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MODIFICATION OF POLYSULFONE ULTRAFILTRATION MEMBRANES WITH PVA AND TiO_2 FOR BETTER ANTIFOULING

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ABSTRACT

The objective of this study was to investigate anti-fouling property of modified polysulfone ultrafiltration (UF) membranes. Polysulfone UF membranes were modified by coating a thin film of polyvinyl alcohol (PVA), or a mixture of polyvinyl alcohol and titanium dioxide (TiO_2) on surface. Effects of curing temperature on the coated membranes were also studied. The modified membranes were tested with 0.5 g/L sodium alginate solution and industrial dye wastewater. Curing temperature influenced remarkably flux and fouling property of the membranes. Among experiments studied, 85 ^oC was the best curing temperature. The PVA and PVA/TiO_2-coated membranes reduced fouling significantly. Dispersion of TiO_2 nanoparticles on membrane surface improved considerably bacteria removal of the membranes.

Keywords: ultrafiltration, fouling, polysulfone membrane, polyvinyl alcohol (PVA), titanium dioxide.

1. INTRODUCTION

Recently, wastewater treatment using membranes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reserve osmosis (RO) is in common use because of its high efficiency [1, 2]. Increasingly, UF, a low-pressure membrane process, is being used for drinking water treatment because it can remove almost all of the solid suspension, sludge, bacteria, and natural organic matter [3, 4]. The challenge of this method is membrane fouling, which is often caused by the irreversible decomposition of the organic compounds on the surface of a hydrophobic membrane. Several strategies have been investigated to establish whether the membrane fouling could be alleviated; these include backwater, chemical cleaning, and modification [5]. Among these methods, the hydrophilic modification of the membrane surface has received most interest due to high efficiency and at a low operating cost over the long term.

Due to chemical stability, high hydrophilic, nontoxic, and biocompatible properties, polyvinyl alcohol (PVA) has been chosen as the appropriate material to modify membrane surface in order to improve the membrane anti-fouling property [6].

Dispersing inorganic nanoparticles on the membrane surface can also improve its performance. Especially, TiO_2 nanoparticles not only can improve permeate flux, but also can improve its self-cleaning properties [7, 8]. It is the purpose of this study to investigate modification of polysulfone (PSf) ultrafiltration membranes with PVA and TiO_2 for better anti-fouling properties.

2. EXPERIMENTAL

2.1. Materials

PSf flat sheet UF membrane with non-woven fabric as the support was purchased from Sepro Co. (USA). Polyvinyl alcohol (PVA) with approximate molecular weights of 32,000 g/mol (degree of hydrolysis: 88 %), malic acid (MA) and sodium alginate (SA) from Sigma-Aldrich Co. TiO_2 P25 Degussa (average diameter ~ 40 nm), Tryptic Soy Broth (TSB) and Tryptic Soy Agar (TSA) medium from a commercial company.

2.2. Preparation of PVA–TiO_2 membrane

The commercial PSf membranes were rinsed initially within de-ionized water, and then stored in de-ionized water.

TiO_2 nanoparticles were dispersed in de-ionized water create mixtures with different TiO_2 contents from 0.003 to 0.07 wt.% (A). A 0.25 g/L PVA solution (B) was obtained by dissolving PVA in de-ionized water at 95 ^oC for 2 h, then cooled down to the ambient temperature. Solution B was mixed with 15 wt% of malic acid, which served as a cross-linker. The resulting solution (C) was vigorously stirred while 0.2 N HCl solution was being added as catalysis to adjust pH of 2 until a homogeneous was obtained. Thereafter, solution C was dropped into solution A and vigorously stirred for at least 1 h (D). The PSf membranes were fixed on glass plate and immersed into solution D in 30 seconds. The coated membranes were dried for 24 h at room temperature, and then cured at different temperatures ranged from 75 to 110 ^oC in an oven for 10 min. After this treatment, the membranes were soaked in NaOH 0.1 N solution for 30 min to remove HCl. After that, the membrane was washed with large volumes of de-ionized water to remove a little unreacted MA and PVA. The modified membranes were stored in de-ionized water for a maximum of 5 days until tested.

2.3. Ultrafiltration experiments

Ultrafiltration experiments were carried out using a cross-flow filtration system.

