

Fabrication and Performance of a Low Operating Pressure Nanofiltration Poly(vinyl chloride) Hollow Fiber Membrane*

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Abstract A low operating pressure nanofiltration membrane is prepared by interfacial polymerization between *m*-phenylenediamine (MPDA) and trimesoyl chloride (TMC) using PVC hollow fiber membrane as supporting. A series of PVC nanofiltration membranes with different molecular weight cutoff (MWCO) can be obtained by controlling preparation conditions. Chemical and morphological characterization of the membrane surface was carried out by FTIR-ATR and SEM. MWCO was characterized by filtration experiments. The preparation conditions were investigated in detail. At the optimized conditions (40 min air-dried time, aqueous phase containing 0.5% MPDA, 0.05% SDS and 0.6% acid absorbent, oil phase containing 0.3% TMC, and 1 min reaction time), under 0.3 MPa, water flux of the gained nanofiltration membrane reaches 17.8 L/m²·h, and the rejection rates of methyl orange and MgSO₄ are more than 90% and 60%, respectively.

Keywords: PVC; Interfacial polymerization; Nanofiltration membrane; Hollow fiber membrane.

INTRODUCTION

Nanofiltration (NF) of membranes is a low pressure-driven filtration process with the separation characteristics between reverse osmosis (RO) and ultrafiltration (UF)^[1, 2]. NF membranes have high rejection to organic molecules with molecular weight from 100 to 1000 Da by their porous dense layer with low energy consuming and high flux. For these characteristics NF membranes have received much attention and widely applied in many areas, such as wastewater treatment^[3], water softening^[4], substances separation^[5] or recovery^[6].

Many methods have been reported to prepare NF membranes included surface grafting^[7], chemical cross-linking^[8], blending^[9], coating^[10, 11], interfacial polymerization^[12–15] and so on. In these methods, interfacial polymerization has been applied for commercial NF membranes and the selective skin layer is a polyamide composite layer. Many membrane materials as a supporting have been used to prepare composite membranes, such as PES^[16], PAN^[17], PS^[18], PVDF^[19] and PP^[20], and most previous research focused on flat sheet membranes. However, the use of interfacial polymerization technology to prepare NF membranes with poly(vinyl chloride) (PVC) hollow fiber membrane as supporting material appears to be seldom studied. PVC is an outstanding material because of its excellent mechanical strength, low cost, low toxicity and excellent chemical resistance properties. PVC membranes have been widely applied in water treatment and exhibited high permeation fluxes and rejections^[20–23]. And the PVC hollow fiber membrane is suitable for preparing low operating pressure NF membrane as a supporting.

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In this study, PVC NF membranes were prepared by interfacial polymerization of *m*-phenylenediamine (MPDA) and trimethyl chloride (TMC) on a commercial PVC hollow fiber membrane supporting. The influencing factors to the filtration performance including surfactant, air-dried time, active monomer concentration and reaction time were examined systematically. Fourier transforms infrared (FTIR-ATR) spectroscopy confirmed the polyamide composite layer on PVC membrane. Scanning electron microscopy (SEM) was used to observed membrane surface morphology. The filtration performance was studied using dye or salt solution.

EXPERIMENTAL

Materials and Reagents

The PVC hollow fiber membrane was provided by Litree Co. (Hainan, China, Table 1 lists the properties.) and stored in water before use. MPDA and TMC were obtained from Aldrich Chemical Company. *n*-Hexane, sodium dodecyl sulfonate (SDS), Congo red ($M_n = 696.68$, the maximum absorption wavelength = 488 nm), methyl orange ($M_n = 327.33$, the maximum absorption wavelength = 463 nm), triethylamine (TEA) and $MgSO_4$ were analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (China). All the reagents were used as received.

Table 1. Characteristics of PVC hollow fiber membrane

Parameter	Value
Configuration	Outside-in hollow fiber
Molecular weight cut-off (kDa)	150
Water flux ($L/m^2 \cdot h$, at 0.3 MPa)	180
Fiber inner/outer diameter (mm)	1.0/1.7

Membrane Preparation

The composite fiber membrane was prepared by the typical interfacial polymerization of MPDA and TMC on PVC hollow fiber membranes. In brief, aqueous phase containing MPDA (0.1–1 wt%) and SDS (0.05 wt%) in water, organic phase containing TMC (0.1–1 wt%) in hexane were prepared separately. Then, the PVC supporting membranes of 50 cm length with one end sealed were immersed into the aqueous phase for about 2 min at 30 °C. The membranes were drained and dried at 25 °C for a certain time until no remaining liquids. At last, the membranes were put into the organic phase for 1 min at 30 °C. The final membranes were air-dried at room temperature for further reaction and hexane evaporation, washed and stored in deionized water before further using.

