

Hydrophilic modification and anti-fouling properties of PVDF ultrafiltration membrane via blending of nano-particle MIL-101 MOFs

H. Wang, H. Chen, Y. Zeng, G. R. Chen, M. B. Cui*

College of Chemistry and Materials Engineering, Xinxiang University, Xinxiang 453003, P. R. China

In this work, a new hydrophilic Polyvinylidene fluoride (PVDF) ultrafiltration membrane was prepared by blending of Metal-Organic frameworks (MOFs) -MIL-101 using the phase inversion method. The effect of the MIL-101 on the morphology and efficiency of the modified membranes was researched. The nano-particle and prepared membranes were all characterized by various physicochemical techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM) and water contact angle. The experimental results showed that the modified membranes showed high hydrophilicity and increased pure water flux (up to 352.8 L/m² •h) compared to the pure membrane. Furthermore, the antifouling properties of the membranes were improved. The 0.2wt% MIL-101/PVDF membrane demonstrated the highest flux recovery ratio (FRR) value (90.4%) and the lowest irreversible fouling resistance (R_{ir}) value (9.6%). The oil rejection >99% for the 10,000 ppm engine oil/water mixture showed the modified membrane has a good treatment effect on oil-water separation. Blending low concentration of MIL-101 could endow the PVDF membranes had higher pure water flux, rejection rate and better antifouling property than the pure membrane.

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1. Introduction

With the development of economy and society, the requirements of drinking water standard have also enhanced rapidly. Nowadays, the freshwater water deficiency has been one of the most important issues affecting many countries in the whole world [1,2]. Membrane separation technology has the characteristics of high separation efficiency, low energy consumption and convenient operation [3,4]. It is widely used in chemical, pharmaceutical, food, biochemical and other fields. Especially in the field of water treatment, membrane separation technology has become the current mainstream technology, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) process[5-7]. In the petrochemical, textile, steel, leather and food industries, the treatment of oily wastewater is a problem. There are many methods for separating oil-water mixtures, but these methods are relatively complex and not efficient [8]. Wettability is an important factor in the separation of oil wastewater. The hydrophilic membrane has good wettability and can be well used in oil-water separation [9-11].

The separation effect and the service life of the device are directly affected by the performance of membrane material as the “chip” of the membrane separation process [12]. Polyvinylidene fluoride (PVDF) has been widely used as membrane materials in recent years because of its advantages such as high temperature resistance, good toughness, good mechanical properties and stable chemical properties[13,14]. The PVDF membrane is generally prepared by non-solvents induced phase separation (NIPS) method. But due to the hydrophobic nature of PVDF, the membrane is easy to fouling during the separation process [15,16]. It is well known that membrane fouling is one of the most intractable problems in membrane processes, it can reduce the flux of membrane and improve the cost. Hence it is necessary to design and prepare a composite PVDF membrane material that can reduce membrane pollution and increase membrane permeation flux [17].

* Corresponding author: wyzhui19@163.com

There are many approaches to decrease the membrane fouling, one of the effective methods is to ameliorate the hydrophilicity of membrane surface, several techniques are reported[18,19]. These approaches include blending hydrophilic polymer or hydrophilic nanoparticles[20,21], coating[22,23], grafting with a photo or plasma polymerization to fix hydrophilic segments on the membrane surface[24,25]. Blending hydrophilic materials to polymer is regarded as a convenient and effective way for hydrophilic modification of polymer membranes. Various hydrophilic polymers such as PVP, PEG have been blended into membranes to improve the hydrophilicity, permeability and antifouling properties. Some nanomaterials such as: TiO₂ [26], graphene oxide/TiO₂[27], Al₂O₃ [28], SiO₂[29], ZnO[30,31], Ag[32,33], Fe₃O₄[34], multi-walled carbon nanotubes (MWCNTs) [35] and metal-organic frameworks[36] were also employed as blending materials to improve anti-fouling performance of membranes.

Metal-organic frameworks (MOFs) which are composed of metal ions and organic ligands, have been intensively researched in the last decade because of their extraordinary high surface area and porosity, capability for functionalization, affinity for certain molecules, tunable chemical composition and flexible structure[37,38]. Compared with traditional inorganic particles with 'rigid' frameworks, the organic nature the framework for MOFs may facilitate interactions with the polymer that allow a good compatibility.

