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Preparation of new 2D MXene/cellulose acetate mixed matrix membrane with excellent performance

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ABSTRACT

Inorganic nanosheets materials are attracting more and more attention to prepare mixed matrix membrane (MMM) with excellent performance. MXene, a new kind of 2D transition metal carbides material, has the similar lamellar structure as graphene oxide and it is a potential material of separation membrane. In this work, the typical MXene material named $Ti_3C_2T_x$ is used to prepare MXene/cellulose acetate (CA) MMM with phase inversion method. The scanning electronic microscopic images of the membrane show the dense functional layer without visible defects. The MXene/CA MMM prepared with 18% CA and 3% MXene shows high rejection to Gentian Violet (408 Da) 100% with flux of 4.2 L/m^2 h at 0.3 MPa. It also has high rejection to Na_2SO_4 89.6% with flux of 4.8 L/m^2 h at 0.3 MPa. After crosslinking with 5% glutaraldehyde at 60°C, the MMM performance does not decline after immersion in 50% dimethylacetamide solution for 12 d, which means excellent solvent resistance of the membrane. Compared with CA membrane, MXene/CA MMM also has better fouling resistance.

Keywords: MXene; Cellulose acetate; Mixed matrix membrane; $Ti_3C_2T_x$; Desalination

1. Introduction

Polymer membranes have the properties of good membrane forming ability, excellent permselectivity, and low cost. They are widely used in the process of wastewater treatment and desalination [1]. Membrane fouling is a major obstacle in membrane separation for water treatment. The chlorination and ozonization of feedwater are the most common antifouling strategies. However, the membrane structures will be damaged by such chemical oxidation [2]. Cellulose acetate (CA) is a kind of hydrophilic material with high resistance to fouling and chlorine resistance. CA membrane also has superior pemselectivity, so it is widely used in microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and gas separation [3]. In order to further improve the performance of CA membrane, a lot of modification methods such as crosslinking, preparation of mixed matrix membrane (MMM) are used [4,5]. Heterogeneous MMM consists of inorganic filler embedded in a polymer matrix. It combines the solvent resistance and thermal resistance of inorganic membranes with the process ability and good permselectivity of polymeric membranes. It has shown great advantages in membrane-based gas separations and pervaporation [6,7]. Recently, MXene, a member of novel inorganic 2D materials, has attracted great research interest, because of its hydrophilic surface, lamellar structure, excellent chemical stability, and electrical conductivity [8–10]. It is often produced with a MAX phase (where M represents an early transition metal, A corresponds to IIIA or IVA group elements, and X is C or N) powders in hydrofloric acid (HF) solutions with Al etched at ambient temperatures. $Ti_3C_2T_x$ is a typical MXene material which is etched by HF from Ti_3AlC_2, where T represents O,

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OH, and/or F groups while x is the number of the terminating groups. MXene has been widely studied in fabrication of super capacitors [11], lithium-ion batteries [12], and heavy metal adsorption [13] because of its layered structure-like graphene oxide and large surface areas. A 2D micrometer-thick MXene membrane has been prepared with the assembling of $Ti_3C_2T_x$ nanosheets to study the selective rejection of ions and molecules. It is demonstrated that the MXene has differential sieving of salts depending on both the hydration radius and charge of the ions [14]. Wu et al. [15] used $Ti_3C_2T_x$ nanosheets as nanofillers to prepare solvent resistant nanofiltration composite membrane. It is found that the uniformly dispersed $Ti_3C_2T_x$ nanosheets enhanced the thermal/mechanical stabilities and solvent resistance of the polymer-based membranes. Wang's group prepared a kind of 2D lamellar membrane with $Ti_3C_2T_x$ MXene nanosheets supported on anode aluminum oxide substrate for the first time. The MXene membrane shows excellent water permeability (more than 1,000 L/m^2 h) at vacuum of 0.1 MPa and favorable rejection rate (over 90%) for molecules with sizes around 2.5 nm because it has been modified with nanosized particles and shows extremely short transport pathway and large amounts of nanochannels [16]. A kind of MXene/polyether sulfone composite membrane has been prepared in our previous work, which shows excellent hydrophilicity and flux which has great potential in wastewater treatment [17].

