Development of composite thin-film nanofiltration membranes based on polyethersulfone for water purification

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Abstract

Composite thin-film nanofiltration membranes were prepared by interfacial polymerization of trimesoyl chloride (TMC), polyvinyl pyrolidone (PVP) and montmorillonite (MMT) composite on the porous polyethersulfone (PES) membrane. The effect of preparation parameters were studied as; reaction time, PVP concentration and MMT content. The properties of the prepared composite thin film membranes were analyzed in terms of their chemical structure, surface morphological features, pure water contact angel, zeta potential, pure water permeation flux (PWP) and solutes rejections. The composite thin film membranes had smoother surfaces, different surface functionality and amphoteric surface with point of zero charges within pH 7-7.5. The PWP was found to increase with increasing MMT content up to 0.10 wt. %. The rejection of crystal violet dye (CV) was studied using the prepared membranes, where the membrane with 0.5 % PVP, 0.10% MMT at reaction time 6 min showed PWP of 18.1 (L/m².h.bar) and CV rejection of 80.01 %. The rejection of Na$_2$SO$_4$ and MgCl$_2$ was found to increase with MMT content and reached 96% and 35.4 %, respectively. The steady state flux was decreased by 5% with increasing MMT content from 0.10 to 0.12 wt. % reflecting antifouling improvement with MMT.

Introduction

The dyeing process and dying industries produce a mass of wastewater containing dyes and salts as sodium chloride (NaCl) and sodium sulfate (Na$_2$SO$_4$) which are used in the dyeing process. The wastewater produced from dying industry must be treated and separated using efficient separation methods. The organic dyes do not degrade naturally and the presence of dyes in aqueous systems prevents the entrance of light to water, which affect the ecosystems [1, 2]. Crystal violet (CV) is one of the dyes used in paint industry, textile industry and biotechnology, so it comes to the aqueous system through the effluent of these industries. CV has many hazards as it has a known mitotic poisoning nature, mutagenic and teratogenic effects. Many procedures were studied for dye removal from aqueous solutions.

Membrane technology was considered as an attractive separation process for wastewater treatment and decontamination. Membrane technology is developed increasingly and applied in different fields [3]. Membrane separation processes have important characteristics as high efficiency, feasible operation and produce low environmental pollution.

Nanofiltration (NF) membranes have been studied for industrial water treatment, water desalination [4–8] and pharmaceutical industries [9, 10]. The NF membranes should verify certain permeability, retention, mechanical stability and operational stability. Different procedures have been potentially studied for developing NF membranes through deposition of surface nanocomposite layer or interfacial polymerization of composite layer on porous support [11]. Different methods were applied for membrane development and fabrication of certain unique surface layer structure as; interfacial polymerization, dip coating, and layer by layer assembly [12, 13].
Nanofiltration membranes have showed efficient performance and wide applications in water purification and wastewater treatment [14, 15]. The NF technology showed efficient removal of perfluorooctanoic acid (PFOA), achieved a significant environmental impact, applied in drinking water decontamination and ground water purification [16, 17]. The process was shown to be affected by size exclusion and electrostatic interactions as well, where PFOA has relatively higher molecular weight (414 g/mol). The rejection of PFOA using NF membranes reached 90% and was found to be affected by membrane surface charge through electrostatic repulsion mechanism [18].

Composite thin film NF membranes were prepared by interfacial polymerization of sericin polymer and trimesoyl chloride (TMC) onto commercial porous support of polysulfone [19]. This study declared that the fabricated composite thin film supported membranes has smooth surface with isoelectric point of pH 4.1 and showed salt rejection of 22.5%, 40.5%, 40.8% and 95.4% for MgCl₂, MgSO₄, NaCl and Na₂SO₄, respectively at neutral pH. Composite thin film of organically bridged silica was deposited on commercial polymeric membrane (NTR-7450) [20] using a low temperature sol–gel spin-coating curing process. The produced composite thin film NF membranes were studied for the vapor permeation dehydration of water-isopropanol solutions, and the results declared a water flux of 2.3 kg/(m² h) and showed highly enhanced separation factor of 2500.

