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Cellulose acetate butyrate membrane containing TiO_2 nanoparticle: Preparation, characterization and permeation study

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Abstract−Cellulose acetate butyrate/TiO_2 hybrid membranes were prepared via phase inversion by dispersing the TiO_2 nanoparticles in casting solutions. The influence of TiO_2 nanoparticles on the morphology and performance of membranes was investigated. The scanning electron microscope images and experiments of membrane performance showed that the membrane thickness and pure water flux were first increased by adding the TiO_2 nanoparticles to the casting solution up to 4 wt% and then decreased with the addition of further nanoparticles to it. The obtained results indicated that the addition of TiO_2 in the casting solution enhanced the rejection and permeate flux in filtration of bovine serum albumin solution. Furthermore, increasing the TiO_2 nanoparticle concentration in the casting solution increased the flux recovery and consequently decreased the fouling of membrane.

Key words: Cellulose Acetate Butyrate, Membrane, TiO_2 Nanoparticle, Blending

INTRODUCTION

Cellulose is one of the best materials for constructing membranes. It is a most abundant organic resource, naturally degradable, biologically compatible, hydrophilic, foul resistant and has good resistance to acid, alkali and organic solvents [1]. Cellulose esters are one of the derivatives of cellulose. Cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) are the most common commercial cellulose esters which are widely used in the manufacture of membranes [1]. Because of good chlorine tolerance and chemical stability, CAB can be considered as one of the appropriate membrane materials [1,2]. Relatively few researches have been done on this polymer as membrane material [1-8].

Preparing hybrid membrane is a way to improve the properties and performance of neat membrane. Nanocomposite membranes are a group of the membranes which are formed by in situ generation or the addition of nanoparticles to polymeric casting solution.

Among inorganic oxide nanoparticles, titanium oxide is a material that is highly regarded because of its particular features such as antifouling and antibacterial properties and also good chemical stability [9-12]. So, many efforts have been done to investigate the effect of adding TiO_2 on morphology and performance of membrane. Some of these works are described below.

Abedini et al. prepared CA/TiO_2 hybrid membranes by blending TiO_2 nanoparticle, solvent and CA. They investigated the influence of TiO_2 on the membrane structure [12]. Rahimpour et al. studied three methods of preparation of the polyethersulfone (PES) membrane modified with TiO_2. They investigated the morphology and performance of membranes and compared the preparation methods with each other [13]. Bae et al. prepared nanocomposite membrane of sulfonated polyethersulfone (SPES)/TiO_2. An analysis proved lower cake layer formation and irreversible membrane fouling for the nanocomposite membrane as compared with the polymeric membrane [9]. Yang and Wang prepared polysulfone (PSf)/TiO_2 hybrid membranes by sol-gel process. They found the optimum TiO_2 concentration for achieving the best performance of the membrane [14]. Also, Yang et al. investigated the influence of TiO_2 nanoparticles on the morphology and properties of PSf ultrafiltration membranes. They found a relationship between the structure and performance of membrane and casting solution viscosity [11]. Pourjafar et al. prepared poly (vinyl alcohol) (PVA)/PES thin film composite membranes and then modified them by the deposition of TiO_2 nanoparticles on their surfaces. They reported that the contact angle, water permeability and flux decline of PVA/PES composite membrane were improved by coating of TiO_2 nanoparticles [15]. Rahimpour et al. prepared TiO_2 entrapped nanocomposite polyvinylidenefluoride (PVDF)/SPES membranes and investigated the membranes' antifouling and antibacterial properties by adding TiO_2 to the membrane structure [16]. Shi et al., in two separate researches, prepared the PVDF/TiO_2 hybrid membranes with different nano-TiO_2 dosages [17] and ionic liquid modified nano-TiO_2 (IL-TiO_2) contents [18] via thermally induced phase separation. They studied the effect of TiO_2 and IL-TiO_2 on the membrane morphology and also the properties such as permeability, porosity and stability. Zhang et al. prepared TiO_2 nanoparticles entrapped PVDF hybrid membranes by impregnating the pre-treated PVDF film in TiO_2 suspension. They studied the structure, permeability and antifouling performance of the hybrid membranes and also explored the adsorption and desorption behavior of Cu^{2+} on the hybrid membranes [19].