In this work, the $Ti_3C_2T_x$ is produced by etching Ti_3AlC_2 with HF. After ultrasonication, it is introduced in the CA casting solution for the first time to prepare the MXene/CA MMM with simple phase inversion method. The morphology, ATR-FTIR, hydrophilicity, and separation performance of the MMMs are studied in detail. The solvent resistance and antifouling performance are also investigated in the experiment.

2. Experimental

2.1. Materials and instruments

The average particle size of the Ti_3AlC_2 used in the experiment is about 3 μm (98%, Beijing Fusiman). CA (content of acetyl group 39.8 wt%, content of hydroxyl group 3.5 wt%) and HF (49 wt%) are purchased from Aladdin (Shanghai, China). Other chemicals used in the experiments are analytical purity grade and used without further purification.

2.2. Membrane preparation

The $Ti_3C_2T_x$ is produced by etching Ti_3AlC_2 with 49 wt% HF at 50°C for 4 h and it is filtrated and neutralized to at least pH 6, then dried in the air at room temperature to obtain MXene. It is delaminated in dimethyl sulfoxide (DMSO) with ultrasonication for 1 h. Then, the solution is filtrated and dried to obtain lamellar MXene material. CA solution (18 wt%) is prepared with dimethylacetamide (DMAc) used as solvent. MXene is added in the CA casting solution with strong stirring and ultrasonication to prepare MMM. The membrane is prepared with phase inversion method and ice-water bath is used as coagulation bath with 30 s evaporation time. All the membranes are immersed in 4% glutaraldehyde solution at 60°C for 20 min to improve the solvent and chemical resistance of the membranes. Effect of MXene content on the membrane performance and morphology is studied in detail.

2.3. Membrane characterization

The performances of the membrane are mainly described by product water flux, J, and rejection, R. The membranes were characterized in the dead-end membrane module after they were pretreated under the pressure of 0.3 MPa for 30 min. The membrane performances including water flux, salt rejection (1 g/L), and dye rejection (100 ppm) were measured under the pressure of 0.3 MPa at 20°C. The permeation flux, F, is calculated as follows:

$$F = \frac{W}{At} \tag{1}$$

where W is the total weight of the water or solution permeated during the experiment; A is the membrane area; and t is the operation time. Rejection, R, is calculated using the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right)\% \tag{2}$$

where C_p and C_f are the concentration of the permeate solution and the feed solution, respectively. All the experiments on flux and rejection were repeated for three times. The relative standard deviation of the data is lower than 15%. The membrane rejection is tested with conductivity meter (DDS-11A, Shanghai Rex Electric Chemical Instrument Co., Ltd.) and UV-Vis Spectrometer (721, Shanghai Youke). The membranes are tested with scanning electronic microscopy (SEM, NanoSEM 450, FEI) and FTIR-ATR (Nicolet-20DXB).

3. Results and discussion

3.1. Characterization of MXene

In order to obtain lamellar MXene, Ti_3AlC_2 is etched with 49 wt% HF at 50°C for 4 h and it is neutralized and filtrated, then dried in the air at room temperature. SEM is used to analyze the change of morphology. As shown in Fig. 1, the particles of Ti_3AlC_2 are very dense solid materials without any ion channel. After treatment, the lamellar $Ti_3C_2T_x$ is successfully formed with the enlarged interplanar spacing because Al is etched with HF. The lamellar MXene is a potential water and ions transport pathway which is meaningful for membrane preparation.

3.2. Characterization of the MMMs

In order to prepare MXene/CA MMMs, MXene is delaminated in DMSO with ultrasonication and added in the CA solution with strong stirring. The constitutions of the casting solution with MXene content changed from 0 to 4% are listed in Table 1. The top surface and cross-section morphologies of the MMMs are shown in Fig. 2. When the polymer content is fixed 18%, the membrane surface changes from smooth to rough with the increase of MXene content. No defect is observed in the top surface of the membrane because the inorganic particles and the CA are all hydrophilic