The permeate flux is calculated by the following equation:

$$J = \frac{V}{At} \quad (1)$$

where: V (L) is the volume of permeate; A (m^2) is the effective area of the membrane and t (h) is the filtration time.

The resistance of membrane is determined using the formula below [9, 10]:

$$R_t = \frac{\Delta p}{\mu J} \quad (2)$$

where, J is the steady state permeate flux ($m^3/m^2.s$); Δp is the trans membrane pressure (kPa); μ is the viscosity (Pa.s) of feed solution at 24 ^oC; and R_t is the total filtration resistance (m^{-1}).

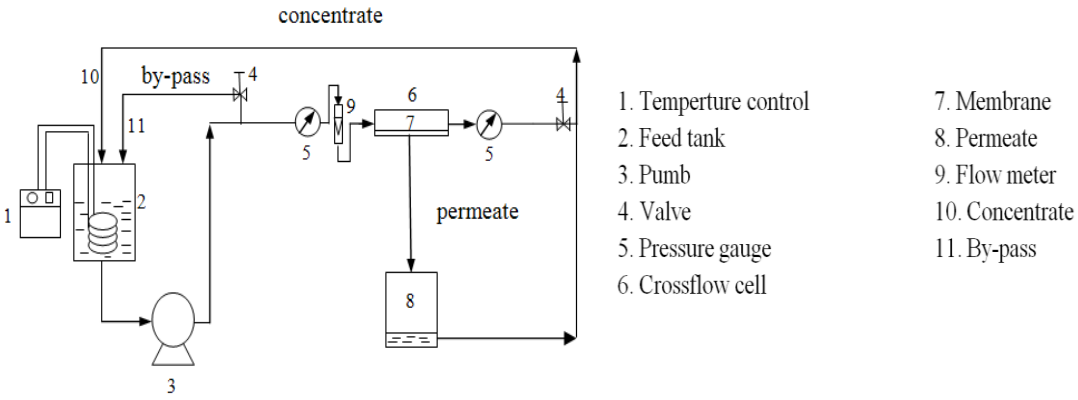


Figure 1. Diagram of cross-flow filtration system.

2.4. Evaluation of photocatalysis

Photocatalysis tests were carried out in an aseptic room. *Escherichia coli* (*E. coli*) cells were precultured in 10 ml of TSB medium at 37 ^oC for 24 h. The membrane was cut and place at the bottom of reactor. 299 ml distilled water was pipetted onto reactor which contained 1 ml E. Coli suspensions at 10^8 CFU/mL (CFU – colony forming units). The test was carried out under a 10 W UV-C lamp (AQUA PRO – USA) which was the light intensity at the peak of 365 nm. The sample was taken out and diluted. The sample was then incubated at 37 ^oC for 24 h. Number of survival *E. coli* was counted.

3. RESULTS AND DISCUSSION

3.1. Preparation of membranes

FTIR spectra of the different membranes are shown in Fig. 2. It can be seen in Fig. 1 that in a wavenumber range from 3500 to 3200 cm^{-1}, same peaks appear in all of the membrane samples. However, the 1719.57 cm^{-1} (b), 1720.81 cm^{-1} (c), and 1725.74 cm^{-1} (d) peaks which are with respect to the (-CO-O-) band just appear in the modified membranes, but not in the original membrane. It is evidence for crosslinking reaction between the hydroxyl group of PVA and the carboxylic group of MA.

The SEM pictures of the original and modified PVA 0.25 g/L membrane in Fig. 3a and 3b show that the surface of modified PVA membrane (b) becomes smoother compared to the unmodified membrane (a).