Compared to the pristine membrane, blending MOFs into membrane matrix are expected to exhibit enhanced permeability and possibly selectivity. Up to now, there have been several researches partially related to MOFs blending membranes for liquid separation application [39,40]. Gholami[41] fabricated a new hydrophilic polyethersulfone (PES) ultrafiltration membrane by blending of TMU-5 Metal-Organic frameworks (MOFs). The results showed TMU-5 nanoparticles were added at low concentrations (0.1 wt%), the pore size and porosity of the membrane increased, pure water flux increased to 182(kg/m² •h), the flux recovery ratio (FRR) value was the highest (98.74%), the irreversible fouling resistance (RIR) value was the lowest (1.25%).The membrane had a >98% retention of the solution of 40,000 ppm engine oil / water mixture, which had a great advantage in oil-water separation compared with the unblended PES membrane. Soto [42] prepared a series of Zn-Co MOFs materials, which were blended with polyethersulfone (PES), and the composite membranes were prepared by phase inversion method. The contact angle of Co 100 blend membranes had the highest hydrophilicity, water flux, porosity and BSA rejection. Makhetha[43] prepared two nanocomposite Cu(tpa) MOFs loaded on graphene oxide (Cu(tpa)@GO), and produced a series of Cu(tpa)@GO polyethersulfone (PES) composite membranes by phase inversion method. The composite membrane exhibited high hydrophilicity and pure water flux relative to the pristine PES and GO/PES membranes. In addition, the selective anionic dye rejection rates of Congo Red and Methyl Orange were >80% and 50% for these Cu (tpa)@ GO/PES membranes, and the selective anionic dye rejection of Methylene Blue <20%. In membranes modified with MOFs, the combination of highly selective pores and hydrophilicity can result in both high selectivity and antifouling properties, which is very helpful for manufacturing competitive industrial separation membranes.

In this research, a novel PVDF membrane by blending of nanosized metal-organic frameworks (MOFs) -MIL-101particles was fabricated. Firstly, the MIL-101 particles were synthesized via a facile synthesis process and characterized. Secondly these nanomaterials were blended with PVDF to prepare membranes using the NIPS method. The effect of MIL-101 nanoparticles on the casting solution on the hydrophilicity, separation performance and antifouling properties of the membranes was investigated. The membrane structure and morphology were characterized using water contact angle, atomic force microscopy (AFM) and scanning electron microscopy (SEM).

2. Experimental section

2.1. Materials

4-nitroimidazole, Terephthalic acid, Chromium nitrate and Polyvinyl pyrrolidone (PVP) were all bought from Aladdin Chemical Co. Ltd., (Shanghai, China). PVDF (Mn=81,000 g/mol)were supplied by Sanai fuxin Group Co., Ltd., (Shanghai, China)which were dried in a

vacuum oven at 40°C for 24 h. N,N-dimethylformamide (DMF) were purchased from Aladdin Chemical Co. Ltd., (Shanghai, China). Bovine serum albumin (BSA, $M_w = 66,000$ g/mol) were purchased from Sinopharm Group Co., Ltd. (Shanghai, China). All chemicals in the experiments were of analytical grade and were used without further purification. Water used in all experiments was deionized water.

2.2. Synthesis of MIL-101

MIL-101 was prepared by a 4-nitroimidazole-assitant route according to previously reported methods[44]. The 4-nitroimidazole was added to 80 ml of deionized water and stirred until dissolved. Terephthalic acid (0.20 mol/L) was added and stirring was continued for 15 min. Chromium nitrate (0.20 mol/L) was added and stirred for another 15 min. The resulting mixture was transferred to a high-pressure reactor lined with polytetrafluoroethylene and sealed, and subjected to a constant temperature treatment in a thermostatic oven for a certain period of time. After cooling to room temperature, the autoclave was taken out, and the mixture in the autoclave was centrifuged, washed repeatedly with deionized water, and the resulting green solid product was dried at 90°C for 12 hours to obtain a sample of MIL-101.