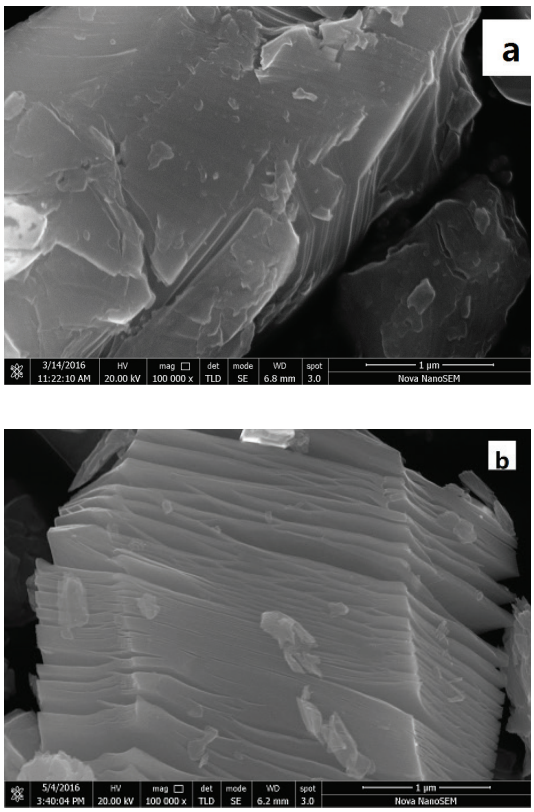

Fig. 1. The morphology of the materials (a) Ti_3AlC_2 and (b) $Ti_3C_2T_x$.

Table 1
Substance constitution of the MMMs

Membrane	CA content (wt%)	MXene content (wt%)
M0	18	0
M1	18	1
M2	18	2
M3	18	3
M4	18	4

and the particles are uniformly encapsulated in the polymer matrix. The cross-section morphologies of the MMMs also demonstrate the good compatibility of the membrane materials. With the increase of MXene content, the membranes become denser and a lot of nanosized particles are observed uniformly encapsulated in the cross-section of MMM [18].

The sharp peak that can be seen in Fig. 3 around 1,750 cm^{-1} is a typical acetate peak (C–O) of CA. The smoother peak that can be seen around 3,400 cm^{-1} is a O–H peak of CA. However, with the increase of MXene content, there are little new peaks observed. It may be caused by that the main functional group of MXene is O–H and the most of the MXene particles are encapsulated in polymer matrix.

The contact angle is tested with three parallel data after the drops stabilize for 5 s. MXene has good hydrophilicity with functional group in the surface of material. With the increase of MXene content, the contact angle decreases accordingly as shown in Table 2, which partially confirms the increase of hydrophilicity of the MMM.

3.3. The separation performance of the MMMs

With the polymer content fixed 18 wt%, the performance of membrane with different MXene contents is investigated. As shown in Fig. 4, when the MXene content increases from 0 to 4%, the rejection to Na_2SO_4 increases first then declines. When the MXene content is 3%, the membrane has the largest rejection of 89.6% to the Na_2SO_4 solution with suitable flux 4.8 L/m^2 h at 0.3 MPa. The hydrophilic inorganic additive causes instantaneous phase separation and induces the denser functional layer. When the MXene content is further elevated, the viscosity of the casting solution is too high to obtain defect-free membrane. So the MXene content is fixed below 4% to prepare MMMs with different performance. The desalination performance of the MMMs is also tested with $MgCl_2$ and NaCl solution as shown in Figs. 5 and 6. The rejections and fluxes show similar law as Na_2SO_4 testing process. The membrane has high rejections to Na_2SO_4 and $MgCl_2$ and suitable flux at 0.3 MPa, which means the MMMs are typical nanofiltration membranes and potential candidates for desalination.

The performance of the MMMs is also tested with typical dye solution including Congo Red (697 Da) and Gentian Violet (408 Da) at 0.3 MPa as shown in Figs. 7 and 8. With the increase of MXene content, the rejection to Congo Red dye is elevated from 92% to 99% and the membrane flux dose not decline obviously. The MMMs also have high rejections to Gentian Violet dye as shown in Fig. 8. The introduction of MXene particles in the polymer matrix improves the hydrophilicity of the membrane and lowers the membrane fouling obviously. The dye molecules adsorbed in the membrane pores are little. So the membrane has similar flux as desalination process.

