide was kindly obtained from the distributor of Arkema, Turkey. Graphene nanoplates with a surface area of 750 m²/g and acetic acid (analytical grade) were purchased from Aldrich Chemicals, Turkey. The seawater was taken from the North coast of Marmara Seawater in Turkey.

2.2. Membrane preparation

PEBA-graphene nanoplate membranes with different ratios of GNPs were fabricated using phase inversion technique. Firstly, a PEBA-acetic acid solution with the polymer concentration of 10 wt% was prepared and stirred at 60 °C for 5 h until a homogeneous polymer solution was obtained. Separately, GNPs were dispersed in acetic acid for 15 min using a sonic mixer. The polymer solution was then added to the acetic acid-GNPs solution and further stirred at room temperature for 2 h at a stirring rate of 500 rpm. Following the homogenization, the solution was cast on to a Teflon plate and allowed to evaporate all acid at the room conditions. After the evaporation, flat-sheet membranes formed with an average thickness of 120 µm ± 5.

2.3. Membrane characterization

Morphological properties and the homogeneous phase continuity of the pristine and nanohybrid membranes were analyzed by means of scanning electron microscope (JEOL JSM-6335 F). Before the analysis, membrane samples were covered with platinum. For the cross-sectional analysis, samples were fractured using liquid nitrogen.

The influence of GNPs addition on the surface's hydrophilicity of PEBA matrix was investigated by means of contact angle measurements (Attension KVS) using the Sessile Drop Method. For the measurement accuracy, each test was repeated for three times.

The effects of temperature on weight losses of the pristine and nanohybrid membranes were analyzed using thermogravimetric analysis (TGA) (Mettler Toledo) in the temperature range from 25 °C to 600 °C at a heating rate of 10 °C/min.

The influence of GNPs addition on the degradation temperatures of the polymeric matrix was examined by means of differential scanning calorimetry (DSC) (Mettler Toledo). For DSC analysis, membrane samples were cut into a constant diameter (3 mm). Then, samples were weighed and encapsulated in aluminum pans. DSC experiment was performed with the temperature rising from – 60 to 200 °C at a heating rate of 20 °C/min under nitrogen atmosphere [40].

2.4. Analysis of permeate water

After the pervaporative desalination experiment, the ion concentration of the desalinated water was determined using inductively coupled plasma mass spectrometer (Perkin Elmer Elan DRC-e ICP-MS). The chloride (Cl[–]) amount in the desalinated water was measured using Hach Dr. 5000 UV–Vis spectrophotometer. The total conductivity of the desalinated water was measured using a Mettler Toledo Seven Compact S230 model conductivity meter with an accuracy of ± 2 µS/cm. Resistances of membranes before and after desalination were recorded using VersaStat 3 Potentiostat Galvanostat.

2.5. Seawater desalination experiment

Desalination experiments were performed using laboratory-scale pervaporation unit as seen in Fig. 1.

The experimental desalination unit consists of a stainless steel membrane cell equipped with a mechanical stirrer and thermocouple.

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