NF membranes with surface composite thin film have been prepared by interfacial polymerization of polyethyleneimine and trimesoyl chloride onto microporous supporting of polyethersulfone [21]. The prepared membranes showed improved performance as; high salt rejection (95.1% for MgCl₂, 94.4% for MgSO₄, 85.1% for NaCl and 80.5% for Na₂SO₄) and higher pure water permeation flux of 24.5 L/(m² h). Poly(vinyl alcohol)/poly(vinylidene fluoride) composite membranes modified with TiO₂ were prepared through dip-coating and applied for dye removal and wastewater treatment [22]. These membranes showed sharp performance enhancement in dye removal, salt rejection and antifouling properties.

Montmorillonite (MMT) is a layered silicate and can be easily assembled into stacked layers with defined interlayer distance providing good separation possibilities in membrane techniques. MMT has been studied as reinforcement material in polymeric composites and different matrices for various applications. The MMT polymeric nanocomposites showed important properties enhancements as liquid barrier and mechanical stability [23–26]. MMT has good swelling properties, high cation exchange capacity and has been studied for water treatment. The embedding of nanoparticles within NF membranes has been provided higher hydrophilicity, higher membrane performance and improved antifouling properties as well [27, 28]. It has been reported that the incorporation of MMT within PVC membrane showed improved performance with respect to water flux, salt rejection and antifouling properties [29]. Different studies have been performed for membrane modification using TiO₂ nanoparticles [30]. The nanoparticles modified membranes showed highly improved antifouling characteristics and high absorption properties. PVA/PSE membrane modified by depositing surface layer of TiO₂ nanoparticles were prepared and showed higher flux and higher salt rejection than the unmodified PVA/PSE [31].
In this study commercial polyethersulfone (PES) membrane was modified by interfacial surface polymerization of composite thin film of trimesoylchloride (TMC)/polyvinylpyrrolidone (PVP)-Montmorillonite (MMT). The composite thin film membranes properties were optimized in terms of reaction time, PVP concentration, MMT content and consequently the membrane performance. The structural features and surface properties of the produced membranes were analyzed by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), atomic force microscope (AFM) and surface zeta potential. The membranes performance was studied in terms of pure water permeation, salt rejection and crystal violet (CV) dye rejection. The antifouling properties were studied through antifouling experiment.

**Experimental**

**Materials:**

Polyethersulfone (PES) ultrafiltration membranes with diameter of 47 mm and pore size of 0.45 µm was purchased from GVS, USA, m-phenylenediamine (m-MPD) was obtained from Sigma Aldrich, trimethoyl chloride (TMC) was obtained from Sigma Aldrich, and hexane, dimethylformamide (DMF) as solvents were obtained from Across organics. Montmorillonite (MMT) was purchased from Sigma-Aldrich.

**Composite thin film membranes preparation:**

The PES membranes were soaked in distilled water for 5 min followed by immersion in m-PDA solution (2 wt. % in deionized) for 2 min. PVP solution of (1 wt. % in DMF) was mixed with varied amount of MMT, stirred for 1 h and sonicated for 30 min at ambient. The PVP-MMT solution was mixed with TMC solution (0.15 wt. % in hexane) with continuous stirring for obtaining the polymerization mixture. The polymerization mixture was dropped onto one side of the pretreated membrane and left for different reaction times (2, 4 or 6 min).

**Membrane characterization:**

The fabricated composite thin film membranes were analyzed for their surface structural properties by Fourier Transformed Infrared Spectroscopy-FTIR (NICOLET 6700 Thermo Scientific) at wave number range of 400–4000 cm\(^{-1}\). The surface morphological properties of the composite thin film membranes were analyzed using JEOL 6340 Scanning Electron Microscopy (SEM). The surface roughness of the prepared membranes was studied using AFM-NT-MDT (Type Next, Russia) Atomic force microscope (AFM) in non-contact mode and the analysis of film roughness were determined by the attached NT-MDT software.

**Membrane characterization:**

The filtration performance of the fabricated membranes was measured by a laboratory designed dead end filtration device. The effective testing membrane area was 12.56 cm\(^2\). Firstly, the membrane was prestabilized for 20 min with the feed sample. Appropriate concentration of CV dye 100 mg/L or the
concerned salts (MgCl\textsubscript{2} and Na\textsubscript{2}SO\textsubscript{4} 500 mg/L) were applied as feed solutions. These solutions were passed through the membrane at 40 psi, where the permeation flux (J, L/m\textsuperscript{2}·h) and rejection (R, %) were calculated by the following equations:

\[ J = \frac{V}{A\Delta t} \]

\[ R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \]

Where \( V \) is the permeated volume, \( A \) is the effective membrane area and \( \Delta t \) is the permeation time period.