In spite of the aforementioned advantages for CAB, because of relatively poor hydrophilicity of CAB membrane, it has a tendency to be fouled during the filtration process. Therefore, in order to increase the hydrophilicity, CAB membranes blended with TiO_2 hydrophilic nanoparticle were prepared. The effects of TiO_2 concentration on the morphology, performance and antifouling properties of the

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prepared membranes were investigated in detail.

MATERIALS AND METHODS

1. Materials

CAB (average M_n~65,000) was procured from Sigma-Aldrich. Solvent of dimethylformamide (DMF) was purchased from Akkim Company. TiO_2 nanoparticles with particle size of 25 nm and polyethylene glycol (PEG) with molecular weight of 25,000 g mol^{-1} were supplied from Degussa and Merck, respectively. Bovine serum albumin (BSA) was obtained from Equitech-Bio Inc. (USA). Distilled water was used as non-solvent in all experiments.

2. Preparation of Membrane

The CAB membrane without TiO_2 nanoparticles and CAB membrane blended with TiO_2 nanoparticles were prepared using the phase inversion method. The casting solutions consisting of CAB, DMF and different concentrations of TiO_2 nanoparticle (0, 2, 4 and 6 wt%) were prepared in the presence of PEG (at 2 wt% constant concentration) by stirring at 200 rpm and room temperature for 12 h. The composition of casting solutions is shown in Table 1.

After formation of homogeneous solutions, they were held at ambient temperature for 6 h to remove their air bubbles. Afterwards, the films were cast on a smooth glass plate by a casting bar. The prepared films were left to evaporate for 5 s and then immersed in the non-solvent bath for precipitation. The immersion process was carried out at room temperature.

3. Membrane Characterization

3-1. Scanning Electron Microscopy (SEM)

The membrane top surface and cross section were observed with a KYKY-EM3200 scanning electron microscope. The membranes were cut into small pieces. For this purpose they were immersed in liquid nitrogen to give a generally consistent and clean cut by freezing. After that the membranes were kept in air for drying and then sputter-coated with thin film of gold. Finally, the coated samples were fixed on plates with adhesive and photomicrographs were taken in very high vacuum conditions at 25 kV.

3-2. Membrane Performance Tests

Membrane performance studies were carried out in a batch mode by applying the set-up presented in Fig. 1. A flat sheet membrane module made from stainless steel was used in the set-up. The effective area of membrane in the module was 10 cm^2. Pure water flux

Table 1. Composition of casting solutions

Membrane	CAB (wt%)	PEG (wt%)	TiO_2 (wt%)	DMF (wt%)
M1	18	2	0	80
M2	18	2	2	78
M3	18	2	4	76
M4	18	2	6	74

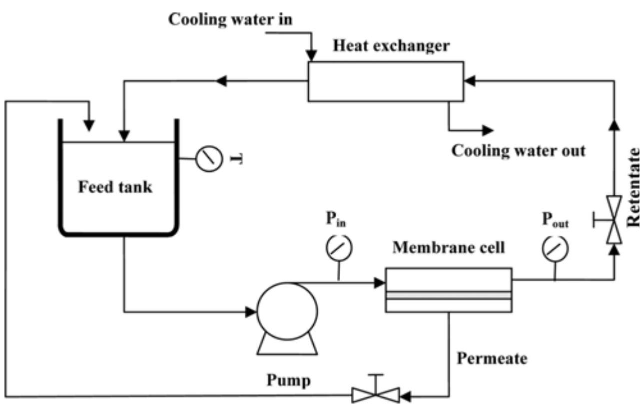

Fig. 1. Scheme of membrane filtration apparatus.

