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RESEARCH NOTE

Nanofiltration Membranes Synthesized from Polyethyleneimine for Removal of $MgSO_4$ from Aqueous Solution

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ABSTRACT

A novel work was performed for fabrication and modification of composite nanofiltration (NF) membrane by polymerization reaction between polyethyleneimine (PEI) and triphthaloyldechloride (TPC). The main purpose of this work was water treatment. Polysulfone was the main polymer applied as substrate. The result of reaction between PEI and TPC was the formation of polyamide layer on the membrane surface. SiO_2 nanoparticles were used as modification agent. The fabricated membranes were characterized by Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM), contact angle measurement and FTIR analysis. Removal of$MgSO_4$ as one of the dissolved salts in water was investigated and these fabricated membranes were utilized to remove $MgSO_4$ from water. Properties of substrate in addition to properties of NF membrane such as steric-hindrance and Donnan exclusion led to a rejection of 89% for $MgSO_4$.

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1. INTRODUCTION

The need for safe and high quality drinking water supply is obvious. As the knowledge of drinking water quality hazards rises and the availability of high quality water resourcesreduces, the demand for more efficient water treatment processes intensifies. The quality of drinking water can be improved either by enhancing the present processes by a refining treatment phase, or by adopting totally new treatment methods. $MgSO_4$ is one of the extra solutes dissolved in water and its removal from water is an important concern for governments. One promising option for divalent ions removal from conventionally treated surface water is the introduction of nanofiltration (NF) as a refining treatment phase.

Nanofiltration is a new membrane separation method advanced in the 1980s similar to reverse osmosis (RO). It is a pressure-driven membrane process typically appropriate for splitting dissolved fractions having a molecular weight in therange of 200 to 1000. The process is determined as a new and capable water treatment technique and a potential alternative to traditional water treatment methods [1, 2]. The main benefits of this process are low operating pressures, high fluxes, high rejections of multivalent salts, low investment and operation costs leading to gaining attention in many other separations, and treatment processes namely waste water treatment, color removal, pharmaceutical and biochemical industries [3].

Most NF membranes fabricated so far are composite naturally,with a selective layer on top of the porous support. Interfacialpolymerization is the main technique in manufacturingthe NF membrane. The interfacial polymerizedNF membranes are usually produced by condensingwater-soluble amines and water-insoluble acyl chlorides in a water–organic boundary [4-6]. Thus produced nanofiltrationmembranes usually have thin and highly cross-linked layers [7]. Separation process in NF membranes occurs based on size differences. It means molecules larger than pore size of membrane are not able to permeate through the membrane wall. Although this mechanism is applicable for separation of solutes, NF membranes present another separation mechanism due to their surface charge, called Donnan exclusion. This feature allows membrane to reject

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solutes smaller than pore size of membrane [8, 9]. This study attempts to explore the possibility to obtain a membrane possessing high rejection to $MgSO_4$ and high water permeation. Polyethyleneimine (PEI) as an amine monomer and triphthaloyldechloride (TPC) as an acyl chloride monomer were used for interfacial polymerization. SiO_2 nanoparticles were added to membrane for improving membrane performance. Performance of the fabricated membranes was examined by 2000 ppm $MgSO_4$/water solution. Eventually, morphology and roughness of membrane, its hydrophilicity and presence of functional groups on the membrane surface were investigated by Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM), contact angle measurement and FTIR analysis.

2. EXPERIMENTAL

2. 1. Materials Polysulfone waspurchased from Solvay Advanced Polymers and used as a membrane support polymer. N-dimethylformamide (DMF) as a solvent of polymer, Polyvinylpyrrolidone (PVP, MW 25,000 g/mol), N-hexane and TPC as an acyl chloride monomer were supplied by Merck. PEI as an amine monomer with molecular weight of 60000 (Acros organics, USA) and TPC as an acyl chloride monomer were used for polymerization reaction. SiO_2 nanoparticles were purchased from US Research Nanomaterial, Inc. $MgSO_4*7H_2O$ (MW 246.48 g/mol) was supplied by Merck.

2. 2. Characterization The top surface of the fabricated NF membranes was observed by SEM (KYKY-EM3200). Surface roughness of the fabricated membrane, modified and unmodified NF membranes were observed using AFM (Nanosurf AG, Switzerland) apparatus. For indicating the presence of polyamide functional group and SiO_2 nanoparticles on membrane surface, FTIR (BFRLWQF - 510A) analysis was carried out. Also, contact angle measurement were performed to confirm improvement in hydrophilic properties of modified membranes using a Dataphysics-OCA 15 Plus contact angle measuring instrument.