2.3. Preparation and Characterization of PVDF and MIL-101/PVDF ultrafiltration membranes

The PVDF and MIL-101/PVDF ultrafiltration membranes were prepared using immersion precipitation phase inversion method. The compositions of casting solutions for the membranes are listed in Table 1. The appropriate amount of MIL-101 was mixed into DMF and well dispersed by sonication for 60 min to achieve a good solute dispersion using KQ 2200DV ultrasonic (China). Then, ultrasonic treatment, PVDF and polyvinylpyrrolidone (PVP) were dissolved in the dope solution by continuous stirring at 60 °C for 12h. Finally, the casting solution was degassed under vacuum at room temperature overnight to remove air bubbles. After that, the solutions were casted using a scraper with 200 μm thickness on a clean glass plate and immediately immersed in a coagulation bath (deionized water) at 30°C. After primarily phase separation and membrane formation, the membranes were rinsed with fresh distilled water for 24 h to wash out solvent and water soluble components in the membranes, and then stored in distilled water for further characterization.

Table 1. The compositions of casting solutions.

Membrane type	PVDF (wt%)	PVP (wt%)	MIL-101 (wt%)	DMF (wt%)
M0	18	1.0	0	81
M1	18	1.0	0.1	81
M2	18	1.0	0.2	81
M3	18	1.0	0.3	81
M4	18	1.0	0.4	81

2.4. Characterization of the synthesized MIL-101 and prepared PVDF ultrafiltration membranes

The surface and cross-sectional morphology of the prepared membranes were observed by scanning electron microscope (SEM) (FEI, QUANTA FEG250, USA). The membranes were cut in pieces of small sizes and frozen with liquid nitrogen, to produce a cryo-fracture on the cross section. The membrane surface and cross-section were gold sputtered before observation. The roughness of the prepared membranes was measured by atomic force microscopy (AFM, Dimension ICON, Germany). All the membranes were dried for 6 h in a vacuum oven before the AFM analysis was performed.

The crystalline structures of MIL-101 were determined by X-ray diffraction (XRD). A D8 Advance diffractometer (Germany) with PSD Vantec-1 detectors and Cu $K\alpha$ radiation ($\lambda = 1.5406$), a tube voltage of 40 kV, a current of 40 mA and a V20 slit were used. The samples were scanned in

locked couple mode with 20 increment in 0.5 s steps.

The hydrophilicity of the membrane surface was quantified by water contact angle measurement (JC-2000D6M, China). The deionized water droplets were injected on the membrane surface, the optical video was employed to record the status of the water. The contact angle measurements were performed 5 times at different locations on each membrane to calculate the average value.

2.5. Pure water flux and antifouling experiments

The water flux, separation and fouling performance of the membrane were tested in a dead-end stirred cell from Millpore at 25°C. the membrane is pre-pressed under 0.2MPa pressure for 30min, to get a constant permeate flow and then the pressure is adjusted to 0.15MPa, The water flux (J_{w0} , $L \cdot m^{-2} \cdot h^{-1}$) was determined by measuring the volume change (V_w) of the permeate within a time period (t):

$$J_{w0} = V_w / (S \cdot \Delta t), \quad (1)$$

where, V_w (L) is the volume of permeated water, S (m^2) is the effective membrane area (15 cm^2), and Δt (h) is the permeation time.

Each reported J_{w0} was based on at least three measurements. For fouling resistance tests, water was replaced with $1.0 \text{ g} \cdot L^{-1}$ of BSA solution. The volume of the permeate was recorded every 15 min and the permeate flux (J_p) was calculated. After 1h filtration with BSA solution, the membrane was washed with deionized water for 30 min and the water flux of the cleaned membrane (J_{w1}) was measured again. BSA concentrations of the feed (C_{feed}) and permeate (C_{permeate}) solutions were measured by a UV-vis spectrometer at a wavenumber of 280 nm. The BSA rejection (R_{BSA} , %) was calculated by:

$$R_{\text{BSA}}(\%) = (1 - C_{\text{permeate}} / C_{\text{feed}}) \times 100\%, \quad (2)$$

In order to evaluate of antifouling properties of prepared membrane, the flux recovery ratio (FRR), the total fouling ratio (R_t), the reversible fouling ratio (R_r), the irreversible fouling ratio (R_{ir}) can be calculated as follow:

$$\text{FRR}(\%) = J_{w1} / J_{w0} \times 100\%, \quad (3)$$

$$R_t(\%) = (1 - J_p / J_{w0}) \times 100\%, \quad (4)$$

$$R_r(\%) = (J_{w1} - J_p) / J_{w0} \times 100\%, \quad (5)$$

$$R_{ir}(\%) = (J_{w0} - J_{w1}) / J_{w0} \times 100\%. \quad (6)$$

2.6. Oil-water emulsion separation test

To further study the separation property, the membranes were subjected to filtration tests for oil-water emulsion. The process was same to the protein filtration test. 10g engine oil was dissolved in 1L deionized water and stirred together for 1 (h), finally a milky oil-water emulsion (10000 ppm) was prepared. A dead-end stirred cell was employed to test oil-water separation of the membranes using nitrogen gas as driving force under constant pressure of 3bar. The effective separation area was 15 cm^2 .