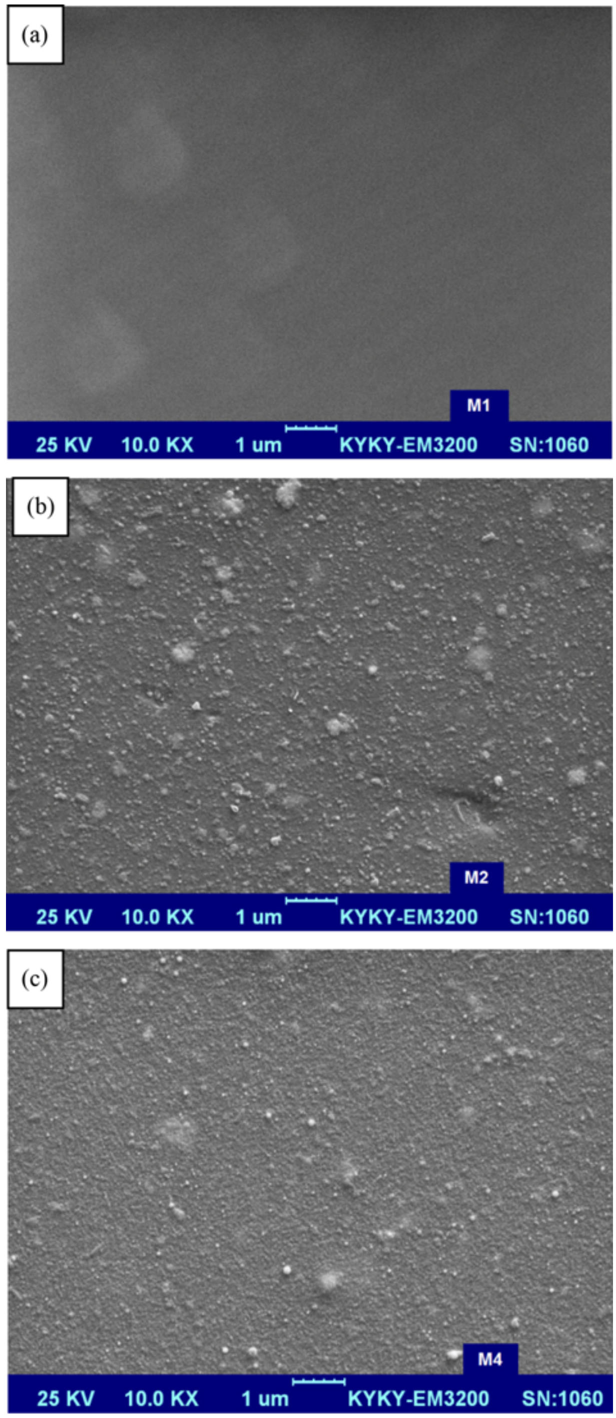

Fig. 2. Surface SEM images: (a) CAB membrane without TiO_2, (b) CAB membrane with 2 wt% TiO_2, and (c) CAB membrane with 6 wt% TiO_2.

(PWF) was calculated by using the following equation [20]:

$$\text{Flux} = \frac{V}{A.\Delta t} \quad (1)$$

where V is the permeate volume (l), A is the effective membrane area (m^2) and Δt is the sampling time (h).