Characterization

FTIR-ATR measurements

Fourier transforms infrared (FTIR-ATR) spectroscopy was employed to investigate the surface chemical composition changes of PVC membranes before and after interfacial polymerization. The spectra with a wave number ranging from 4000 to 1000 cm^{-1} were collected by cumulating 32 scans at a resolution of 2 cm^{-1} using a Bruker Vector22 FTIR spectrophotometer.

Scanning electron microscopy (SEM)

The morphology of the pristine and modified PVC hollow fiber membrane samples was observed by field emission scanning electron microscope (FESEM, FEI SIRION-100). To avoid destroying the cross section structure, the membrane samples were fractured in liquid nitrogen and then sputtered with gold before SEM observation.

Separation and permeation properties

Permeation tests were carried out under 0.3 MPa using an end-flow NF test cell with a filtration area of 60 cm^2 or so (Scheme 1). Then a dye or salt solution of 1000 mg/L was flowed at 25 °C across the membrane. The flux

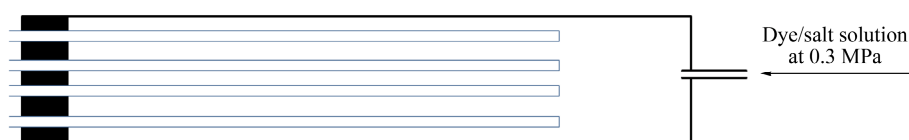
and rejection rate were measured by collecting the permeation water after being compacted under 0.35 MPa for 1 h. The permeation flux (F) was calculated according to the following equation:

$$F = V/(A_m t)$$

Where V is the total volume of the solution penetrated through the membrane, A_m is the membrane area, and t denotes the collection time (0.5 h). The rejection rate (R) of dye or salt was calculated as follows:

$$R = (1 - C_p/C_f) \times 100\%$$

Where C_p and C_f are the solute concentrations in the permeate and feed, respectively. Dye and salt concentrations were tested by UV-Visible spectrophotometer (UV-1601) and electrical conductivity instrument DDS-11A (Shanghai Leichi Instrument, China), respectively. All experiments were carried out at room temperature.



Scheme 1 Schematic representation of the nanofiltration evaluation cell

RESULTS AND DISCUSSION

Effect of Absorbing Time in the Aqueous Phase on Absorbing Degree of MPDA

In order to increase prepare efficiency and get to maximum absorbing of MPDA, absorbing degree (AD) and absorbing time in the aqueous phase were investigated first. A certain weight PVC membrane was dipped into the aqueous phase at 30 °C from 10 s to 180 s, then air-dried at 25 °C for 30 min, the AD was calculated by:

$$AD = (W_1 - W_0)/W_0$$

where W_0 and W_1 are the weights of the initial PVC membrane and the MPDA absorbed membrane, respectively. All results were the average of three parallel experiments at least, and the results are shown in Fig. 1. As the absorbing time increased, AD increased fast at the beginning and leveled off at 120 s. Further increasing the absorbing time shows little influence on AD because of reaching a saturation value. AD reached the maximum value at 120 s, so it was chosen as the absorbing time.

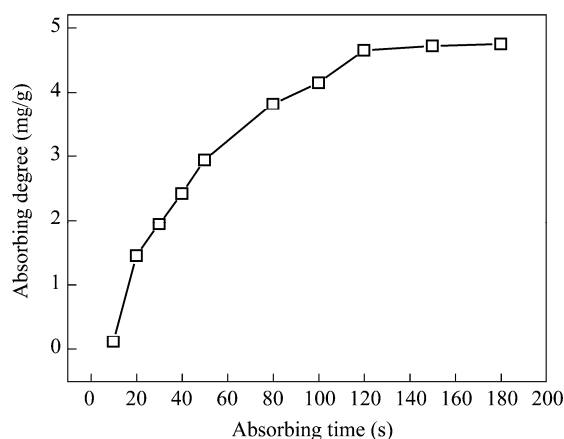


Fig. 1 Effect of absorbing time in the aqueous phase (MPDA, 0.5 wt%; SDS, 0.05 wt%) on absorbing degree of MPDA