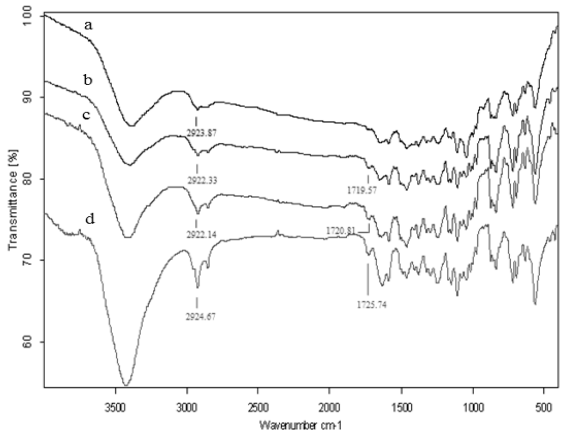
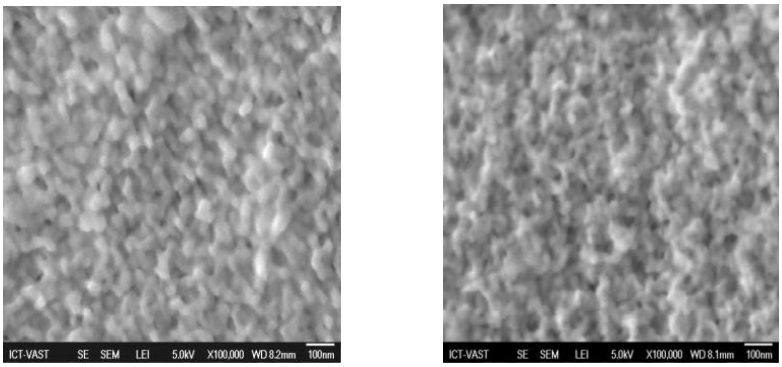


Figure 2. FTIR spectra of the different membranes: (a) Original polysulfone, (b) PVA (0.25 g/L) modified, (c) PVA (0.25 g/L)–TiO_2 (0.003 wt. %) modified and (d) PVA (0.25 g/L)–TiO_2 (0.005 wt. %) modified.



(a) 100,000 x (b) 100,000 x

Figure 3. SEM image of membrane surface: a) Original polysulfone, b) PVA (0.25 g/L) modified.

3.2. Resistance analysis and filtration performance

3.2.1. Resistance analysis

Figure 4 shows relationship between the steady state flux and the trans membrane pressure (TMP) of the different membranes. With pure water, the slope of the line with respect to the neat PSf membrane is highest, followed by the PSf-PVA 0.25, then the PSf-PVA 0.25-TiO_2 0.005 %, the PSf-PVA 0.25-TiO_2 0.003 % and the PSf-PVA 0.25-TiO_2 0.007 % modified membrane. The presence of PVA layer and inorganic particles on membrane surface was an obstacle to water permeability and made membrane resistance increased.

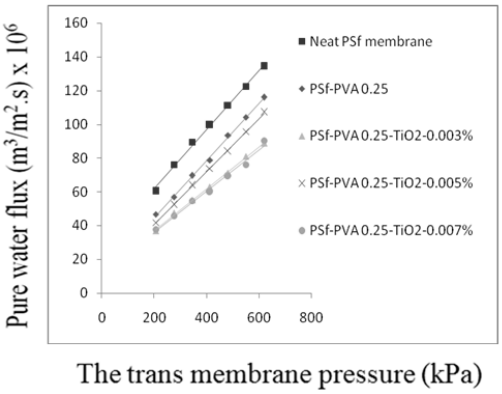


Figure 4. Steady state Flux-TMP profile of different membranes for pure water.

3.2.2. Filtration performance

a. Effect of curing temperature on flux

Membrane was modified with 0.25 g/L PVA aqueous solution and treated at different temperatures. Filtration of pure water with the modified membranes was tested. The measured water fluxes are showed in Fig. 5. The results show that the steady state flux of the membrane cured at 85 ^{o}C is highest, followed by what of the membrane cured at 75 ^{o}C, 100 ^{o}C and 110 ^{o}C. Within temperatures studied, 85 ^{o}C could be considered to be the best curing temperature and therefore the membrane PSf-PVA 0.25 cured at 85 ^{o}C was chosen for next experiments.

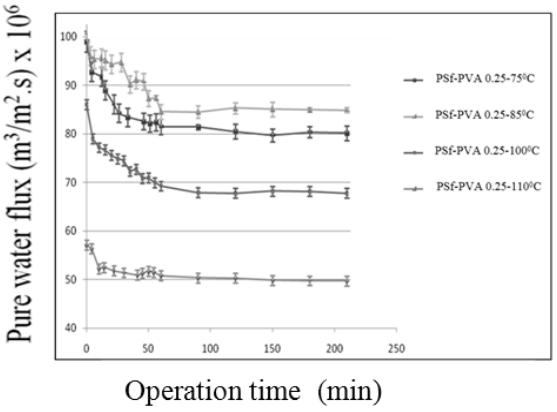


Figure 5. Pure water flux for PSf-PVA 0.25 g/L membranes cured at different temperatures.

b. Fouling mitigation effect

Fouling of the PVA-TiO_2 modified membranes in sodium alginate solution and due wastewater were studied.