Then, the experiments were carried out by applying BSA solution. BSA was dissolved in distilled water and its concentration was kept constant at 1 gl^{-1} in all the experiments. The permeate flux and BSA rejection were calculated by using Eq. (1) and the following equation, respectively [20]:

$$\%R = \left(1 - \frac{C_p}{C_F}\right) \times 100 \quad (2)$$

where, C_p and C_F are the BSA concentrations in permeate and feed, respectively. The BSA concentrations in permeate and feed were measured by applying a UV-Vis spectrophotometer Unico UV-2100 at the absorbance of 280 nm. After filtration of BSA solution, the membranes were washed with distilled water for 15 min and the PWF of fouled membranes was measured. To evaluate the fouling resistance of membranes, flux recovery (FR), which indicates the recycling property of membrane, was calculated as follows [13]:

$$\%FR = \left(\frac{J_{w2}}{J_{w1}}\right) \times 100 \quad (3)$$

where J_{w2} and J_{w1} are the pure water fluxes of fouled and virgin membranes, respectively.

All experiments were carried out at 14±1 °C and a transmembrane pressure of 5 bars; and the average of two replicates was presented.

RESULTS AND DISCUSSION

1. The Effect of TiO_2 Nanoparticle on Morphology and PWF

The SEM images of top surface of membranes are observed in Fig. 2. With respect to this figure, by increasing the TiO_2 concentration in polymeric solution, the content of TiO_2 nanoparticles in the skin layer of membrane is increased.

The effect of TiO_2 nanoparticle amount on the PWF of mem-

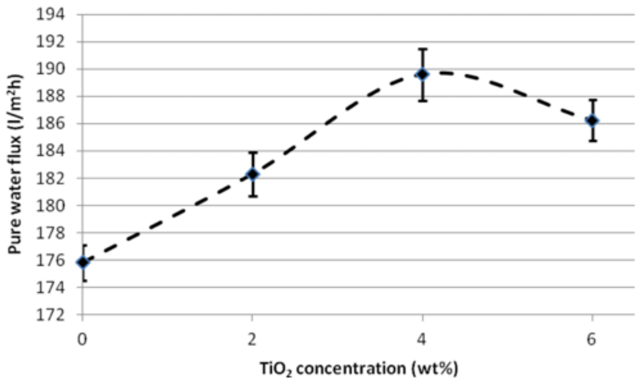

Fig. 3. Effect of TiO_2 concentration on pure water flux.

