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A Novel Nanofiltration Membrane Prepared with PAMAM and Graphene oxide for Desalination

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ABSTRACT

Nanofiltration is increasingly gaining attention in many separation and treatment processes such as water softening, color removal and separation of medicines. Nanofiltration membranes are often negatively charged, displaying separation characteristics in the intermediate range between reverse osmosis and ultrafiltration. In this research, a novel nanofiltration membrane prepared with poly(amidoamine) (PAMAM) dendrimer and graphene oxide (GO) on amidoximated acrylic ultrafiltration membrane was investigated. Scanning Electron Microscopy (SEM) and contact angle of the water were employed to characterize the chemical and physical changes of resulting membranes. The flux and rejection of resulting membranes increased with increasing generation numbers of PAMAM for NaCl concentration. The salts rejections order of resulting membrane is $CaCl_2 > MgSO_4 > NaCl > Na_2SO_4$, which shows that resulting membranes were all positively charged NF membrane. The PAMAM/GO NF membrane is especially suitable for separating cationic solutes from others. This kind of membrane is also particularly suitable for treating acidic feed. The studied membrane possesses maximum operating pressure lower than 4 bar and excellent stability during continuous filtration at 27±2°C.

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INTRODUCTION

Nanofiltration (NF) is increasingly gaining attention in many separation and treatment processes such as water softening, color removal, chemical oxygen demand (COD) reduction and separation of medicines [1–3]. NF membranes are often negatively charged, displaying separation characteristics in the intermediate range between reverse osmosis (RO) and ultrafiltration (UF). NF membranes generally have a thin skin layer enabling higher fluxes and lower operating pressures than RO membranes and are able to reject small organic molecules having molecular weights as low as 200–500 Da such as many medicines (streptomycin, penicillin etc.). Moreover, NF membranes are also able to reject ions, especially bivalent ions, due to the Donnan effect [4] stemming from the membrane charge [5, 6].

There are many methods for the preparation of composite membranes for NF including vapor deposition [7], plasma-initiated polymerization [8–11], photo-initiated polymerization [12], the radiation polymerization [13], the dip coating process [14], interfacial polymerization [15,16], electron beam irradiation [17], atom transfer radical polymerization [18], resin-filled chelating [19], and in situ amines cross-linking [20]. Interfacial polymerization, however, is still a key

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method to produce commercial NF membranes such as the NF series (Filmtec Corporation), the NTR series (Nitto Denko Company), the UTC series (Toray Industries) and so forth. Although they have been used in many fields successfully, it should be an important promising work for membrane manufacturing to develop a novel NF membrane with special properties using high performance materials.

Dendrimers developed as novel high performance materials over the past decade have received a great deal of attention because they have numerous terminal functional groups and a highly branched structure. The most-studied dendrimer is probably the so-called poly(amidoamine) (PAMAM) dendrimer, which has a global shape containing much higher amino group densities on the surface than conventional macromolecules. These dendrimers are typically synthesized by the repetitive Michael addition and aminolysis [21]. The high density of their terminal groups provides a large number of reactive sites [22] for potential application as nanoscale catalysts, micelle mimics, drug delivery agents, chemical sensors, high-performance polymers, and adhesives [23,24]. In recent years, some studies have appeared in the literature describing the applications of PAMAM in the membrane separation field, including PAMAM supported UF to improve separation performance of UF [25], PAMAM dendrimer-induced crosslinking modification of polyimide membranes to enhance CO_2 permeability [26], using PAMAM as liquid membrane to improve separation performance of CO_2 from gas mixtures [27–29], and grafting PAMAM and poly(acrylic acid) onto Au-coated Si wafer to prepare pH-switchable modified electrode for probing both cationic and anionic redox-active molecules [30]. Up to now, few researchers prepared NF membranes with dendrimers, Willem and co-workers presented their primary study on NF membrane formation with poly(propyl imine) (PPI) dendrimers polymerized with TMC [31]. However, Preparation of PPI dendrimer suffered from the shortcoming of material cost, higher pressure operation and low yield. On the contrast, PAMAM can be synthesized under normal pressure at room temperature, and possesses the similarity to PPI in its chemical structure and physical properties. Using PAMAM to develop a novel NF membrane with special properties is expected to be a promising method in the future.