The salt solution concentrations after and before permeation were measured by an electrical conductivity meter, where, CV dye concentrations were measured using UV-visible spectrophotometer.

**Antifouling experiment**

The antifouling properties of the composite thin-film membranes were studied through permeation experiments using aqueous solution of sodium alginate (SA) with 100 mg/L as fouling agent solution. The fouling results of the membranes were presented in terms of the normalized permeate fluxes with time \( J_t/J_o \), where, \( J_o \) and \( J_t \) are the water fluxes at initial and after time \( t \) of the fouling test, respectively. The values of the normalization flux should declare the antifouling behavior of the studied membrane and reflect the fouling agent deposition onto the membrane surface.

**Results And Discussion**

**Preparation of composite thin PES-TMC/PVP membranes:**

Composite thin film membranes of PES-TMC/PVP-MMT were prepared on the front side of porous support PES membrane through interfacial polymerization. The film thickness was controlled by limiting the reaction time between PES and TMC/PVP-MMT and the membrane performance was studied as a function of film thickness. The thin film has an important role in the structural properties and morphology of the membrane interface and consequently the membrane performance [32].

The reaction time, PVP concentration and MMT content, were optimized with respect to the membrane performance. The effect of reaction time and PVP concentration on the membrane performance are given in Table 1.
The results in Table 1 obviously demonstrate that both the reaction time and PVP concentration have a clear effect on the membranes performance. It is obvious that increasing reaction time decreases the PWP as a result of increasing thin film thickness and reaction time of 6 min was considered where, PWP of 13.9 L/m².h.bar was obtained. The C.V. rejection was found to be clearly improved from 68.9% at reaction time of 2 min to be 79.5% at reaction time 6 min, which refer to the increased thickness of the interface, polymerized composite thin film. The effect of MMT content in the composite thin film on the membrane performance was studied at fixed reaction time of 6 min and fixed PVP concentration of 0.5%, and the results are given in Table 2.

The results given in Table 2 demonstrate a clear improvement of membranes performance with increasing the MMT nanoparticles content up to 0.10 wt.%, where the PWP increased with increasing the MMT within 0.04–0.10 wt.%. Furthermore, the CV rejection appeared improved with the presence of MMT while a slight decrease in the rejection percentage with increasing MMT concentration up to 0.12 wt. %. The presence MMT showed sharp increase in pure water flux of PES-TMC/PVP-MMT in comparison to PES-TMC/PVP at the same reaction time and PVP concentration. These results could be explained
depending on the properties of MMT, where the surface hydrophilic properties of the interfacial layer increase with MMT and consequently enhance the water permeation through the thin-film [33–35]. The results given in Table 2 clearly illustrate the significant effect of the interfacial thin film content on the membrane performance (water flux and salt rejection). It could be deduced that the improved structural and morphological properties affect the hydraulic resistance and so affect the water permeation.

The effect of MMT content on the permeation flux was presented in Fig. 1, reflecting important role of MMT on the pure water permeability.

The membrane surface hyrophilcity was measured through determining the pure water contact angel against the MMT content in the composite thin film and the results are given in Fig. 2. The obtained results showed that the water contact angel decreases with increasing the MMT content (wt.%) which could be due to the increased hydrophilicity of the surface layer with incorporation of hydrophilic MMT nanoparticles. Notably, the water contact angel of PES-TMC/PVP membrane with zero content of MMT was found to be 83°, where the water contact angel for PES-TMC/PVP-MMT with 0.12 wt % decreased to be 62°.

**Structural and morphological properties of PES-TMC/PVP-MMT composite thin film membranes:**

The structural changes of the modified membranes were appeared in the FTIR spectrum of PES-TMC/PVP-MMT compared to the virgin PES membrane (Fig. 3). The characteristic peaks for the virgin PES appeared in Fig. 3a, where the peak appeared at 3096 and 3065 cm\(^{-1}\) assigned for the stretching vibration of aromatic –CH. The peaks appeared at 1580 and 1485 cm\(^{-1}\) assigned for the aromatic ring C = C stretching vibration. The aromatic ether band appeared around 1235 cm\(^{-1}\) and the sulfone group appeared at 837, 1110, and 1145 cm\(^{-1}\).