2. 3. Fabrication of Modified Composite Membranes The polysulfone/DMF solution was made by dissolving 18 Wt.% polysulfone and 1.5 Wt.% PVP in DMF at room temperature. PVP was used as a pore forming agent [10]. Then, the solution was cast on polyester non-woven and put into the water bath. After the fabricated membranes dried, two solutions containing PEI/SiO_2/water and TPC/N-hexane were prepared. For fabrication of composite membrane, polysulfone substrate was glued onto the glass support. Then, it was immersed in the amine solution for 15 min. In the next step, it was placed vertically in the air for removing excess amine molecules. Next, it was immersed into the acyl chloride solution for 1 min for proceeding interfacial polymerization process. As a final stage, membrane was heated for further interfacial polymerization reaction.

2. 4. Filtration Experiments A solution was prepared by dissolving $MgSO_4$ in deionized water with concentration of 2000 ppm and used as a feed stream. Unmodified and modified membranes were cut off in an appropriate size and put into the dead-end nanofiltration cell for performing experiments. All the experiments were carried out in the presence of nitrogen gas and under operational pressure of 5 bar. For reaching to steady flux, the experiments were performed for certain time of 25 min. Stirring speed kept constant at 300 rpm to reduce influences of concentration polarization (CP). Flux of $MgSO_4$/water solution was calculated by the following equation;

$$J=Q/A.t \quad (1)$$

where, J is the flux (l/m^2h), Q is the volumetric quantity of permeate (l), t is the running time (h) and A is the membrane effective area (m^2). The permeate was gathered and concentration of $MgSO_4$ was measured by conductivity meter instrument. The $MgSO_4$ rejection ratio was calculated by

$$R(\%)=1-(C_P/C_F) \quad (2)$$

where, C_F and C_P are the $MgSO_4$ concentrations in the feed and permeate solutions, respectively.

3. RESULTS AND DISCUSSION

3. 1. Morphological Studies Hydrophilicity of membrane surface was studied by data obtained from contact angle measurement. In this work, 12 samples of membrane with different concentration of amine and acyl chloride monomer were fabricated and their compositions are shown in Table 1. The water contact angle declining trend is shown in Figure 1. As can be seen in Figure 1, by increasing content of SiO_2 nanoparticles from 0 Wt.% to 0.1 Wt.%, the water contact angle decreased to a good value of 46° that is desired for a higher water flux.FTIR analysis was performed for investigating the functional groups existing on the membrane surface. Figure 2 shows FTIR analysis of modified and unmodified NF membranes. Figure 2a shows analysis of unmodified membrane which has characteristic amide group peak at wave number of around 1663 cm^{-1} due to the C═O stretching [11]. This peak can alsobe seen in Figure 2b. Figure 2b shows analysis of SiO_2 modified membrane which has peaks around 1080 cm^{-1} due to the asymmetric stretching of Si─O─Si groups [12]. FTIR analysis

confirms formation of polyamide layer on the polysulfone substrate and dispersion of SiO_2 nanoparticles into the polyamide layer.

TABLE 1. Conditions for fabrication of modified NF membranes

Sample No.	Reactant's concentrations	Sample No.	Reactant's concentrations
1	0.1 Wt. % TPC 0.01 Wt. % SiO_2 nanoparticles	7	0.3 Wt. % TPC 0.05 Wt. % SiO_2 nanoparticles
2	0.1 Wt. % TPC 0.03 Wt. % SiO_2 nanoparticles	8	0.3 Wt. % TPC 0.1 Wt. % SiO_2 nanoparticles
3	0.1 Wt. % TPC 0.05 Wt. % SiO_2 nanoparticles	9	0.5 Wt. % TPC 0.01 Wt. % SiO_2 nanoparticles
4	0.1 Wt. % TPC 0. 1 Wt. % SiO_2 nanoparticles	10	0.5 Wt. % TPC 0.03 Wt. % SiO_2 nanoparticles
5	0.3 Wt. % TPC 0.01 Wt. % SiO_2 nanoparticles	11	0.5 Wt. % TPC 0.05 Wt. % SiO_2 nanoparticles
6	0.3 Wt. % TPC 0.03 Wt. % SiO_2 nanoparticles	12	0.5 Wt. % TPC 0. 1 Wt. % SiO_2 nanoparticles

PEI concentration: 2 Wt. %, time of interfacial polymerization: 1min, heat treatment temperature: 110°C, time of heat treatment operation: 15min

TABLE 2. Effect of SiO_2 nanoparticles on roughness of membrane surface.