Graphene oxide (GO) is a derivative of graphene, but they have differing properties. Sheets of GO possess numerous oxygen-containing functional groups: hydroxyl and carboxyl groups are located around the edges, whereas carbonyl and epoxide groups are in the center [32, 33]. The existence of various types of hydrophilic groups allows GO to be easily exfoliated when it is in the wet state. These active groups can be used to induce chemical reactions and provide GO with additional functional groups after the modification, thereby increasing the flexibility and diversity of GO applications. For example, GO layers can be intercalated or cross-linked with primary aliphatic amines, amino acids, diaminoalkanes, boronates, acyl chloride, and isocyanates [34−42] or they can be covalently linked with polymers through esterification [45−47]. In this case, these nanoplates can be utilized for the preparation of nanofiltration membranes.

In this research, graphene oxide (GO) nanoplates were used as selective layer and PAMAM dendrimers as an antifouling agent for the preparation of novel nanofiltration membranes. These nanoscale plates were deposited on the amidoximated acrylic membranes, PAMAM dendrimers were grown above them and their performance was measured for desalination via nanofiltration process. The task of cross-flow mode filtration experiments was used in order to ensure the maximum permeability and rejection efficiency.

MATERIALS AND METHODS

Acrylic waste fibers were supplied by Paitakht Carpet Company (Kashan, Iran). N, N-dimethylformamide (DMF, Mw=73.09 g/mol, industrial grade) was purchased from Kimia Zist Azma Company (Tehran, Iran). Graphite powder (1 µm) was bought from local company (Tehran, Iran). Deionized water was also used as non-solvent agent in the coagulation bath. Methyl acrylate and ethylene diamine as monomers of PAMAM dendrimers and methanol as solvent were supplied by Merck (Germany).

Preparation of acrylic membrane support

Casting solution for the preparation of acrylic membrane support was prepared by dissolving 18% wt. of acrylic waste fibers in DMF at the temperature of 75°C. The solution was magnetically stirred for at least one day to guarantee complete dissolution of polymer. The homogenous solution stayed for 1.5 h where its bubbles were removed. After that, the prepared homogeneous solution was cast using a film applicator to 200 µm clearance gap on a glass plate substrate. Temperature and relative humidity of casting environment were ~24°C and 23%, respectively. The cast film was immediately (without a gap time) immersed in a deionized water bath to complete the phase separation, where the exchange between solvent (DMF) and non-solvent (water) was induced. After complete coagulation, the membrane was transferred into a pure water bath. The bath was refreshed frequently for at least 24 h. This was done to ensure the complete removal of the residual solvent from the membrane.

Synthesis of Graphene oxide

GO sheets were synthesized as a procedure published previously. Briefly, a mixture of graphite, $NaNO_3$, and concentrated H_2SO_4 was continuously stirred at 0°C. Then, $KMnO_4$ was added to the mixture gradually. The mixture was stirred for 90 min at 0°C. After that, the temperature of mixture was reached to 35°C and stirred for 2 h. Distilled water was used to dilute the resulting solution. H_2O_2 solution was poured to the suspension to obtain graphite oxide. The graphite oxide was separated from the solution by centrifugation at 12000 rpm for 10 min, and washed with distilled water repeatedly until the pH reached to 7. Graphite oxide powder was dispersed by sonication to obtain a GO mixture. Thick multilayer flakes of GO were removed by centrifugation at low speeds (2000 and 4000 rpm). To obtain uniform large-area GOs, a low-speed centrifugation at 3000 rpm was first used to remove thick multilayer flakes until all the visible particles were removed (3-5 min).

Amidoximation of acrylic membrane support

The acrylic membrane was washed thoroughly with pure water before reacting with hydroxylamine. Aqueous solutions were prepared from hydroxylamine hydrochloric with concentration of 1 M and this membrane was immersed in this solution for given times (3.5 h). The membrane was reacted with hydroxylamine solution at temperature of 70°C and pH=7. For adjusting pH of reaction solutions, sodium hydroxide was used in these experiments.