3. Results and discussions

3.1. Characterization of MIL-101

The shape, size and volume of pores have an important influence on the function of porous compounds in special applications. In order to determine the crystalline phase of MIL-101, X-ray diffraction (XRD) measurements were performed at the diffraction angle (2θ) of 0-40°.

Fig.1 shows the XRD patterns of MIL-101(4NIm), which are similar to the simulated pattern of MIL-101[45] (CSD number: 415697). The diffraction peaks of recrystallized H2-BDC at $2\theta = 17.4, 25.2$ or 27.9 were not found. The d-spacing values of the powder diffractogram of Cr-MIL-101(4-NIm) are along with the values calculated from the orthorhombic unit-cell parameters determined by Férey et al [46]. The diffraction peaks of Cr-MIL-101(4-NIm) shifted slightly toward the lower angle, inferring that the crystal parameter was a little larger than that of Cr-MIL-101 as that in literature [46].

The SEM image of Cr-MIL-101(4-NIm) was shown in Fig.2. It can be seen that Cr-MIL-101(4-NIm) is octahedral in shape. The particles are rather uniform in size, in the range of 500-600 nm in axial and 750-900 nm in radial direction. The needle-like crystal of recrystallized H2-BDC was not founded in the scope.

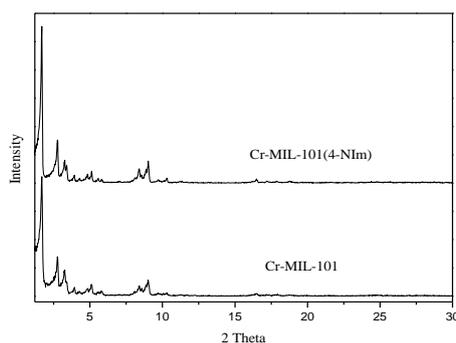


Fig. 1. XRD graph of MIL-101.

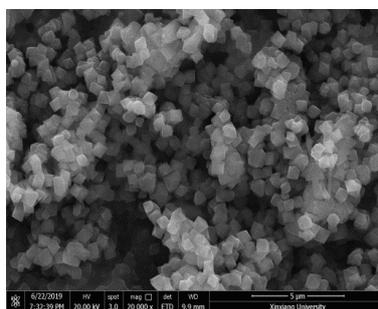


Fig. 2. SEM graph of MIL-101.

3.2. Morphology analysis

The SEM morphologies and cross sections of the PVDF membranes are illustrated in Fig.3. The PVDF membrane surfaces were homogeneous and with regularly distributed pores, as shown in Fig.3, all the membranes exhibit a typical asymmetric morphology of a thin skin layer and a porous sublayer structures. The porous structure of PVDF membranes prepared by non-solvent induced was constructed through substitution between the solvent (DMF) and non-solvent (water). With the increase of the content of MIL-101, the porosity was increased and finger like structure was changed to spherical macro-voids. This can be explained that the hydrophilic MIL-101 could accelerate the exchange of solvent and non-solvent in the phase inversion process. It is obvious that the 0.1 wt% MIL-101 were scattered well in the polymer matrix. However, more than 0.2wt%, the blended MIL-101 may generate agglomerations and result in heterogeneous membrane surfaces. This is because of an increment in viscosity of the casting solution and the low affinity of to the bulk polymer containing 0.3 and 0.4 wt% MIL-101 amount, which hinders the exchange of DMF and water, resulting in a decrease in the precipitation of the membranes.

