



## Methyldiethanolamine Solution Filtration Using Blended PVDF Membranes with Improved Antifouling Properties

Moaaz A. Abdelwahab <sup>a,b\*</sup>, Heba Abdallah <sup>c</sup>, Fatma Khalifa Gad <sup>a</sup>,  
Amr F.M. Ibrahim <sup>a\*</sup>

<sup>a</sup> Faculty of Petroleum and Mining Engineering, Suez University, Suez, 43512, Egypt

<sup>b</sup> Belayim Petroleum Company (PETROBEL), Egypt

<sup>c</sup> Chemical Engineering Department, Engineering and Renewable Energy Research Institute, National Research Centre, Dokki, Giza, Egypt, PO box 12622



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### Abstract

Alkanolamine solutions are widely used to remove acid gases (primarily H<sub>2</sub>S and CO<sub>2</sub>) from natural gas and light hydrocarbon streams. Removal of impurities and entrained solids is crucial to the effective operation of gas-treating plants. In this work, flat sheet ultrafiltration membranes were prepared from a polyvinylidene fluoride (PVDF) backbone blended with polyethylene glycol (PEG) and polyacrylonitrile (PAN) using the phase inversion method. The influence of blending proportions on the morphology and antifouling properties of the membranes was investigated. The prepared membranes were characterized using scanning electron microscopy and contact angle measurements and their mechanical properties and porosity were also evaluated. Membrane performance tests were carried out using an unstirred laboratory scale dead-end filtration setup fed with deionized water and real industry lean methyldiethanolamine solution. It was found that applying the right amounts of PAN and PEG to the casting solution increases PVDF membrane water flux and enhances its mechanical and antifouling properties. The addition of 1 wt. % PAN and 2 wt. % PEG400 to the casting solution of PVDF membranes results in 18% increase in pure water flux and ~97% rejection of the solids in the amine solution. This accomplishment was ascribed to the increased porosity and surface hydrophilicity of the blended PVDF membranes. The membrane showed improved surface antifouling properties with a high flux recovery ratio of 85.6% and a low irreversible resistance of 0.14.

**Keywords:** Poly(vinylidene fluoride); polyacrylonitrile; Polyethylene glycol, Ultrafiltration membranes; Methyl diethanolamine; Anti-fouling properties

### 1. Introduction

The removal of acid gases (mainly H<sub>2</sub>S and CO<sub>2</sub>) from natural gas and light hydrocarbon gas streams in the industrial sector is mostly conducted using chemical solvent absorption [1]. The process involves a chemical reaction of acid gases with a continuously circulated aqueous amine solution leading to the sweetening of the natural gas stream and the rich amine solution is then regenerated to separate acid gases [2]. The lean amine solution is then purified using filters to remove particulates such as dirt, debris, active carbon, condensed hydrocarbons, pieces of metal, and corrosion products in the form of black powder of iron sulfide. Contaminants increase amine foaming tendency and corrosion problems and induce thermostable salts formation [3,4]. These operational problems thereby reduce amine absorption capacity and negatively affect plant productivity and

profitability. Therefore, the purification of amine solutions is an urgent task to guarantee the effective operation of natural gas treatment plants and expand the service life of the absorbent and equipment.

Membrane separation processes have emerged as a competitive technology for the purification of amine solutions [5]. Previous reports showed that electrodialysis could have a great potential in removing contaminants of an ionic nature. For example, the Dow Chemical Company reported a reduction of ~ 88% in the concentration of thermostable salts at the regeneration of a mixture of tertiary amines [6]. Grushevenko and coworkers [7] showed that using two-step electrodialysis reduces mono-ethanolamine loss and allows the concentration of heat stable salts to be maintained at permissible levels. Nevertheless, electrodialysis is limited to the recovery of charged pollutants only and further

\* Corresponding authors' E-mail: Amr.Ibrahim@suezuni.edu.eg or Moaaz.AAAAb@pme.suezuni.edu.eg

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treatments are required to remove the neutral species and oligomers. Kentish and coworkers [8] showed that nanofiltration can be used to concentrate heat-stable salts in a contaminated mono-ethanolamine solution and thus reduces the circulating solution viscosity and corrosivity. Nanofiltration also allows delivering a lower volume and more concentrated solution to a downstream thermal reclamation, but the low flux and fouling issues make it less attractive [9]. The above-mentioned membrane processes are mostly inefficient if the amine solution contains appreciable amounts of solid particulates.