Synthesis of PAMAM

Poly(amidoamine) dendrimers were synthesized on the amidoximated acrylic membrane. by means of the procedure described by Tomalia et al. [22] where ethylene diamine was used as a nitrogen core, and a repeated stepwise reaction was conducted including Michael addition and aminolysis. Repetition of these sequences was used to make successively higher generations. It should be noted that a layer of graphene oxide was coated on this membrane before synthesizing dendrimers.

Membrane performance

Permeability and rejection experiments were carried out by a nanofiltration setup (Fig. 1). It offered an effective filtration area of 32 cm^2, a feed velocity on the membrane surface of 4.5 L/min, a pressure of 4 bar and an operating temperature of 25±2°C. For the measurement of rejection, the concentration of calcium chloride, sodium chloride, magnesium sulfate and sodium sulfate in feed was kept constant at 1000 ppm. The concentration of inorganic salts was obtained through the measurement of aqueous solution conductibility by the use of a conductometer (WTW inoLab Cond 720, Germany). Morphology of the dried membranes was examined using scanning electron microscopy (SEM, Hitachi S-4160, Japan).

RESULTS AND DISCUSSION

In ester-terminated dendrimer polymer grafting samples G0.5 and G1.5, the absorption at about 1718-1723 cm^{-1} suggested the presence of ester bonds ($–CO_2CH_3$). A broad band in the region of 3454 $cm^{–1}$, which is attributed to the stretching vibrations of the OH groups of the hydroxyls groups of the structure, in addition to physiosorbed water. The characteristic absorption peaks of ester bonds disappeared in the corresponding amino-terminated samples G1.0 and G3.0 and amide characteristic peak at about 1645-1654 $cm^{–1}$ appeared indicating that the ester bonds were almost inverted into amino-terminated products. Based on the above analysis, it was concluded that ester and amino-terminated hyperbranched PAMAM were grafted successfully on the GO surface via the step by step divergent approach.

The active skin layer and cross-section morphology of the novel NF membrane are shown in SEM patterns (Fig. 2). The active skin

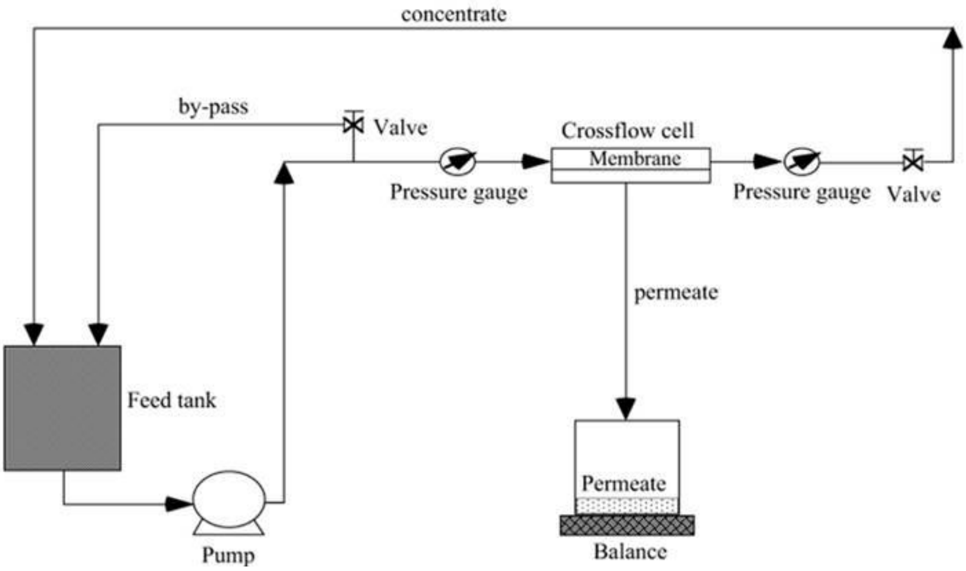

Fig.1. Used NF setup for measurement of novel nanofiltration membrane performance