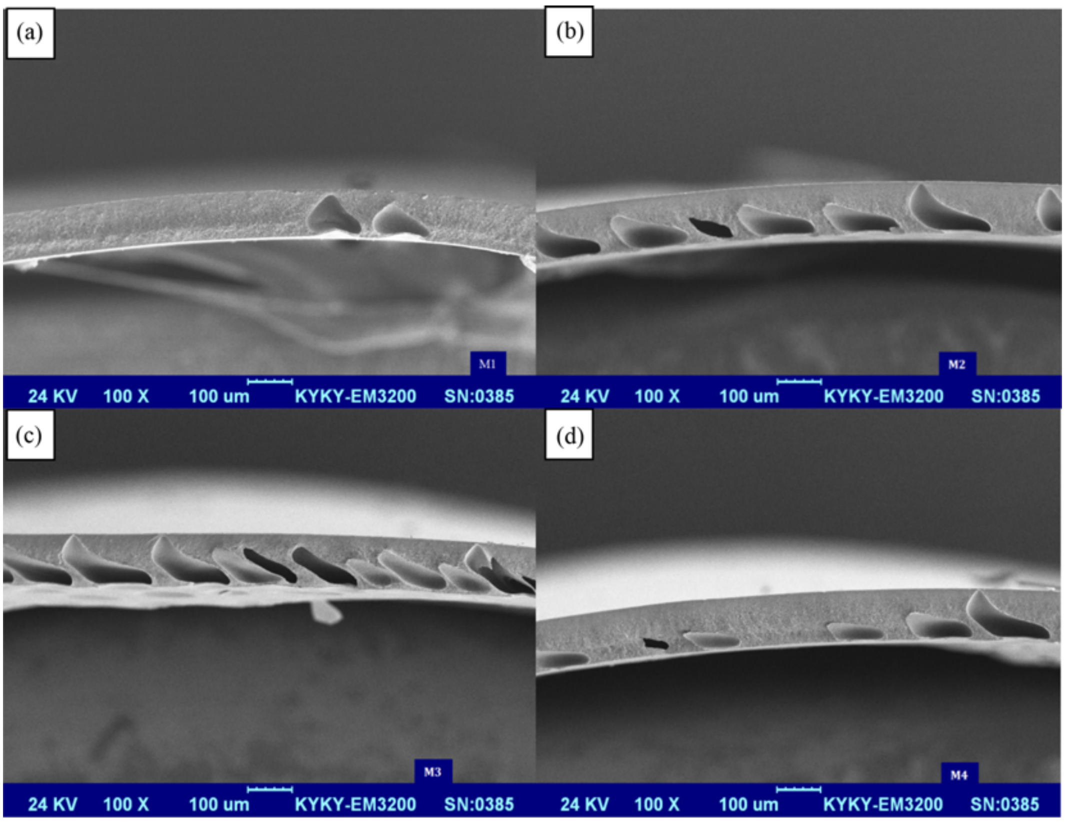

Fig. 4. Cross sectional SEM images of the CAB membranes with 100 X magnification: (a) TiO_2 wt%=0, (b) TiO_2 wt%=2, (c) TiO_2 wt%=4, and (d) TiO_2 wt%=6.

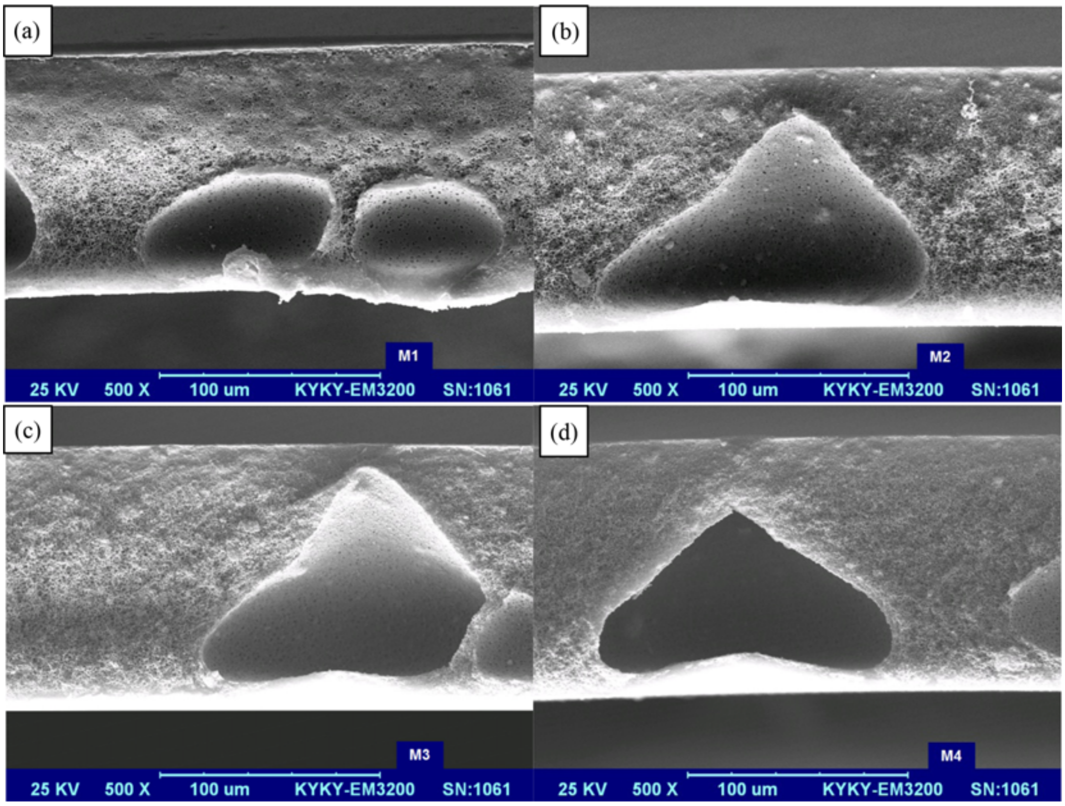

Fig. 5. Cross sectional SEM images of the CAB membranes with 500 X magnification: (a) TiO_2 wt%=0, (b) TiO_2 wt%=2, (c) TiO_2 wt%=4, and (d) TiO_2 wt%=6.