Existing amine particle filtration best practice proposes that 10  $\mu\text{m}$  absolute filter is essential to ensure adequate removal of iron sulfide and other solid particulates from a circulating amine solution [4]. This size specification is based only on the hypothesis that the majority of the solid particulates in amine solution fall in a size range that will permit effective capture by 10  $\mu\text{m}$  filter. While in actual plant practice, a 10  $\mu\text{m}$  filter may provide an inefficient performance allowing solid particles to pass through or being fouled and plugged so rapidly which calls for replacement, labor, and disposal related costs. These issues could be solved by further research to characterize the entrained solid particulates in the amine solution and with the synthesis of membranes with appropriate pore size and surface wetting properties to insure clean permeates and long filter lifetime. Since few reports were found addressing this point, this research gap of selecting an appropriate filter for amine solution filtration will be fulfilled by further research.

Herein, we investigated the removal of solid particulates from real industry methyldiethanolamine solution using polyvinylidene fluoride (PVDF) ultrafiltration membranes. PVDF is a frequently used membrane material for the preparation of microfiltration and ultrafiltration membranes for solid-liquid separation applications [10]. Commercial PVDF membranes are almost dominating the market due to their exceptional mechanical, thermal, chemical, and hydrophobic properties [11]. The prepared membranes are produced using the well-established non-solvent induced phase inversion method to insure simple and flexible production in the commercial sector [11,12]. Non-solvent additives such as polyethylene glycol (PEG) and polyacrylonitrile (PAN) were used to tailor the specific properties of PVDF membranes to ensure high performance and improved antifouling properties [12]. While PAN and PEG seems to be a good candidate for modification of PVDF membranes and enhancing their hydrophilic properties, only few studies have addressed blending PVDF/PAN [13-16] or PVDF/PEG [17-19]. To the best of our knowledge, no other studies has focused on the tertiary blends of PVDF, PAN and PEG with PVDF as the main polymer. The objective of this work is to synthesize PVDF ultrafiltration membranes with

improved anti-fouling properties and investigate their filtration characteristics for real plant lean methyldiethanolamine solution.

## 2. Experimental

### 2.1. Material

Polyvinylidene fluoride (PVDF, CAS #: 24937-79-9, Alfa Aesar) was used as the main polymer and N-Methyl 2-pyrrolidone (NMP, >98%, Loba Chemie) was used as a solvent for the casting solutions. Polyethylene glycol, (PEG, Mw. 400 g/mol, Carl Roth GmbH) and polyacrylonitrile (PAN, Mw. 150,000 g/mol, Sigma Aldrich) were used as additives in the casting solution to tune the properties of the membrane. Methyldiethanolamine (MDEA) solution was obtained from a natural gas field in Egypt. The solution was regenerated after the capture of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  from the natural gas stream.

### 2.2. Amine solution characterization

The nature of the total suspended solid has been investigated using atomic emission spectrometry, AES according to ASTM D6595 "Standard Method for Determination of Metals and Contaminants". The particle size distribution of the entrained solids has been investigated using HORIBA- LA-960 laser scattering particle size distribution analyzer. Solid-state spectrometry designed for the analysis of elements dissolved or suspended as fine particles using the rotating disc electrode (RDE) technique. Turbidity measurements for the feed sample was obtained using a TL2300 tungsten lamp turbidity meter.