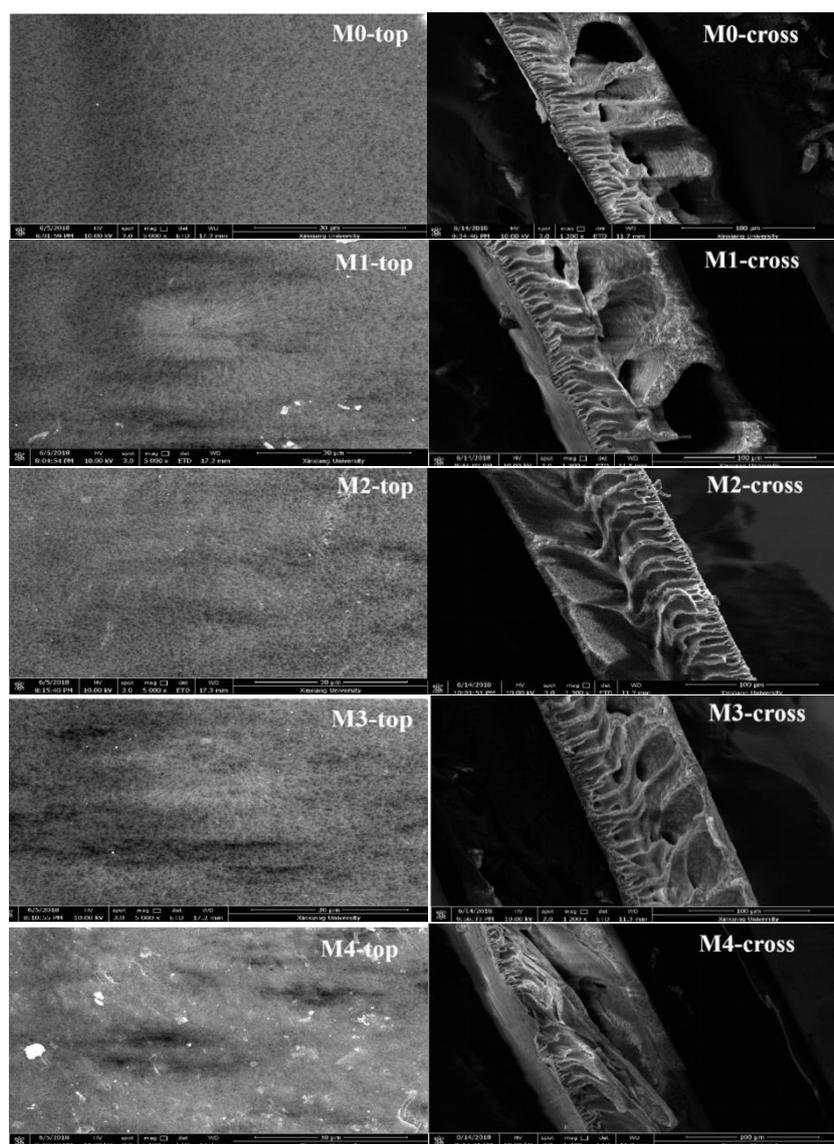


Fig 3. Surface and cross-section SEM images of the PVDF and MIL-101/ PVDF membranes with different concentrations.

Roughness is another important surface property that determines the interaction between the retained components and the membrane surface [47]. The roughness of the prepared membranes was measured using AFM technique. The AFM images and roughness parameters are shown in Fig. 4 and Table 2. The R_a values of M0, M1, M2, M3 and M4 were 29.4, 18.5, 13.1, 14.2 and 25.1 nm respectively. As can be seen from the figure, there are many large peaks and valleys on the surface of the pure PVDF membrane(M0), and many small peaks are shown in the MIL-101/ PVDF membranes, which indicates that the roughness of the membrane is obviously reduced. The surface roughness of the membrane decreases, which can theoretically reduce the contact area between the membrane surface and pollutants resulting improve the anti-fouling property of the membrane. When the MIL-101 concentration is low, the electron electrostatic interaction between them is very small, exists symmetrically in the membrane, and the surface of the membrane is relatively smooth. As the concentration increases, the pore size of the MIL-101 increases and agglomerates, which increases the surface roughness of the MIL-101/ PVDF membranes, but it is still smaller than that of the unmodified film. The surface roughness of PVDF membrane with 0.2 wt% MIL-101(M2) is the lowest. When the concentration is greater than 0.2 wt%, the roughness of the modified

membranes(M3 and M4) begin to increase and the membrane fouling intensifies, because of the accumulation of high MIL-101 in the membrane surface.

Table 2. Surface roughness parameters of PVDF and MIL-101/ PVDF membranes.