Sample No.	Roughness (nm)		
	S_a	S_q	S_z
Unmodified NF	4.61	5.91	87.2
1	5.63	7.2	136.1
2	10.22	13.45	200.2
3	17.13	22.51	283.23
4	22.76	30.8	353.13

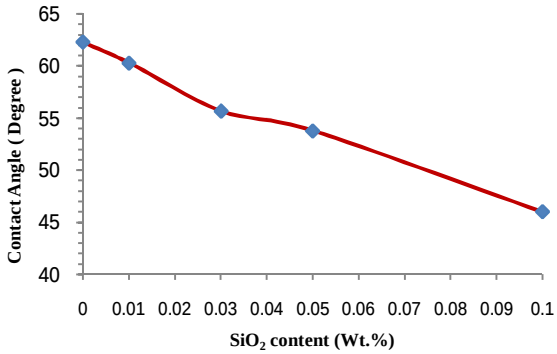

Figure 1. The water contact angle of the fabricated membranes at 0.1 Wt.% TPC and 2 Wt.% PEI.

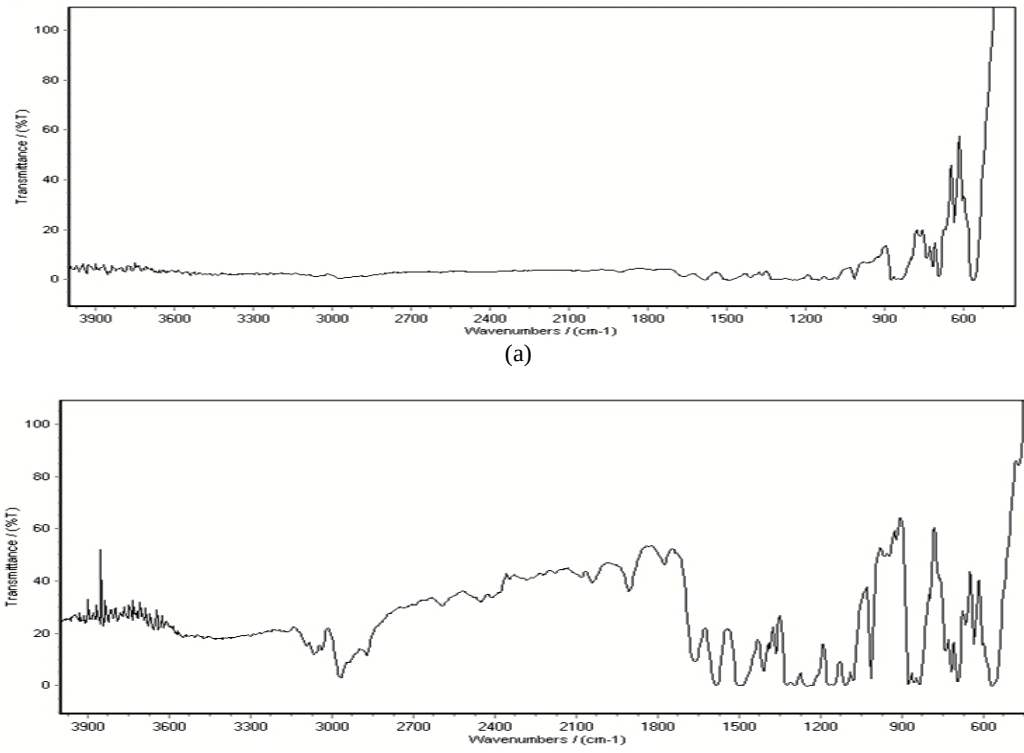

Figure 2. FTIR analysis of (a) unmodified NF membrane and (b) SiO_2 modified membrane

For investigating whether the fabricated membrane surface becomes rougher or smoother, AFM analysis was done and roughness parameters are shown in Table 2. As can be seen in Table 2, S_a, S_q and S_z represent the mean roughness, the root mean square of the Z data and the mean difference between the highest peaks and lowest valleys, respectively.As displayed in Table 2, by adding SiO_2 nanoparticles to the unmodified NF membrane, the membrane surface became rougher. As content of SiO_2 nanoparticles increased, roughness of the membrane surface increased too. The two-dimensional top surface AFM images of unmodified NF and four modified membranes are shown in Figure 3.

Figure 4 shows the top surface SEM images of an unmodified NF membrane and SiO_2 modified membrane. As can be seen in Figure 4, SiO_2 nanoparticles were well dispersed onto the membrane surface. From Figure 4, it is clear that the surface of the SiO_2 modified NF membrane is rougher than the surface of the unmodified NF membrane. Also it can be found that the SiO_2 nanoparticles tend to form aggregates on membrane surface.