Chemical and Morphological Characterization of the Membrane Surface

The virgin and modified PVC membranes were characterized by FTIR/ATR spectroscopy to confirm the polyamide composite which was formed by the reaction between MPDA and TMC (Fig. 2). As shown in Fig. 3, it is clear that, after interfacial polymerization, strong new peaks appeared for modified membrane surface at 1610 cm^{-1} (aromatic ring breathing), 1660 cm^{-1} (amide I, C=O stretching), 1545 cm^{-1} (amide II, N—H bending)^[13]. All these results suggest that polyamide composite layer was formed on the membrane surface.

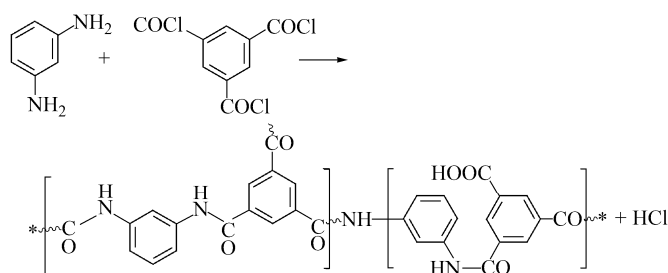


Fig. 2 Interfacial polymerization reaction between MPDA and TMC

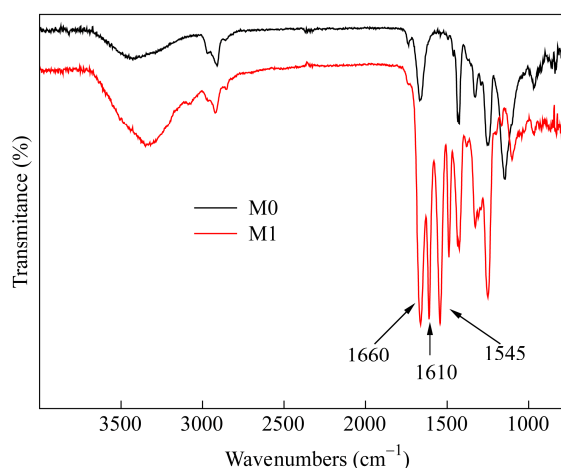


Fig. 3 FTIR-ATR spectra of virgin membrane (M0) and modified membrane (M1)

Surface Morphologies of PVC Membranes

Since polyamide composite layer was formed on membrane surface, the surface morphologies of the membranes must be changed obviously. For PVC is a hydrophobic polymer material, water cannot well spread on PVC membrane surface or permeate into pores. Without SDS in aqueous solution, the composite layer has defect and it is undesirable because of the poor rejection performance in nanofiltration. In order to prepare a uniform and defect-free composite layer, surfactant is needed in our case.

The membrane surface morphologies with SDS in aqueous solution were observed by SEM. Compared to virgin PVC membrane's smooth and porous surface (Fig. 4, M0), interfacial polymerization generates a dense, uniform and thin polyamide defect-free layer on outer-face of the PVC hollow fiber membrane supporting. The pore distribution of polyamide layer is similar to that of virgin membrane. The formation mechanism is shown in Fig. 5. After absorbing in the aqueous phase, the solution not only spread on membrane surface but also permeated into pores. Then the membranes were dried in air, water on outer surface drained and MPDA was remained, but the aqueous solution in pores could not be drained completely during the air-dried time. MPDA on outer surface and in solution reacted simultaneously with TMC. At last the polyamide layer was formed as shown in Fig. 4 (M1–M4) and Fig. 5 (C).