Membranes	Roughness parameters	
	R _a (nm)	R _q (nm)
M0	29.4	36.4
M1	18.5	23.6
M2	13.3	16.8
M3	14.2	17.8
M4	25.1	30.3

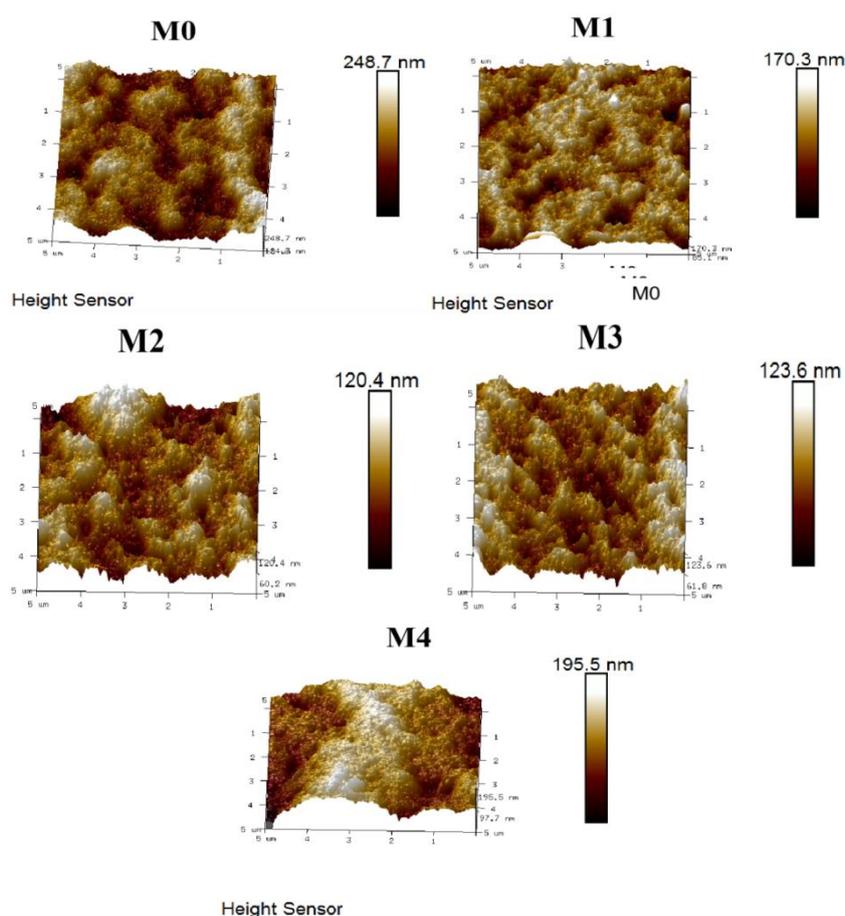


Fig. 4. Surface AFM images of the PVDF and MIL-101/ PVDF membranes with different concentrations.

3.3. Membrane hydrophilicity and pure water flux

The hydrophilicity is an important feature of membrane, which is favor of the water flux and antifouling ability of the membranes. The water contact angles of the prepared membranes are described in Fig.5. It can be seen that M0 was hydrophobic and showed the highest water contact angle at approximately 95.9°. Blending MIL-101 nanoparticles to the casting solutions significantly reduces the water contact angle of the membrane, the hydrophilicity of the blended membranes was improved. By adding 0.1, 0.2, 0.3and 0.4 wt% MIL-101, the water contact angels of M1, M2, M3 and M4 decreased to 78.5°, 75.8°, 77.6° and 79.1° respectively, It seems that the hydrophilicity of PVDF membranes increased with the content of MIL-101 additive, but addition of 0.3 wt%

MIL-101 increased the water contact angle. This phenomenon is attributed to the hydrophilicity of the MIL-101. During the membrane formation, the hydrophilic functional groups of MIL-101 migrates towards the top surface of the membrane, and increased the hydrophilicity. However, the compatibility of the MIL-101 and PVDF is deteriorated, when adding excess MIL-101, the casting solution becomes uneven, which affected the surface of the membrane, and the contact angle becomes large.