The MXene/CA MMM prepared with 3% MXene has relatively high permselectivity and its performance is listed in Table 3. The MXene/CA MMM has rejection to Na_2SO_4 and $MgCl_2$ and dye molecules. It will be a potential membrane for heavy metal ions and dye wastewater treatment.

3.4. The solvent resistance and antifouling performance of the MMMs

DMAc is used as solvent to prepare the MXene/CA MMM because it is the good solvent of CA. In this work, the solvent resistance of the membrane is tested with membrane static immersed in 50% DMAc solution at room temperature. It is found that, after crosslinking with glutaraldehyde at 60°C for 20 min, the membrane shows good solvent resistance. As shown in Fig. 9, the performance of membrane with static immersion in 50% DMAc solution does not decline during 12 d, which demonstrates the good solvent resistance of the prepared MXene/CA MMM.

As shown in Fig. 10, the antifouling performance of M0 and M3 is compared with Congo Red testing. Both the membranes have good antifouling performance at dye filtration and the flux does not decline obviously with the operating time. And the rejections to the dye are all 100% during the filtration. The M3 membrane has low initial flux, however, its flux declines much less and easier to clean compared with M0 membrane which confirms the positive effect of MXene on membrane fouling.

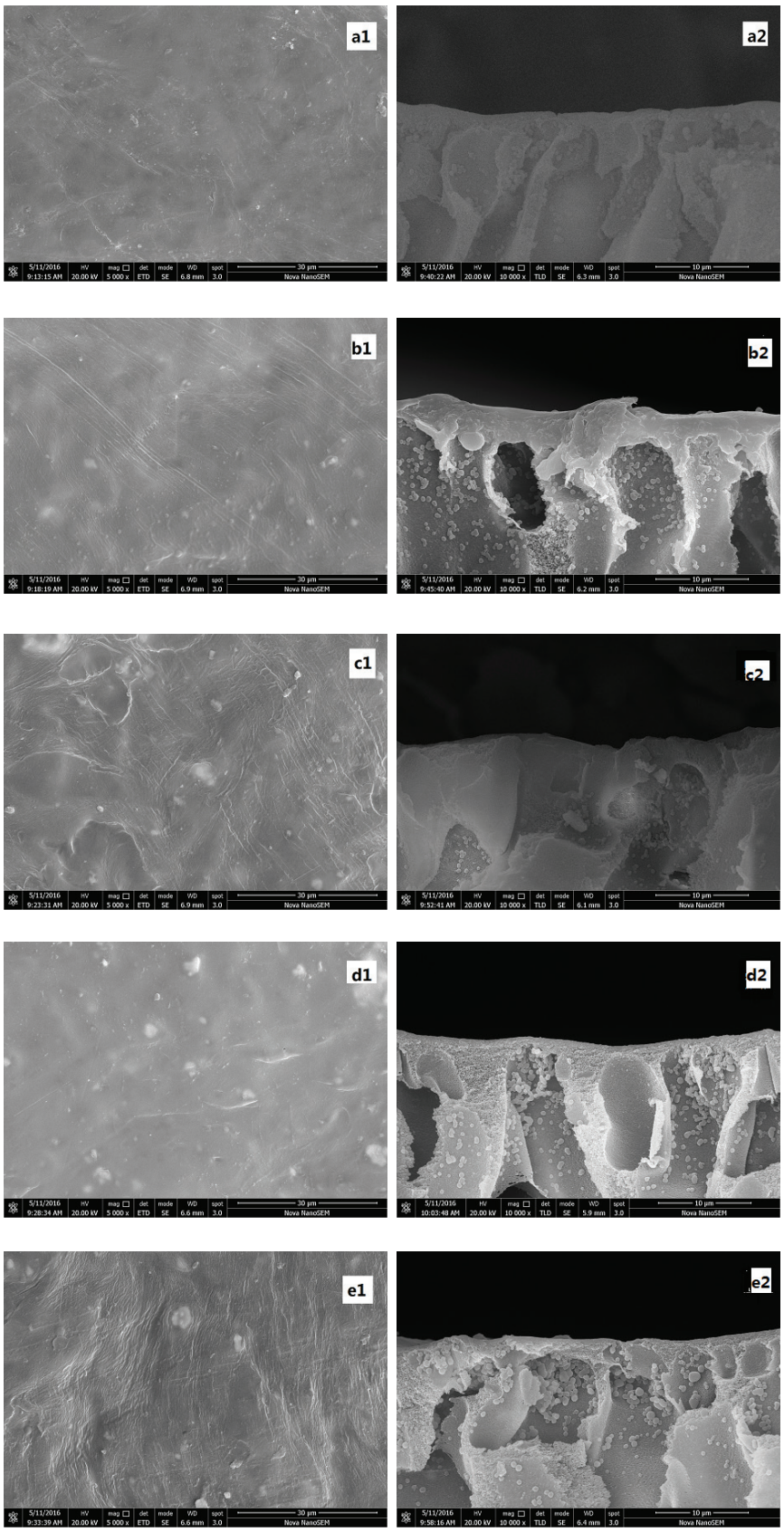

Fig. 2. The morphology of the prepared MXene/CA MMMs (a) no MXene; (b) 1% MXene; (c) 2% MXene; (d) 3% MXene; (e) 4% MXene; (1) top surface; and (2) cross-section.

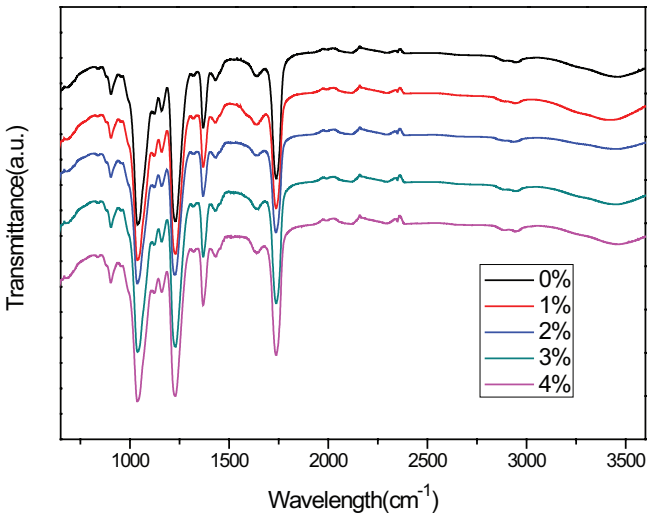

Fig. 3. The FTIR-ATR spectrum of MMMs.

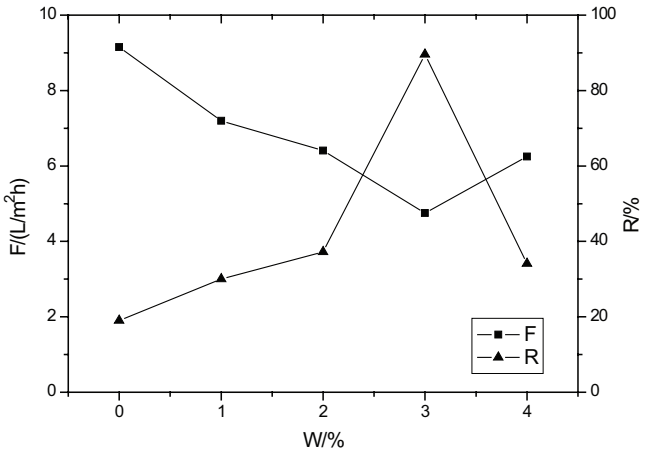

Fig. 4. The performance of the MMMs with different MXene contents (1 g/L Na_2SO_4 solution and 0.3 MPa).

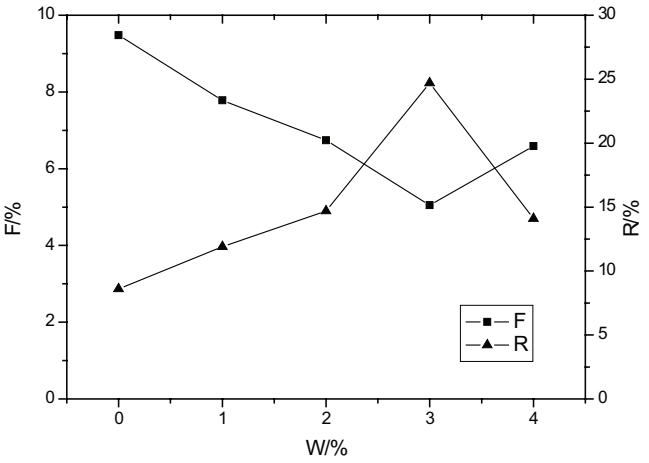

Fig. 5. The performance of the MMMs with different MXene contents (1 g/L NaCl solution, 0.3 MPa).