layer in NF acrylic membrane became a uniform, smooth and dense layer, no pore structure could be found on the active layer, so there was no pore filling found in the NF membranes by synthesizing PAMAM dendrimers. In fact, the pore sizes on the active skin layer of the NF membranes were usually in the magnitude of nanometers. It is often difficult to observe the pore structure of NF membrane surfaces using SEM. It must be noted that a layer of graphene oxide was coated on this functionalized membrane. The graphene oxide nanoplated act like a net on the pores. On the other hand, the cross-section photos showed that the amidoximated acrylic UF membrane was a good microporous membrane because it had regular finger-like pores and sponge-like pores in the walls of pores enabling good flux. Also, a fused nodular structure was well developed in the rim of macrovoids. As suggested by Smolders et al., the spherical structure is presumably related to the clustering of entanglement of polymer molecules during spinodal decomposition.

The contact angles of PAMAM/GO NF membranes with difference generations are listed in Table 1. The contact angles of the NF membranes were lower than those of the amidoximated acrylic UF membrane. This indicates an increase in membrane surface hydrophilicity due to the introduction of NH_2 groups to the membrane active layer, and hydrophilicity increased with increasing PAMAM concentration and/or the number of PAMAM generations.

The rejection for different salts and their solution flux was compared for NF membranes with different generation of dendrimers as shown in Table 2. The salts rejections order of these membranes is $CaCl_2$ > $MgSO_4$ > NaCl > Na_2SO_4 which is similar to the sequence developed by Runhong Du [48], whereas this order is opposite to the one developed by Yu [49, 50], i.e. Na_2SO_4 > NaCl > $MgSO_4$ > $CaCl_2$, where the negatively charged NF membranes was used. This sequence shows that PAMAM/GO NF membranes used were all positively charged nanofiltration membrane. This order can be explained by Donnan exclusion [51]. A positively charged nanofiltration membranes have higher rejections for high-valence cations and low-valence anions than low-valence cations and high-

Table 1. The contact angles of NF membrane for water.

Membranes	Contact Angle (°)	Flux (LHM)
Amidoximated acrylic membrane	40	140.6
Generation 0.5	37	49.7
Generation 1	33	55.8
Generation 1.5	30	61.2
Generation 2	24	68.2