The PES-TMC/PVP-MMT spectra showed a sharp peak with high intensity at 1647 cm\(^{-1}\) which could assigned for the stretching vibration of amidic C = O and the shoulder appeared at 1722 cm\(^{-1}\) could be ascribed for the –C = O stretching of the carboxylic acid resulted from the hydrolysis of the acyl chloride (-COCl). The peaks at 2848 and 2928 cm\(^{-1}\) could be ascribed for the stretching vibration of C-H from the methylene (-CH\(_2\) ) of PVP. The characteristic peaks for MMT appeared in the spectra of PES-TMC/PVP-MMT at 3448 cm\(^{-1}\) for the adsorbed humidity and the peak at 1640 cm\(^{-1}\) assigned for the bending –OH of the clay surface water. The peaks at 1100 and 1050 cm\(^{-1}\) are assigned for the stretching vibration of Si-O and were found overlapped. These observations confirm the presence of interfacial polymerization of the composite thin film of TMC/PVP-MMT on the surface of PES and the formation of the amidic linkages of (-CONH-) on the active surface layer.

The surface morphological features of the produced composite thin film membranes were studied using SEM and AFM. The SEM images of PES and PES-TMC/PVP-MMT are presented in Fig. 4(a-f). The images
show that the interfacial polymerization of TMC/PVP-MMT onto the PES surface produces highly dense and smooth surface and declared the formation of surface active layer of TMC/PVP-MMT onto the porous surface of PES. The SEM images of PES-TMC/PVP-MMT demonstrate the formation of thin film with considerable thickness, and no particles agglomeration. The presence of MMT showed no clear folds or wrinkles, where PVP could coat the surface composite thin film. The SEM images refer to the fast growth of the surface thin film, which indicate that the polymerization may occurred not only on the PES surface but also within the MMT layer which cause more layer thickness and decrease the MMT interlayer distance. However, the improved surface properties due to the presence of MMT content appeared up to 0.1 wt% and the effect diminishes at higher MMT content of 0.12 wt%. The presence of MMT with low content in the thin film composite may increase the thermodynamic incompatibility between polymer and solvent due its hydrophilic nature, which could affect the surface morphological properties [36]. The hydrophilic properties of MMT particles may also affect the entrance of water into the membrane body and facilitate the water-solvent exchange and so decrease the formation of sponge like structure, while instead larger finger like macro-voids could be formed [37].

Furthermore, the variation of pure water permeability relative to the variation was of pure water contact angel depending on MMT content refer to the potential surface structural and morphological changes due to the interfacial polymerization of the composite thin film [38–40].

The AFM images of the prepared membranes are given in Fig. 4(g-j) depecting further information about the membrane surface morphology. The images clearly depict that the surface of the composite surface layer appeared smoother after the formation of thin film composite. The surface roughness was determined as the root mean square roughness (RMS) to indicate the surface roughness of the prepared composite membranes and was found to be 51.16 nm for PES and 48.28 nm for surface modified membrane PES-TMC/PVP-MMT.

These results refer to a smooth surface layer produced through interfacial polymerization, which may due to the limited depth of the reaction and the formation of barrier layer. The smooth surface represent an advantage for the membrane fouling resistance [36].

The surface charge is an important parameter depending on the membrane content which could affect the membrane performance. The prepared composite membrane surface charges was studied by measuring the potential at different pH (3.5–10) and the results were given in Fig. 5. Obivously, the prepared membranes with interfacially formed surface composite thin film showed amphoteric surface with point of zero charge at pH 7-7.5. The results showed that the membranes are positively charged at pH below 7 and are negatively charged at pH higher than 7.5 and the isoelectric points were found shifted towards higher pH with increasing the MMT content.