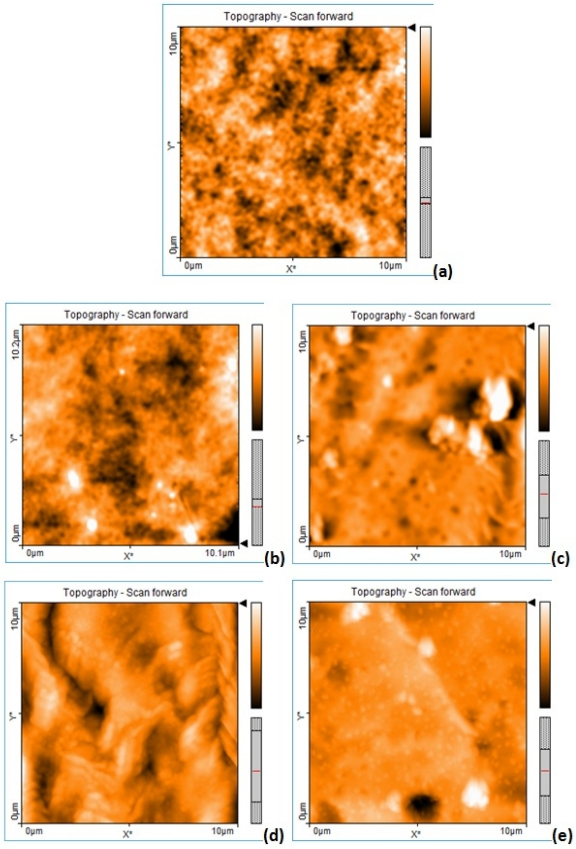

Figure 3. The two-dimensional surface AFM images of (a) unmodified NF, (b) 0.01 Wt.% SiO_2, (c) 0.03 Wt.% SiO_2, (d)0.05 Wt.% SiO_2 and (e) 0.1 Wt.% SiO_2 at 0.1 Wt.% TPC and 2 Wt.% PEI.

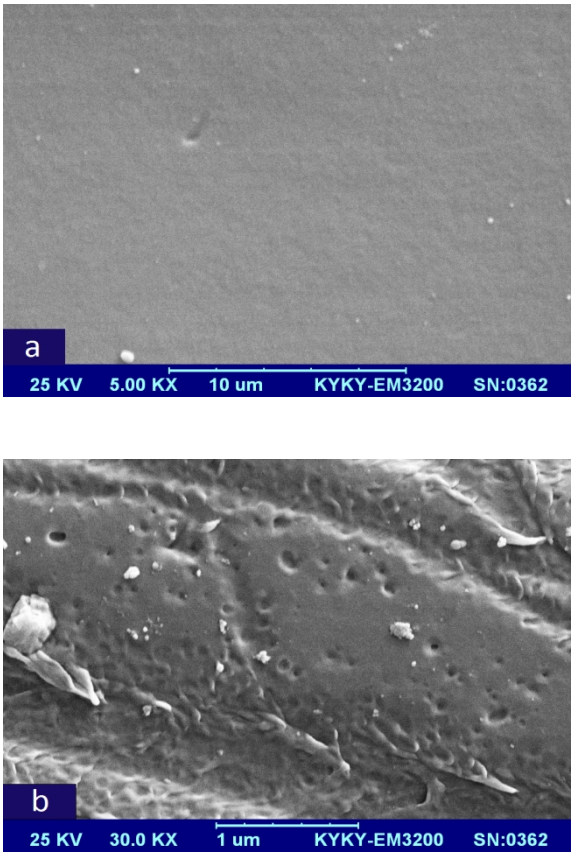

Figure 4. The surface SEM images of (a) unmodified NF membrane and (b) SiO_2 modified membrane.

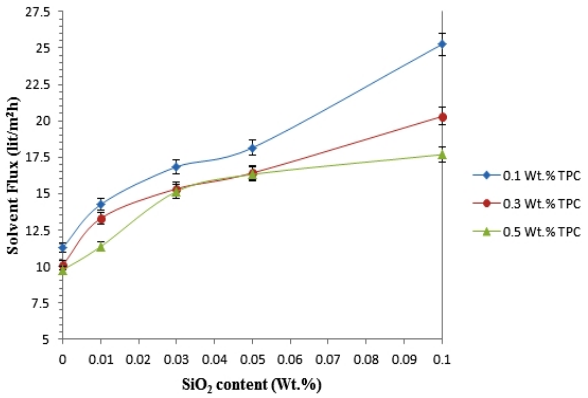

Figure 5. Influences of SiO_2 contents on solvent flux at 2 Wt.% PEI.