### 2.3. Membrane preparation and characterization

Blended PVDF/PAN/PEG membranes were prepared using the immersion precipitation phase inversion method. Certain amounts of PVDF, PAN and PEG are added to NMP solvent prepare casting solutions with the weight proportions given in Table 1. Membranes are given names starting with the letter M followed by the weight percentages of PVDF, PAN and PEG. The mixture is continuously stirred for 12 h to achieve complete dissolution and mixing of the components. The polymer solution was then cast on a non-woven substrate on top of a glass plate at room temperature using a film applicator with a gap of 200  $\mu\text{m}$ . Using non-woven support in membrane preparation improves membrane mechanical properties and decrease the membrane wrinkling and shrinkage for all prepared membranes [20]. The glass plate with the substrate and the applied thin film was immersed immediately in a distilled water coagulation bath at 25  $^\circ\text{C}$ . After the membrane was completely detached from the glass plate, the membrane was removed from the water bath to a tray containing fresh water to remove the residual solvent and polymeric additives. After stabilizing for 24 h the membranes were removed from the tray and dried in air at room temperature. After

drying, the membranes were ready for characterization and performance tests.

Membrane surface and cross section images were obtained using a scanning electron microscope (SEM, JEOL 5410). Membranes were fractured after immersion in liquid nitrogen before sputter coated with gold element to provide electrical conductivity. The mechanical properties of the prepared membranes were studied to provide the effect of the blending percentage on the membrane tensile strength and elongation properties. The membrane was loaded under slightly applied load till breakage using H5KS Tinius Olsen tensile tester. Three samples were tested for each membrane blend to ensure reproducibility of the data. Contact angle measurements were obtained for the prepared membrane using Biolin Scientific Goniometer equipped with automated microsyringe. By dropping 4  $\mu\text{L}$  water, the contact angle was measured at four different spots for each sample and the average value has been reported.

Table 1 The composition of modified PVDF membranes' casting solutions

Membrane symbol	Casting solution composition (weight percentage)			
	PVDF	PAN	PEG 400	NM P
M15,0,0	15	0	0	85
M14,1,2	14	1	2	83
M14,2,1	14	2	1	83
M15,0,5,3	15	0.5	3	81.5

The membrane porosity was determined applying the gravimetric method [13] using three 1  $\text{cm}^2$  samples for each membrane and the average porosity was reported. The membrane samples were kept immersed in deionized water for one day and then taken out and the wet weight ( $w_1$ ) of the sample is measured immediately after removing water droplets from the sample surface. The membrane samples were then dried in an oven at 80  $^\circ\text{C}$  overnight. The samples were then moved directly to a desiccator for 10 minutes till the samples cooled down and the dry weight ( $w_2$ ) was then recorded. Porosity calculations were conducted according to Equation 1.

$$\text{Membrane porosity, \%} = \frac{w_1 - w_2}{A \cdot L \cdot d_w} \quad (1)$$

Where A and L represent the membrane cross-sectional area and thickness respectively. The membrane thickness was measured using a lab micrometer at three points of the membrane and an average thickness was reported.  $d_w$  stands for the water density.

#### 2.4. Permeation and separation experiments

To evaluate the separation, permeation, and antifouling properties, filtration experiments were conducted using a lab-scale dead-end filtration setup shown in Figure 1. A flat sheet membrane was placed in a stainless-steel cell supported by a porous metal plate and sealed in position using O-ring. A pump was used to circulate the amine solution from a reservoir to the membrane surface and the clarified amine solution went through the permeate side of the membrane. A pressure valve was used to control the transmembrane pressure at 3.4 bar for all experiments. The effective membrane area of the experiments was 17.34  $\text{cm}^2$ . Filtration experiments were conducted at ambient temperature. The membranes were tested first using distilled water, and flux measurements were recorded until steady state flux was reached. Water was then displaced with the amine solution and amine filtration experiments were conducted for one hour where steady state amine flux could be attained. Flux calculations for the initial water,  $J_{w1}$ , ( $\text{L}/\text{m}^2\text{h}$ ) at steady state and the amine solution  $J_a$  ( $\text{L}/\text{m}^2\text{h}$ ) at steady state were made using Equation 2 and membrane rejection in amine permeation experiments was calculated as in Equation 3 [21].