The salt rejection behavior of the PES-TMC/PVP-MMT with varied MMT content ratio was studied through permeation experiments for salt solutions containing MgCl$_2$ and Na$_2$SO$_4$. The results presented in Fig. 6 showed that the rejection for Na$_2$SO$_4$ was found to be greatly higher than that for MgCl$_2$. The
rejection of electrolyt solution is related to membrane pore size and the electrostatic interaction between the membrane and the diffusion coefficient of the salts\cite{20, 41}. The observed high rejection for Na$_2$SO$_4$ than MgCl$_2$ could be explained due to membrane surface charge and the effect of diffusion coefficient of studied salts as well. Where, the diffusion coefficient in the membrane can be considered to be approximately as in aqueous solutions. The diffusion of Na$_2$SO$_4$ is slightly lower than that for MgCl$_2$ which contribute in the higher rejection of Na$_2$SO$_4$.

**Crystal violet dye removal characteristics of PES-TMC/PVP-MMT membrane:**

The rejection behavior of CV dye from aqueous solution was studied using the prepared composite thin film membranes PES-TMC/PVP-MMT containing different MMT content ratio (PES-NF3, PES-NF4, PES-NF5). The permeation of CV dye solution (100 mg/l) was studied at pH 7 and 0.276 MPa. The dye solution permeate flux was studied at different permeation time and the results are given in Fig. 7.

| Membrane  | Steady state flux (l/m$^2$.h) | Steady state CV removal (%) |
|-----------|-----------------------------|-----------------------------|
| PES-NF3   | 58                          | 95.3                        |
| PES-NF4   | 54                          | 97.8                        |
| PES-NF5   | 52                          | 99.6                        |

The results in Fig. 7 showed that the PES-TMC/PVP-MMT membranes effectively remove the CV dye especially NF5 and the dye solution flux decreased clearly with increasing the MMT content in the interfacial polymerized thin film and reached steady state. It was reported that both the electrostatic interaction and steric hindrance highly affect both the rejection and permeation of CV dye via PES-TMC/PVP-MMT membrane \cite{42, 43}. The results showed slow rate of flux decrease, which reflect the potential antifouling behavior of the composite thin film based membrane towards the CV aqueous solution and the possible high rejection of higher molecular weight organic dyes. This finding could be explained to be due to the surface smoothness of the surface thin film and the electrostatic interaction under these experimental conditions and the dye predominate species under the experiment pH.

**Antifouling behavior of PES-TMC/PVP-MMT membrane:**

The antifouling behavior of the fabricated PES-TMC/PVP-MMT membrane was evaluated in permeation process of aqueous solution of 100 mg/l SA at pH 7.0 and temperature of 25 °C. Where, PES-NF4 and PES-NF5 membranes were applied for fouling experiments and the fouling agents have larger molecular size compared with nanofiltration membrane pore size. Consequently, the fouling molecules couldn’t pass through the membrane pores during the solution permeation and causes fouling for the membrane surface. The surface fouling process was performed at permeation flux of 70.01 l/m$^2$h to verify the
required permeation driving hydrodynamic force on the fouling process. The normalized flux \(J_t/J_0\) of the studied membranes NF4 and NF5 to SA solutions are presented Fig. 8.

The results in Fig. 8 showed that the membranes fluxes for SA solutions decreased sharply followed by slow decrease with time. These results could be due the deposition of the fouling agent molecules on the surface of membranes till reaching the steady state between 15–25 h. The steady state flux for PES-NF5 membrane decreased with ratio of 5% for SA aqueous solutions. These findings reflect the role of MMT content in the composite thin film in improving the antifouling behavior of the membrane. The membrane with higher MMT content (PES-NF5) showed better performance in fouling resistance. It was previously reported that the fouling agents could be adsorbed onto the membrane surface via hydrophobic actions, hydrogen bond, electrostatic interactions and van der Waals forces. Consequently, the fouling effect could be vanished through decreasing the adsorptive driving forces and enhancing the repulsive interactions of membrane surface with the fouling molecules [44–45]. Notably, the membrane surface tends to be negatively charged under the specified testing conditions so, certain electrostatic repulsive forces could occur between membrane surface and the fouling agent, resulting in lower fouling effect.

The presence of the MMT within the interfacial composite thin film showed improvement in antifouling behavior, resulting in higher flux recovery ratio (FRR). These results could be due to the increased hydrophilic spots within the composite thin film, which inhibit the interaction of fouling molecules with the membrane active surface groups. It has been reported that the surface hydrophilicity is a limiting parameter for surface adsorption behavior [46–47]. The increased hydrophilicity by the presence of MMT was confirmed also by the decreased water contact angle with increasing of MMT concentration.