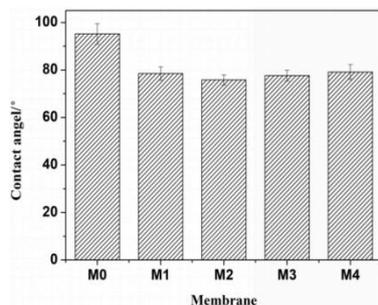


Fig. 5. Contact angle of the PVDF and MIL-101/PVDF membranes.

The results of pure water flux of the prepared PVDF membranes were illustrated in Fig.6. The water flux of the pure PVDF membrane is lower than the PVDF membranes after MIL-101 blending. The MIL-101 concentration was 0.2wt%, the water flux reached the highest, and then decreased. The enhancement of water flux in PVDF membrane can be explained from two aspects. First, the hydrophilicity of the blend MIL-101 improves the surface hydrophilicity of the membrane, adsorbs more water molecules close to the membrane, and promotes the transport of water molecules in the membrane, which is beneficial to the increase of water flux. The water contact angle results of the membrane (Fig. 5) have the same trend as the change of water flux. Second, the MIL-101 affects the pore size and structure of membrane, a wider internal pore and many channels formed in the cross section of the PVDF composite membrane reduce the resistance of water molecules, meanwhile the porous of MIL-101 provides a new flow path for water molecules, easily penetrates through the PVDF composite membrane, and increases the water flux. However continued to increase the concentration, the water flux of the 0.4wt% MIL-101 imprinted membrane dropped compared to the pure membrane (M0). This is due to too much MIL-101 can block the pores of the membrane, reduce the porosity (as shown in Fig. 3) and decrease the water flux.

The rejection was another important parameter for permeability, which was primarily determined by the features of the skin layer. The BSA rejection results of the PVDF membranes were shown in Fig.6. After blending MIL-101, the BSA rejection slightly decreased from 86% to 78%, but the change is little, the membrane maintains high rejection at higher fluxes, the BSA rejection of membrane with high concentration of MIL-101 increased in opposite of the water flux trend.

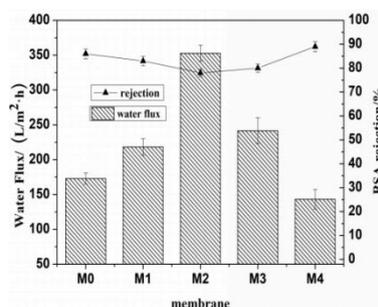


Fig. 6. Pure water flux and BSA rejection of the PVDF and MIL-101/PVDF membranes.

3.4. Antifouling properties of the MIL-101/PVDF membranes during BSA filtration

Membrane fouling is a significant challenge in the ultrafiltration membrane separation processes that resulted in an impressive decrease in permeation flux [48]. The antifouling performance of the prepared PVDF ultrafiltration membranes, was analyzed by measuring pure water flux after fouling by 1000 ppm BSA solution. Fig.7 present the permeate fluxes which consist pure water flux before and after fouling with the protein, the protein solution flux. As shown in Fig 7, the permeability of the membranes greatly reduced when pure water was changed by BSA solution in filtration cell indicating fouling of the membranes. After washing the membranes, the pure water flux of the MIL-101/PVDF membranes decreased lower than the pure PVDF membrane. This may be ascribed to the increase in hydrophilicity of the blended membranes which is in stability with membrane hydrophilicity change as manifested in Fig 4.

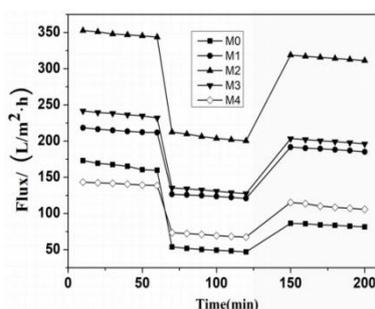


Fig. 7. Flux versus time of the PVDF and MIL-101/ PVDF membranes during the fouling processes.

The water flux recovery ratios of the prepared PVDF membranes are presented in Fig.8. The higher FRR means the better antifouling property for the membrane. The FRR of the PVDF membranes is increased from 49.9% to 90.4% after blending MIL-101. It means that the MIL-101/PVDF membranes possesses the higher filtration efficiency when they were exposed to protein solution.