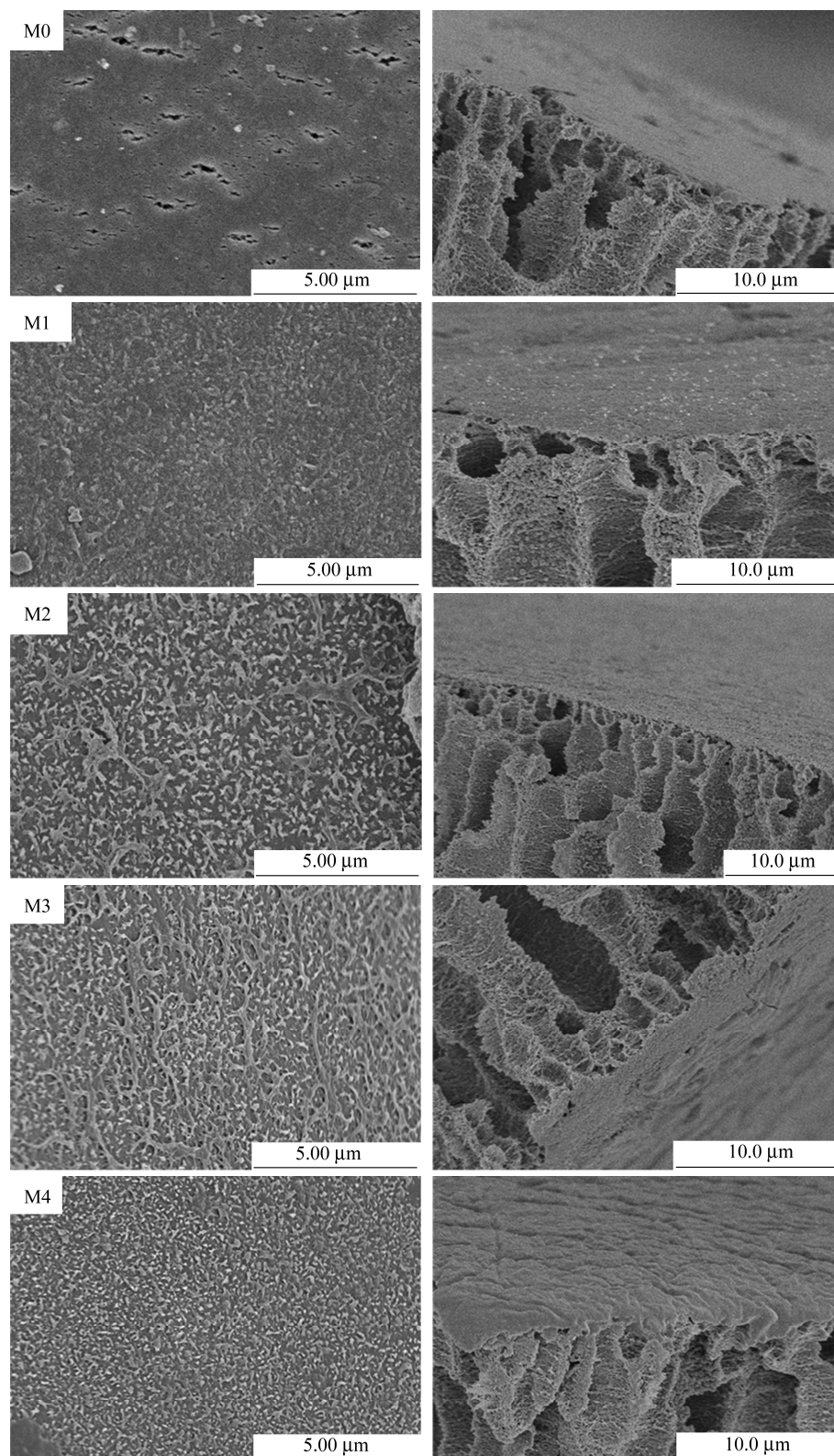


Fig. 4 SEM images of the membranes: surface (left) and cross section (right) of virgin and modified membranes (M1 = 0.1 wt% MPDA, M2 = 0.3 wt% MPDA, M3 = 0.5 wt% MPDA and M4 = 1.0 wt% MPDA)

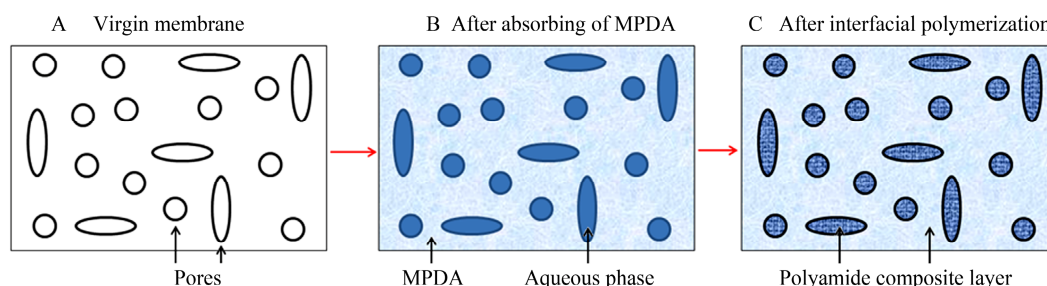


Fig. 5 The schematic formation of polyamide composite layer on PVC membrane surface and in pores