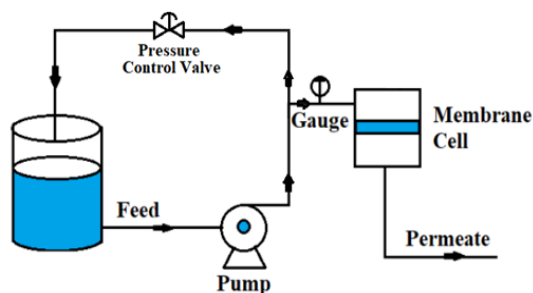


Figure 1 Schematic diagram of the filtration setup used in this work

$$\text{Flux} = \frac{Q}{A \cdot \Delta t} \quad (2)$$

$$\text{Membrane rejection, \%} = \left(1 - \frac{\text{Permeate Turbidity}}{\text{Feed Turbidity}}\right) * 100 \quad (3)$$

where, Q is the permeate volume (L), A is the membrane area ( $\text{m}^2$ ) and  $\Delta t$  is the permeation time (h). Turbidity measurements for the feed sample and the permeate were obtained using a TL2300 tungsten lamp turbidity meter.

To test the fouling of the membrane, the solution tank was refilled with distilled water and the membranes were washed thoroughly with distilled water outside the cell. Pure water flux ( $J_{w2}$ ) measurements were recorded again after membrane cleaning until the steady state flux was reached. The anti-fouling characteristics of the synthesized membranes were investigated in terms of the flux recovery ratio (FRR), and the total fouling resistance ( $R_f$ ) given in Equations 4 and 5 [20,13].  $R_f$  represents total flux decrease due to total fouling. Part of the fouling is reversible and can be removed by physical cleaning (water flushing, back-washing, or using

strong shear force). Irreversible fouling needs more complex washing method that may include solvents, acids and/or alkalines. Reversible and irreversible fouling resistance ( $R_f$ ,  $R_{ir}$ ) were calculated as given in Equations 6 and 7 [13,20,21].

$$\text{FFR, \%} = \frac{J_{w2}}{J_{w1}} * 100 \quad (4)$$

$$\text{Rt, \%} = \left(1 - \frac{J_a}{J_{w1}}\right) \quad (5)$$

$$\text{R}_f, \% = \left(\frac{J_{w2} - J_a}{J_{w1}}\right) \quad (6)$$

$$\text{R}_{ir}, \% = \left(\frac{J_{w1} - J_{w2}}{J_{w1}}\right) \quad (7)$$

### 3. Results and Discussion

#### 3.1. Amine solution characterization

The analysis of the elements dissolved or suspended as fine particles in the amine solution used in this study is given in Table 2. A non-negligible presence of heat stable salts, even if still lower than the maximum specification limit, indicates a partial degradation of the amine. The presence of these heat stable salts explains the high value of total dissolved solids. Also, the relatively low amine concentration, with consequent  $\text{H}_2\text{S}$  loading value close to the maximum recommended limit suggests degradation of the amine and inefficient regeneration process. Moreover, the direct analysis by AES of the filtrated suspended solids reveals the presence of appreciable amounts of suspended solids, identified as black FeS particles. These suspended particles also contribute to the high amine solution turbidity. Scanlan [4] reported that iron sulfide is typically the main component of suspended solids filtered from gas plants or refinery amine solutions. The reaction between iron and hydrogen sulfide produces a layer of iron sulfide that coats the internal surfaces of iron tubes. This layer may be removed mechanically by abrasion or erosion or simply dissolved in the amine solution and circulate as small particles giving the black color to unfiltered or poorly filtered rich-side amine solution [4].

The particle size distribution of the filtered solids is illustrated in Figure 2. The median size is about  $2.9 \mu\text{m}$  (meaning that 50% of the particles have a particle size smaller or equal to  $2.9 \mu\text{m}$ ) and the average (mean) particle size is  $3.43 \mu\text{m}$ . The data presented in Figure 2 also suggest that using a filter with absolute  $10 \mu\text{m}$  size, as already applied in industry, is not suitable for the retention of the majority of the solid particles and a UF membrane would be a good candidate for clarifying the amine solution under consideration.