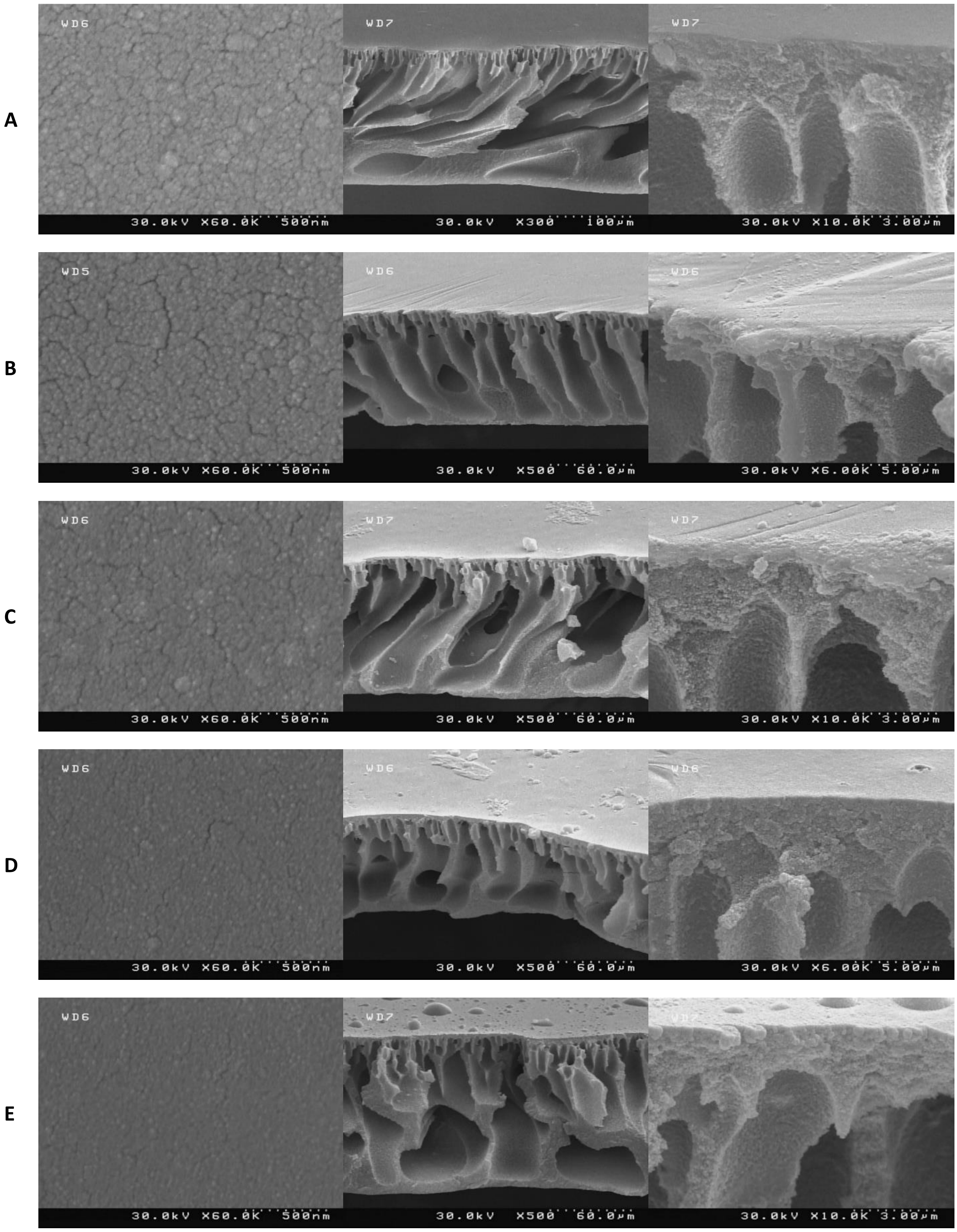

Fig.2. SEM images of A: amidoximated acrylic membrane support, synthesis of PAMAM dendrimers on this support with generation of B: 0.5, C: 1, D: 1.5 and E: 2.

valence anions. These results demonstrate that the rejection to salts for a NF membrane is not only related with the pore size of the membrane, but also largely depends on the electrostatic action between the membrane and ions in solution. Therefore, the separation property to salts of

Table 2. Performances of PAMAM/GO NF membranes for different inorganic salts solution.

Inorganic Salts	Zeroth Generation (R, %)	First Generation (R, %)	Second Generation (R, %)
$CaCl_2$	77.2	84.2	95.7
$MgSO_4$	67.6	72.3	85.1
NaCl	38.2	48.1	72.5
Na_2SO_4	36.2	47.6	58.2

positively charged NF membranes will be very different from negatively charged NF membranes. The rejection of NaCl for second generation of PAMAM dendrimers is 72.5% and the rejection of $MgSO_4$ is 85.1%, showing that this membrane is an excellent NF membrane.

CONCLUSION

In this investigation, a novel nanofiltration membrane has been successfully prepared using PAMAM and graphene oxide on functionalized acrylic UF membrane. Different properties of NF membrane can be obtained by changing the generation numbers of PAMAM. By testing the contact angles of the membrane for water, the hydrophilicity of the PAMAM/GO NF membrane is higher than the amidoximated acrylic UF membrane as an amino group was introduced to the membrane surface. Flux and rejection of the NF membrane increased with increasing generation numbers of PAMAM. The rejection for different inorganic salts and their solution flux was compared for all novel membranes. The salts rejections order of these membranes is $CaCl_2$ > $MgSO_4$ >NaCl>Na_2SO_4. This sequence shows that resultant membranes were all positively charged NF membrane. This resultant membrane is suitable for separating cationic solutes from others. It can be stated that PAMAM/GO NF membrane is also particularly suitable for treating acidic feeds.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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