branes is depicted in Fig. 3. The TiO_2 concentration in the casting solution was increased from 0 to 6 wt%. The PWF is increased with addition of TiO_2 up to 4 wt% and then decreased with further addition of TiO_2. The results can be explained with respect to the cross sectional SEM images (Figs. 4 and 5) and changes in the thickness of membranes (Fig. 6).

According to Figs. 4 and 5, by increasing TiO_2 from 0 to 4 wt% the number of macrovoids in the structure is increased, and also the macrovoids in the structure become larger and closer to the membrane surface. Further increase of the TiO_2 concentration up to 6 wt% results in reduction of the number and size of macrovoids, and consequently the formation of membrane with denser structure. The increase in the membrane porosity and opened structure with increasing TiO_2 from 0-4 wt% enhances the permeability. At the same time, the improved hydrophilicity can attract the water molecules inside the membrane matrix and help them to pass through the structure and therefore enhance the permeability [11]. However, higher TiO_2 concentration produces a highly viscous casting solution, which slows down the membrane formation process and creates a thicker skin layer and a compact sublayer containing the considerable TiO_2 particles blocking the membrane pores, and thereby producing a negative effect on the permeability [13,14]. Furthermore, Fig. 6 proves the above results. The membranes thickness is increased by increasing the TiO_2 concentration in the casting solution from 0 to 4 wt%. However, increasing further TiO_2 nanoparticles in the casting solution causes compaction and decreases the membrane thickness. This means that the porosity of membrane is increased by increasing 0 to 4 wt% TiO_2 to the solution and then decreased in higher nanoparticle concentration and compaction occurs.

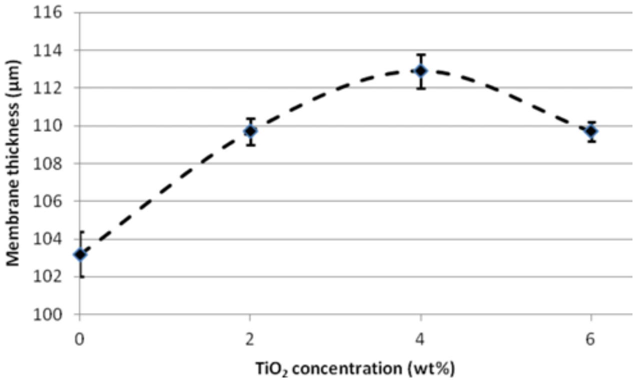

Fig. 6. Effect of TiO_2 concentration on membrane thickness.

2. BSA Solution Filtration

The flux behavior of membranes in the filtration of BSA solution is depicted in Fig. 7. The obtained results clearly show that the antifouling property of membranes with adding TiO_2 is significantly improved. The flux reduction for the CAB membrane without TiO_2 is drastically increased during test, but it for the other membranes is more reasonable.