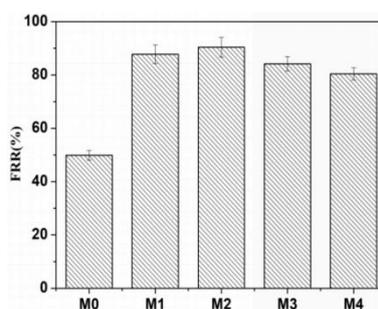


Fig. 8. Water flux recovery ratios (FRR).

Three antifouling parameters: total fouling (R_t), reversible fouling (R_r) and irreversible fouling (R_{ir}) are investigated to study the antifouling property of the membranes in more detail. R_r was defined as the fouling agents were cleaned by backwashing. R_{ir} was defined as the fouling agents were only be removed through chemical cleaning. R_t was the sum of the R_r and R_{ir} . A lower R_t value indicates that the membrane has better antifouling performance, while a higher FRR value indicates that the membrane has better antifouling performance. The R_t , R_r , and R_{ir} values for the pure PVDF and blended membranes are displayed in Fig.9. The results demonstrated the pure PVDF membrane had highest irreversible fouling ratio (50.1%, more than 73% of total fouling) due to the hydrophobic and higher roughness. For the blended membranes, the irreversible fouling ratio (R_{ir}) was sharply decreased from 50.1% to 9.6%, The reversible fouling ratio (R_r) was increased from 18.9% to 30.2%. These results indicate that the blended membrane has better antifouling

performance which is ascribed to the more hydrophilic and smoother surface property, restrained the protein adsorption on the membrane. In general, the recovery ratios (FRR), reversible resistances (R_r), and irreversible resistances (R_{ir}) of MIL-101/PVDF ultrafiltration membranes were increased, the surface properties of the membrane were improved.

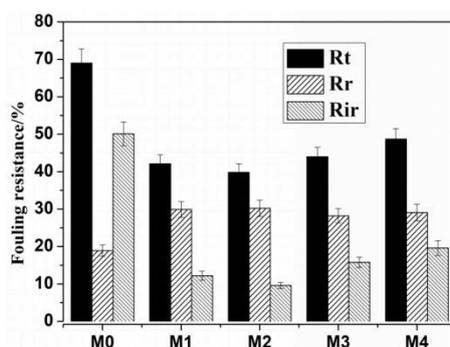


Fig. 9. Fouling resistance ratio of PVDF and MIL-101/ PVDF ultrafiltration membranes.

Using oil-water emulsion as raw material, the separation performance of MIL-101/PVDF membrane for oil-water separation was studied. The result is shown in Fig.10. It can be seen that the MIL-101/PVDF membrane can effectively separate oil from the oil-water emulsion, with a flux of $95.53 \text{ kg/m}^2 \cdot \text{h}$ and the oil rejection rate of 99.74%. This is because that MIL-101/PVDF membrane has strong hydrophilicity, smooth surface and rich microporous morphology, and can be used in the field of oil-water separation.

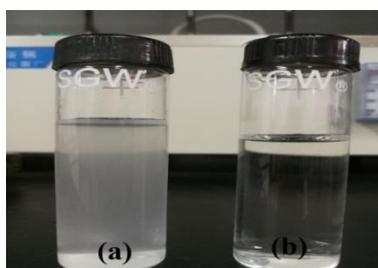


Fig. 10. The photos of (a) feed solution, (b) permeation from 0.5 wt% MIL-101 /PVDF membrane.

4. Conclusions

The preparation of high-performance membranes has been playing an important role in wastewater treatment. In this work, a new MIL-101/PVDF ultrafiltration membrane was successfully prepared by using immersion precipitation method. The modified PVDF membrane was characterized by SEM, AFM and water contact angle, the pure water flux, and anti-fouling of the membranes were also researched. It was illustrated that the roughness of the MIL-101 /PVDF membranes showed a decrease in the roughness of the membrane surfaces and an increase in the hydrophilicity resulting in raising the resistance of membranes to fouling and the permeation flux.

The results showed the MIL-101 /PVDF membranes have higher water permeability and excellent antifouling performance. When the doping amount of MIL-101 was 0.2wt%, the water flux of the MIL-101 /PVDF membrane was $352.8 \text{ (L/m}^2 \cdot \text{h)}$, the BSA rejection rate was 78.1%, and the FRR was 90.4%. It showed that preparation of MIL-101 /PVDF membrane was an effective method to improve the flux and anti-fouling of the PVDF membrane and could be applied in the field of oil -water separation with high efficiency.

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