Effect of Membrane Air-Dried Time on Nanofiltration Performance

Air-dried time from 10 min to 60 min were chosen to investigate the effect on prepared membrane rejection and permeation performance with dye aqueous solution, and the other reaction conditions remained unchanged. As shown in Fig. 6, there is an optimum air-dried time at 40 min or so. Shorter time, there was lots of water remained on surface which might formed the defects; Longer time, MPDA might be oxidized in the air. The two factors caused the rejection rate decrease.

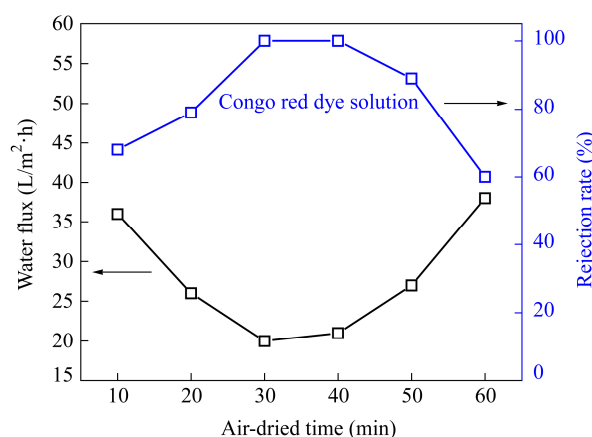


Fig. 6 Effect of air-dried time on nanofiltration performance (TMC = 0.3 wt%, MPDA = 1 wt%, SDS = 0.05 wt%, reaction time = 2 min)

Effect of Interfacial Polymerization Time on Nanofiltration Performance

During the interfacial polymerization, there formed a polyamide composite layer which is very important for the nanofiltration performance. There are many methods to optimize the layer, and it is one of the advantages of interfacial polymerization technique, too. The main factors are reaction time of the interfacial polymerization and the monomer concentration in each solution.

Figure 7 shows the water flux and rejection rate performance as a function of the reaction time. It was found that the water flux decreased and rejection rate increased with increasing the interfacial polymerization reaction time, then leveled off at 60 s^[16], further increasing time shows little influence on the nanofiltration performance because both of the thickness and compactness of the selective skin layer are almost fixed^[24, 25]. So in order to gain good rejection performance and highly efficient membrane preparation process, the reaction time is fixed at 60 s in our study.

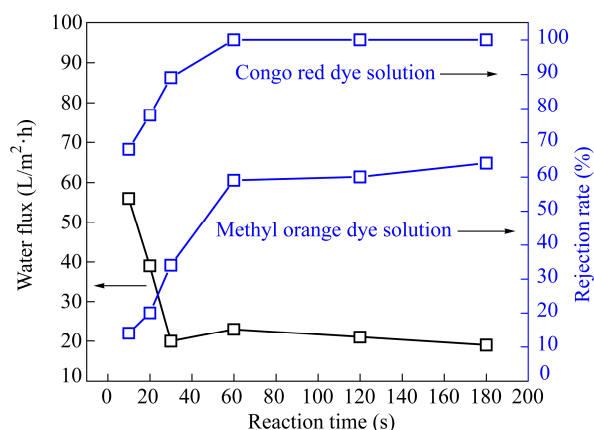


Fig. 7 Effect of reaction time on the performance of the membranes (TMC = 0.5 wt%, MPDA = 1 wt%, SDS = 0.05 wt%)

Effect of TMC and MPDA Concentration on Nanofiltration Performance

Figures 8 and 9 show the water flux and rejection performance as a function of the monomer concentration in both aqueous and organic solutions. There are the same regulations, with increasing monomer concentration water flux decreased, while rejection rate increased, then leveled off. It is worth mentioning that the varying of TMC concentration has significant effect on the performance than MPDA. There will form a dense layer on membrane surface at the concentration of TMC and MPDA at 0.3% and 0.5%, respectively.