3. 2. Performance of Fabricated Membranes

To explore the best performance of the fabricated membranes both in case of rejection of solute and water flux, 12 modified samples were fabricated. Reactants concentrations are shown in Table 1. The data obtained from the experiments are given in Figures 5 and 6.

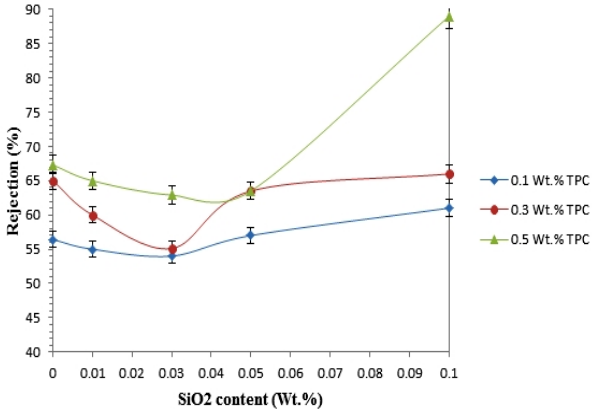

Figure 6. Influences of SiO_2 contents on rejection of $MgSO_4$ at 2 Wt.% PEI.

As can be seen in Figure 5, solvent flux increased by adding SiO_2 nanoparticles to the membrane and by further increasing of SiO_2 content, it also increased. The reason for this behavior might be better hydrophilic properties of the membrane surface due to the presence of SiO_2 nanoparticles. This trend could be observed for each concentration of TPC. It must be noted that the nanoparticles may affect the interfacial polymerization process, and convert the polymerization conditions by releasing additional heat throughout the process which could enhance the solvent flux [13]. Rate of rejection for unmodified and SiO_2 modified membranes to $MgSO_4$ molecules is shown in Figure 6. As expected, membranes fabricated by 0.5 Wt.% TPC possessed higher rejection to the solute due to their thicker selective layer and possessed lower solvent flux compared with others. By adding nanoparticles to the unmodified membrane, a declining trend was observed in case of rejection at first. It is believed that the hydrophilicity of the membrane surface has more effects on the membrane performance in lower contents of SiO_2 nanoparticles whereas Roughness of the membrane surface is more effective in higher contents of SiO_2 nanoparticles which caused decreasing and increasing of rejection to $MgSO_4$. A membrane with 0.1 Wt.% SiO_2, 0.5 Wt.% TPC and 2 Wt.% PEI showed better performance than others and acceptable flux of 17.7 l/m^2h and superior rejection of 89% was obtained.

4. CONCLUSION

This study attempted to fabricate a composite NF membrane by polymerization reaction between PEI and TPC and modification of the membrane by SiO_2 nanoparticles in order to remove $MgSO_4$ from water. AFM images showed that the membrane surface became rougher compared with unmodified membrane due to the presence of SiO_2 nanoparticles. SEM images indicated that the SiO_2 nanoparticles were well dispersed on the membrane surface. FTIR analysis and contact angle measurement confirmed the presence of SiO_2 nanoparticles on the membrane surface and better hydrophilic properties of the membrane. By performing the experiments, the modified membrane showed 89% rejection to the $MgSO_4$ molecules which is an appropriate rejection to divalent salts.

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چکیده

یک کار جدید برای ساخت و اصلاح غشای کامپوزیتی نانوفیلتراسیون به کمک پلی اتیلن ایمین (PEI) و تری فتالویل دی کلرید (TPC) به روش پلیمریزاسیون بین سطحی انجام شد. هدف اصلی این کار تصفیه آب بوده است. پلی سولفون (PS) به عنوان پلیمر به کار رفته در زیرلایه در نظر گرفته شد. لایه حاصل از پلیمریزاسیون بین سطحی از جنس پلی آمید می باشد. نانوذره سیلیکا به عنوان عامل اصلاح کننده غشا مورد استفاده قرار گرفت. غشاهای ساخته شده توسط آزمایشات میکروسکوپ الکترونی روبشی، میکروسکوپ الکترونی اتمی، زاویه تماس آب و آنالیز طیف سنجی مورد بررسی قرار گرفتند.منیزیم سولفات به عنوان یکی از نمک های محلول در آب مورد بررسی قرار گرفت و از این غشای ساخته شده در جهت حذف مولکول های نمک منیزیم سولفات از آب استفاده شد. خصوصیات زیرلایه به علاوه خصوصیات غشای نانوفیلتر مانند خاصیت ممانعت فضایی و اثر دونان میزان پس زنی 89% را برای منیزیم سولفات در پی دارد.

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