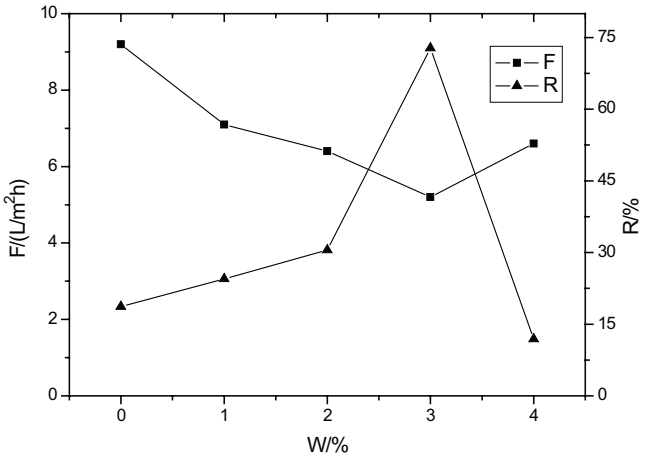

Fig. 6. The performance of the MMMs with different MXene contents (1 g/L $MgCl_2$ solution and 0.3 MPa).

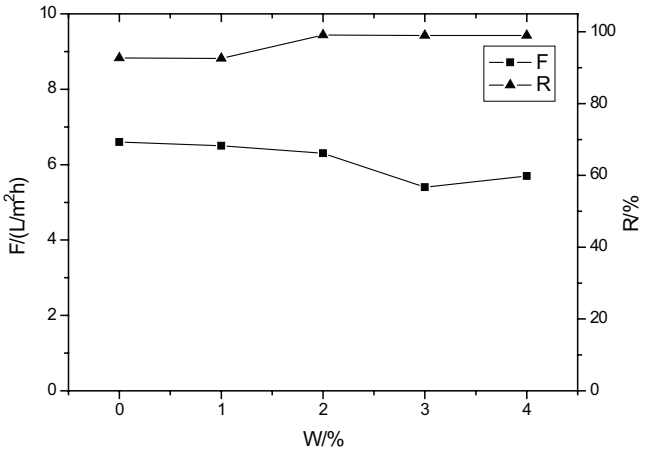

Fig. 7. The performance of the MMMs with different MXene contents (100 mg/L Congo Red solution and 0.3 MPa).

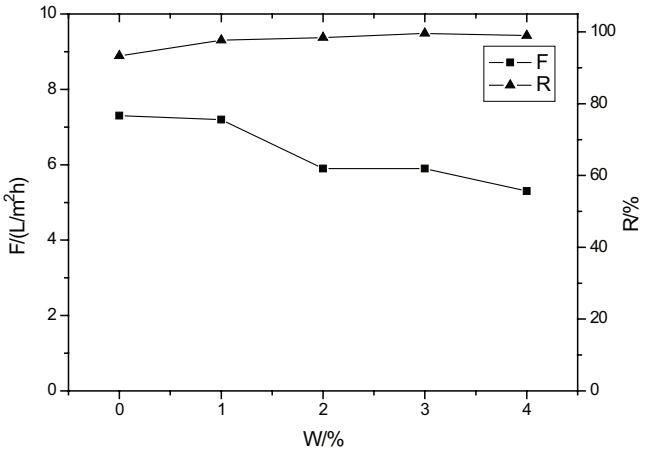

Fig. 8. The performance of the MMMs with different MXene contents (100 mg/L Gentian Violet solution and 0.3 MPa).