The fouling reversibility and membrane durability are mainly dependent on the weak bonding between the fouling molecules and the membrane surface. Consequently, the membranes could be easily washed out and re-applied in repeated fouling experiments to analyze the membrane stability and durability. The SA solution was applied as feed solution till steady state followed by washing all the permeation equipment and the used membrane by distilled water. The washed membrane was applied in pure water permeation to evaluate the pure water flux and determine the flux recovery ratio (FRR %) as below:

\[
FRR\% = \left(\frac{J_{w2}}{J_{w1}}\right) \times 100
\]

where \(J_{w2}\) is the pure water flux after fouling process and \(J_{w1}\) is the pure water flux before the fouling process.

The fouling process was repeated to analyze the membrane durability and stability and the results were given in Table 4.
Table 4
Flux recovery ratio for PES-NF4 and PES-NF5 membranes after repeated SA fouling-cleaning cycles

| Fouling-cleaning cycles | FRR%  |
|-------------------------|-------|
|                         | NF4   | NF5   |
| 1st cycle               | 95%   | 96%   |
| 2nd cycle               | 90%   | 92%   |
| 3rd cycle               | 81%   | 89%   |
| 4th cycle               | 76%   | 81%   |

The results in Table 4 clearly show that the NF4 and NF5 membranes are relatively stable until the fourth fouling-cleaning cycle. The obtained results showed enhanced membrane stability, durability and enhanced FRR performance, which reflects the potential application of the PES-TMC/PVP-MMT membrane for water treatment.

**Conclusion**

In this study the preparation of thin film composite nanofiltration membranes was studied by interfacial polymerization of TMC/PVP-MMT on the porous support PES. Considerable film thickness with improved properties was prepared at 6 min reaction time, 0.5 wt.% PVP and 0.1 wt.% MMT. The structural and morphological analysis using FTIR, SEM and AFM declared the difference between the virgin support PES and the thin film composite membranes PES TMC/PVP-MMT. The pure water contact angel of the prepared PES-TMC/PVP-MMT membrane (with 0.1 wt.% MMT) decreased to 62° compared to 83° for PES-TMC/PVP membrane. The zeta potential of PES-TMC/PVP-MMT showed variation with increasing MMT content and showed amphoteric surface with at pH 7-7.5. The PWP was found to increase with increasing MMT content up to 0.10 wt. %. The rejection of crystal violet dye (CV) reached 80% using PES-TMC/PVP-MMT PWP and the salts (Na₂SO₄ and MgCl₂) rejection was found to increase with MMT content and reached 96% and 35.4%, respectively. The steady state flux was lowered by 5% with increasing MMT content from 0.10 to 0.12 wt. % and the FRR% provided the enhanced membrane stability, durability and antifouling performance.

**Declarations**

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**Declarations Conflict of interest**
The authors confirm that there are no known conflicts of interest associated with this publication.

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Figures

![Graph](image-url)

**Figure 1**

Effect MMT content (wt.%) in composite thin film membrane PES-TMC/PVP-MMT on the pure water permeability.
Figure 2

Effect MMT content ratio on the pure water contact angle of PES-TMC/PVP-MMT composite thin film membranes.
Figure 3

FTIR spectra of virgin PES membrane and PES-TMC/PVP-MMT membrane with 0.1 wt. % MMT

Figure 4

SEM images for PES-(a-c), PES-TMC/PVP-MMT-(d-f) and AFM images for PES-(g-h), PES-TMC/PVP-MMT-(h).
Figure 5

Surface zeta potential for PES-TMC/PVP-MMT membranes of different MMT content ratio in terms of pH.
Figure 6

Effect of MMT concentration in PES-TMC/PVP-MMT modified membrane on the rejection of MgCl$_2$ or Na$_2$SO$_4$. 
Figure 7

Permeation flux of CV dye solutions after different permeation time using PES-TMC/PVP-MMT containing different concentrations of MMT
Figure 8

Effect of filtration time of SA solution on the normalized flux of PES-TMC/PVP-MMT membranes with different MMT concentrations.