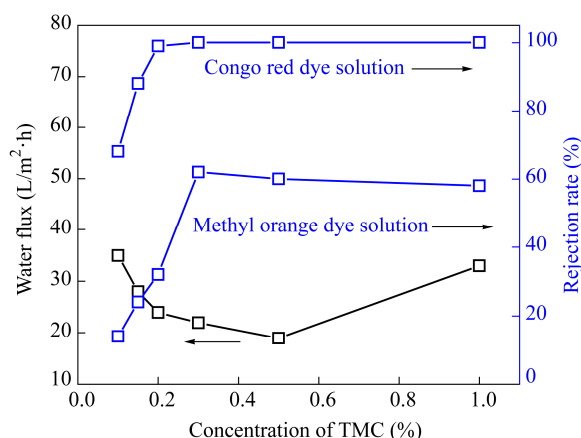


Fig. 8 Effect of TMC concentration on nanofiltration performance (MPDA = 1 wt%, SDS = 0.05 wt% and reaction time = 1 min)

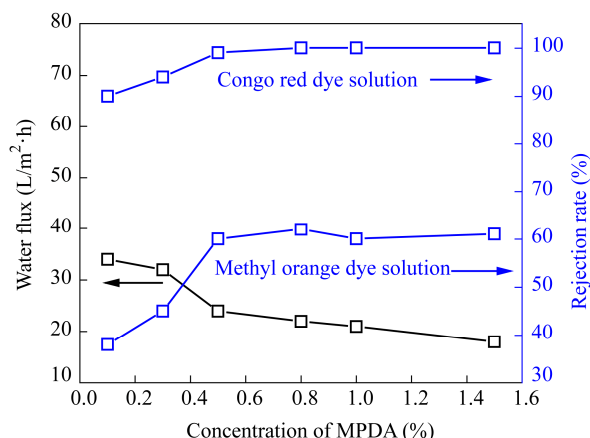


Fig. 9 Effect of MPDA concentration on nanofiltration performance (TMC = 0.3 wt%, SDS = 0.05 wt% and reaction time = 1 min)

Effect of TEA Concentration on Nanofiltration Performance

From the above preparation conditions, higher rejection rate of congo red can be gained, but the rejection performance of methyl orange, rejection rate is 60% or so, is needed to be improved. From Fig. 2, during the interfacial polymerization reaction between MPDA and TMC produces HCl, so, in order to improve reaction process and optimize reaction conditions, TEA is used in aqueous phase to neutralize the HCl. Figure 10 shows the rejection rate increases with the increasing amount of TEA added. The addition of aqueous solution with TEA concentration of 0.6% has higher rejection performance than subsequent addition of TEA, the rejection rates of methyl orange and MgSO_4 solutions are more than 90% and 60%, respectively, and the water flux is $17.8 \text{ L/m}^2\cdot\text{h}$ at 0.3 MPa.

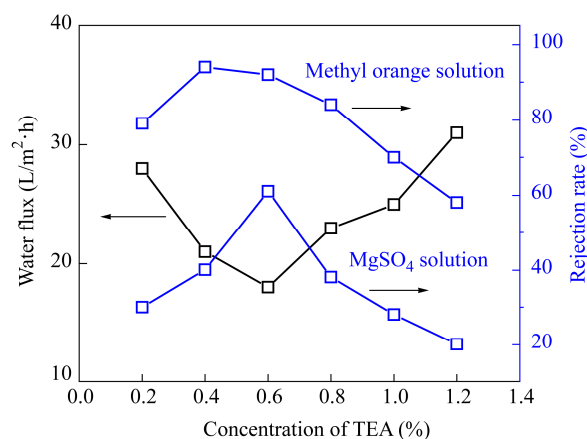


Fig. 10 Effect of TEA concentration on nanofiltration performance (MPDA = 0.5 wt%, TMC = 0.3 wt%, SDS = 0.05 wt% and reaction time = 1 min)

CONCLUSIONS

A low operating pressure PVC NF membrane was successfully prepared by interfacial polymerization between MPDA and trimesoyl chloride. Water flux of the gained nanofiltration membrane reaches 17.8 L/m²·h at 0.3 MPa. The rejection rates of methyl orange and MgSO₄ are more than 90% and 60%, respectively, MWCO is about 320 Da according to the molecular weight of methyl orange. The PVC NF membrane has the potential to be scaled up to industrial level.

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