Table 2
The contact angle of the MMMs

Membrane	Contact angle (°)
M0	68
M1	63
M2	60
M3	57
M4	58

Table 3
Performance of the MMM with 3% MXene (0.3 MPa)

Feed	*F* (L/m² h)	*R* (%)
Congo Red	5.4	99
Gentian Violet	4.2	100
$MgCl_2$	5.2	73
Na_2SO_4	4.8	89.6
NaCl	5.1	25

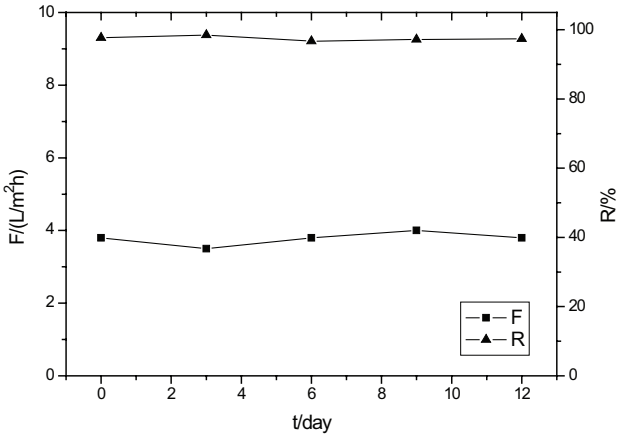

Fig. 9. The performance of the MMMs with immersion in 50% DMAc solution (M2, 100 mg/L, Congo Red solution, and 0.3 MPa).

4. Conclusions

In conclusion, the lamellar MXene material $Ti_3C_2T_x$ is etched with HF from Ti_3AlC_2 and used as inorganic nanosheets additive. A series of a 2D MXene/CA MMMs based on phase inversion method are prepared successfully. The MMMs show rough and dense surface layer and MXene is encapsulated uniformly in the polymer matrix. The MMM exhibits an increased rejection to dyes and inorganic salts when the MXene content is increased. When the MXene is fixed 3%, the membrane shows high rejections to Congo Red dye (99%), Gentian Violet (100%), Na_2SO_4 (89.6%), and relatively high flux (about 4.8 L/m² h) at 0.3 MPa. Its rejection to inorganic salts NaCl is below 25%, which indicates that the membrane can be used with extremely high efficient in dye desalination and wastewater treatment. After cross-linking, the membrane shows good solvent resistance and the membrane performance does not decline with membrane immersed in 50% DMAc solution. It also shows good antifouling performance with hydrophilic MXene used as additive.

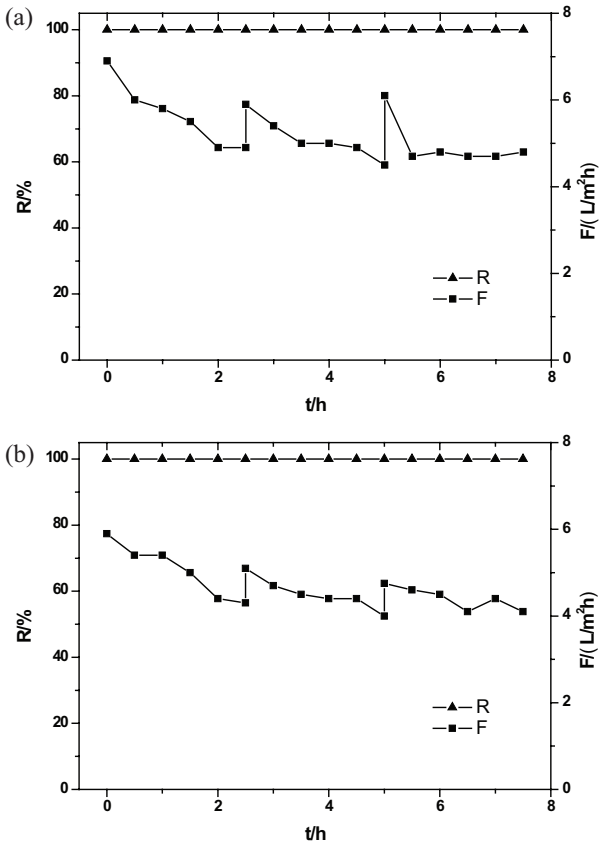

Fig. 10. The antifouling performance of the MMMs (top, M0; bottom, M3; testing solution: 100 mg/L, Congo Red solution, 0.3 MPa; the membrane is cleaned with detergent at 2.5 h, and 1% HCl at 5 h).

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