The BSA rejection by prepared membranes is presented in Fig. 8. It should be noted that the BSA rejection by the CAB membranes containing TiO_2 is higher in comparison with that by the CAB membrane without TiO_2. It means that an increase in the membrane hydrophilicity is also beneficial for increasing the rejection of

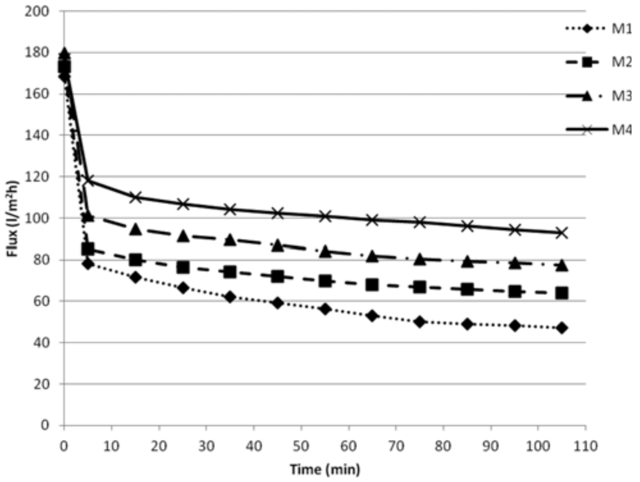

Fig. 7. Flux behavior of CAB membrane without TiO_2 and with TiO_2 during BSA solution filtration.

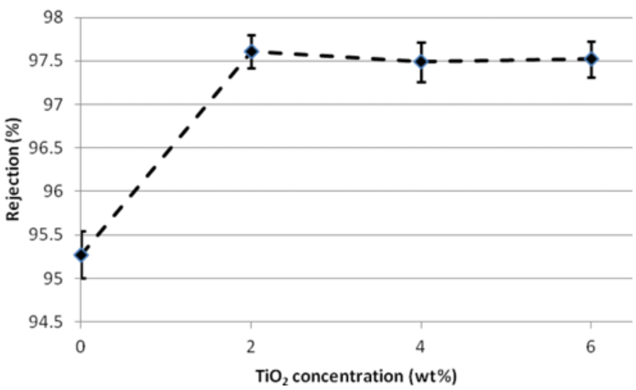

Fig. 8. BSA rejection for CAB/TiO_2 membranes with different TiO_2 concentrations.

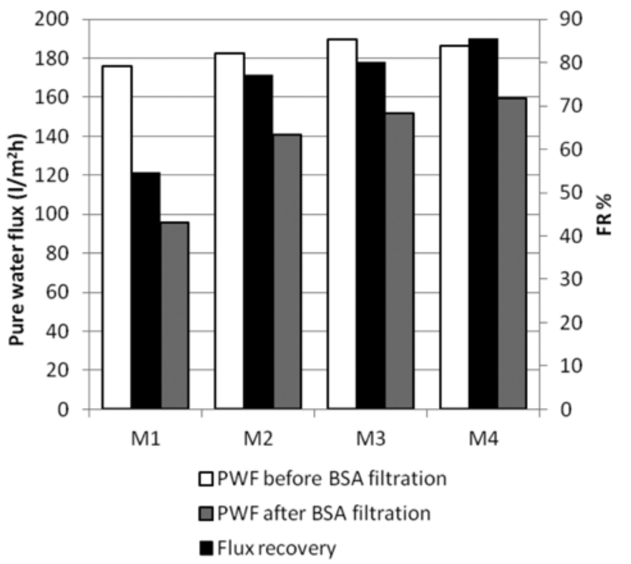

Fig. 9. Pure water flux before and after BSA solution filtration and flux recovery percent.

BSA. Also, the rejections confirm the trends observed in the porosity with respect to the SEM images.

The antifouling property of TiO_2 membranes can also shown by the flux recovery via the test of membranes with pure water after the filtration of BSA solution. The results are presented in Fig. 9.

The results show that the CAB membrane without TiO_2 after the filtration is fouled and PWF is reduced to approximately half initial value. However, for the other membranes because of their antifouling properties and hydrophilicity, the recovery percent is about 80. Furthermore, with increasing the TiO_2 concentration in the casting solution, the recovery is increased due to further accumulation of nanoparticle on the membrane surface.