For sodium alginate filtration, polysaccharide was used as a foulant. Physical cleaning using pure water and chemical cleaning using NaOH were performed in these tests. Figure 6 shows flux and flux recovery for different membranes. It can be seen in Fig. 6 that using NaOH

solution to clean membranes can recover fluxes better than pure water. It also can be seen that after cleaning, flux for the neat membrane declines much quicker compared to the modified membranes. Modification with only PVA could improve anti-fouling property better than with PVA-TiO_2. This may be due to that PVA reinforced hydroxyl group on membrane surface, and the affinity of water – membrane surface increased.

Fouling of the different membranes with dye wastewater treatment was also analyzed. Figure 7 shows fluxes for different membranes. The result reveals that the steady state flux for the unmodified membrane was always lower than the modified membranes. Among the membranes studied, the PVA 0.25 - TiO_2 0.005 % modified membrane has highest flux and the unmodified membrane flux has lowest flux. The average permeates in 845 min for different membranes are showed in Fig. 8. The permeate for PSf-PVA 0.25 - TiO_2 0.005 % is highest, followed by PSf-PVA 0.25, PSf-PVA 0.25 - TiO_2 0.003 %, neat PSf membrane, and PSf-PVA 0.25 - TiO_2 0.007 %.

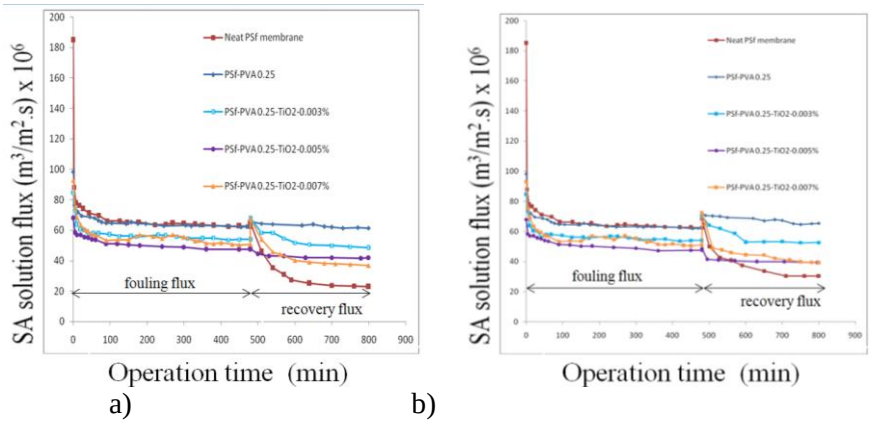


Figure 6. Flux for different membrane in sodium alginate filtration
a) cleaning by pure water and b) NaOH.

Accordingly, the filtration efficiency of PVA or PVA-TiO_2 modified membranes was better than the unmodified membranes. PSf-PVA 0.25-TiO_2 0.007 % was exceptional. High content of TiO_2 nanoparticles might cause the aggregation on membrane surface which decreased permeate water.

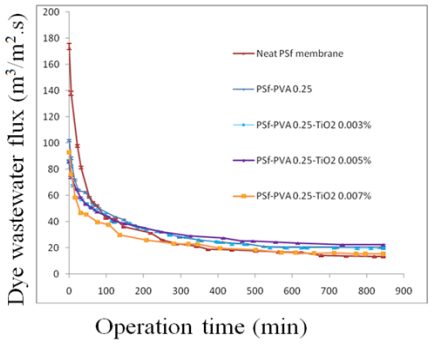


Figure 7. The steady state flux of different membranes for dye wastewater treatment.

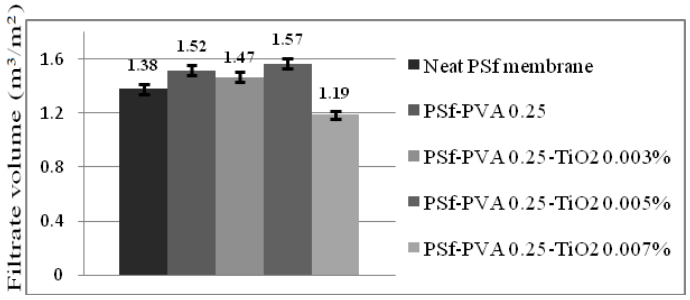


Figure 8. Permeate for different membranes for dye wastewater filtration.

c. Photocatalysis

Figure 9 shows the remainder and survival ratios of *E.coli* bacterium in permeates for different membranes treated with UV light illumination. In Fig. 9, differences in *E.coli* remainder for TiO_2-modified and unmodified membranes are obviously seen. The presence of TiO_2 nanoparticles on membrane surface can improve the bacteria killing. It can be also seen that after about 120 seconds treated with UV light, almost bacteria were killed.

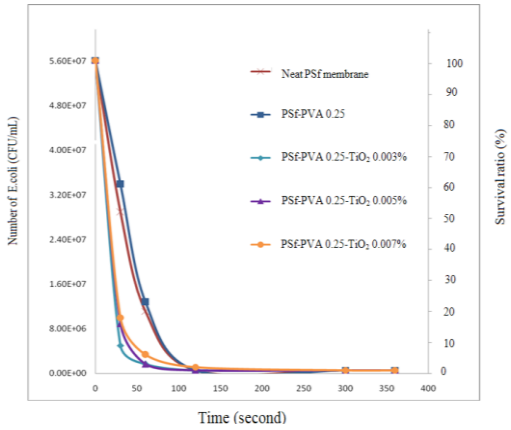


Figure 9. Number and survival ratio of *E. coli* in permeates for different membranes.

5. CONCLUSIONS

In this study, PSf-PVA and PSf-PVA-TiO_2 composite membranes were prepared via dip-coating process. Modification to virgin membrane using PVA and TiO_2 can improve the anti-fouling property of membranes. Not only improve the anti-fouling property, dispersion of TiO_2 nanoparticles can also improve significantly the bacteria killing capability of membranes. However, high content of TiO_2 nanoparticles might cause the aggregation on membrane surface which makes permeate decreased.

Curing temperature may have effects on degree of crosslinking between polyvinyl alcohol and malic acid, and therefore influences filtration performance of membranes. It was found that suitable curing temperature for PVA-MA crosslinking is about 85 ^{o}C.

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TÓM TẮT

BIẾN TÍNH MÀNG SIÊU LỌC POLYSULFONE BẰNG PVA VÀ TiO_2 NHẰM CẢI THIỆN KHẢ NĂNG CHỐNG TẮC NGHẼN

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Mục tiêu của công trình là nghiên cứu quá trình biến tính màng siêu lọc polysulfone nhằm cải thiện khả năng chống tắc nghẽn của nó. Màng siêu lọc polysulfone đã được biến tính bằng

cách phủ lên bề mặt một lớp màng mỏng polyvinyl alcohol (PVA), hoặc hỗn hợp của polyvinyl alcohol với TiO_2 kích thước nano. Ảnh hưởng của nhiệt độ ủ sao khi phủ lớp bề mặt lên đặc tính của màng cũng được nhiên cứu trong công trình này. Màng biến tính thu được đã được lọc thử nghiệm với dung dịch sodium alginate 0,5 g/L và nước thải của ngành dệt nhuộm. Kết quả cho thấy, nhiệt độ ủ có ảnh hưởng đáng kể đến thông lượng và khả năng chống tắc nghẽn của màng. Trong khoảng nhiệt độ đã nghiên cứu, 85 ^oC được cho là nhiệt độ ủ phù hợp nhất. Màng được biến tính bằng PVA và PVA/TiO_2 có khả năng chống tắc nghẽn tốt hơn hẳn màng chưa biến tính. Kết quả cũng cho thấy rằng, việc phân tán các hạt TiO_2 có kích thước nano lên bề mặt màng không những làm tăng thông lượng và khả năng chống tắc nghẽn mà còn cải thiện khả năng loại bỏ khuẩn *E.coli* của màng.

Từ khóa: siêu lọc, tắc nghẽn, màng polysulfone, PVA, TiO_2.