CONCLUSIONS

CAB membranes with and without TiO_2 nanoparticles were prepared by phase inversion via immersion precipitation. The addition of TiO_2 to the casting solution affected the membrane properties. The main conclusions are as follows:

With respect to the SEM images the membrane thickness was increased by increasing the TiO_2 concentration in the casting solution from 0 to 4 wt%. However, adding further TiO_2 nanoparticle in the casting solution caused compaction and decreased the membrane thickness. This result is also proved by PWF test. PWF was increased by increasing the TiO_2 up to 4 wt% in the casting solution and then decreased with further addition of TiO_2.

The results of BSA solution filtration showed that the antifouling property of membrane by increasing TiO_2 was improved and the BSA rejection by the membranes containing TiO_2 was higher than that by the membrane without TiO_2. The antifouling property of the membranes containing TiO_2 could be also shown by flux recovery. The results showed the CAB membrane without TiO_2 was fouled after the filtration and PWF was reduced to approximately half initial value. However, for the other membranes, due to their antifouling properties and hydrophilicity, the recovery value was about 80%.

REFERENCES

1. X. Y. Fu, T. Sotani and H. Matsuyama, *Desalination*, **233**, 10 (2008).
2. A. D. Sabde, M. K. Trivedi, V. Ramachandhran, M. S. Hanra and B. M. Misra, *Desalination*, **114**, 223 (1997).
3. S. M. Xie, W. F. Wang, P. Ai, M. Yang and L. M. Yuan, *J. Membr. Sci.*, **321**, 293 (2008).
4. M. Hashino, K. Hirami, T. Katagiri, N. Kubota, Y. Ohmukai, T. Ishigami, T. Maruyama and H. Matsuyama, *J. Membr. Sci.*, **379**, 233 (2011).
5. W. S. Wu, W. W. Lau, G. P. Rangiah and S. Sourirajan, *J. Colloid Interface Sci.*, **160**, 502 (1993).
6. Y. Fang, S. Sourirajan and T. Matsuura, *J. Appl. Polym. Sci.*, **44**, 1959 (1992).
7. A. J. M. Valente, H. D. Burrows, A. Y. Polishchuk, M. G. Miguela and V. M. M. Lobo, *Eur. Polym. J.*, **40**, 109 (2004).
8. G. S. Luo, M. Niang and P. Schaetzel, *J. Membr. Sci.*, **125**, 237 (1997).
9. T. H. Bae, I. C. Kim and T. M. Tak, *J. Membr. Sci.*, **275**, 1 (2006).
10. G. Fu, P. S. Vary and C. T. Lin, *J. Phys. Chem. B.*, **109**, 8889 (2005).
11. Y. Yang, P. Wang and Q. Zheng, *J Polym. Sci. Pol. Phys.*, **44**, 879 (2006).

12. R. Abedini, S. M. Mousavi and R. Aminzadeh, *Desalination*, **277**, 40 (2011).
13. A. Rahimpour, S. S. Madaeni A. H. Taheri and Y. Mansourpanah, *J. Membr. Sci.*, **313**, 158 (2008).
14. Y. Yang and P. Wang, *Polymer*, **47**, 2683 (2006).
15. S. Pourjafar, A. Rahimpour and M. Jahanshahi, *J. Ind. Eng. Chem.*, **18,** 1398 (2012).
16. A. Rahimpour, M. Jahanshahi, B. Rajaeian and M. Rahimnejad, *Desalination*, **278**, 343 (2011).
17. F. Shi, Y. Ma, J. Ma, P. Wanga and W. Sun, *J. Membr. Sci.*, **389**, 522 (2012).
18. F. Shi, Y. Ma, J. Maa, P. Wanga and W. Sun, *J. Membr. Sci.*, **427**, 259 (2013).
19. X. Zhang, Y. Wang, Y. You, H. Meng, J. Zhang and X. Xu, *Appl. Surf. Sci.*, **263**, 660 (2012).
20. E. Saljoughi, M. Amirilargani and T. Mohammadi, *Desalination*, **262**, 72 (2010).