#### 3.2. Physical and mechanical characteristics of the prepared membranes

The mechanical test was carried out to measure the durability of the prepared membranes on the non-woven substrate by measuring the tensile strength and elongation against a static force. The data presented in Table 3 for the mechanical properties show that the

tensile strength decreases in the following sequence  $\text{M15,0.5,3} > \text{M14,1,2} > \text{M14,2,1} > \text{M15,0,0}$  indicating that increasing PEG content in the casting solution leads to increased strength. The  $\text{M15,0.5,3}$  membrane's tensile strength increased by 13.12 % compared to the bare PVDF membrane. Li et al [22], reported that lower molecular weight PEG can enhance the tensile strength of the PLA/ PEG blends membranes by being easier to be incorporated in the main polymer chains and provide a plasticizing effect.

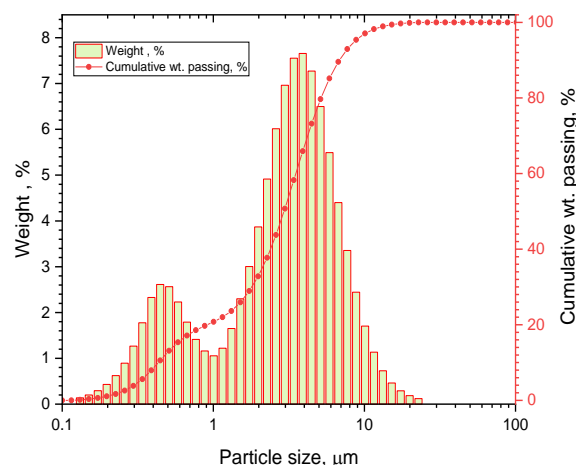


Figure 2 Particle size distribution of the solids entrained in the used amine solution

Table 2 The characteristics of the amine solution used in this work and the accepted limits for each property as recommended by industry limits.

Parameter	Value	Accepted limits
Appearance	black/ turbid	colorless - transparent
pH	10.3	10.0 - 10.5
Amine concentration, %	34.7	min. 40 - 45
$\text{H}_2\text{S}$ loading, %	0.018	max. 0.02
Total dissolved solids (TDS), ppm	706	max. 10
Iron content, ppm	0.2	max. 5
Hydrocarbon content, %	nil	nil
Water content, %	65.3	min. 55 - 60
Turbidity, NTU	517	max. 15
Total suspended solid (TSS), ppm	579	max. 10
Total acid gas, %	0.59	max. 2
Heat stable amine salts, %	0.56	max. 2

On the other hand, elongation was found to decrease in the following order  $\text{M14,2,1} > \text{M15,0.5,3} > \text{M15,0,0} > \text{M14,2,1}$ .  $\text{M14,2,1}$  shows about 19 % increase in elongation compared to the bare PVDF membrane. The data also suggest that the addition of PAN

contributes to the enhancement of the elongation property of the membrane. Abdallah and coworkers [23] reported that small additions of PAN to PES membranes gradually enhances both the tensile and elongation properties of the membrane. However, increasing PAN percentage to 2% resulted in a decrease in the mechanical properties of the membrane. This was attributed to the initiation of microcracks due to a delay in solid-liquid demixing during membrane formation. To sum up, the application of right amounts of PAN and PEG to the casting solution of PVDF can be conducive in enhancing its mechanical properties.

Water contact angle measurements were carried out to evaluate the surface hydrophilicity of the prepared membranes which could have a significant influence on their performance and fouling characteristics [13,21]. As observed in Table 3 the pure PVDF membrane shows the highest contact angle value which suggests a more hydrophobic membrane surface. The contact angle of the prepared membranes decreases in the order  $M15,0,0 > M14,2,1 > M14,1,2 > M15,0,5,3$  indicating that the blend membranes are more hydrophilic by tuning the percentage of PAN and PEG [14,16,13,18]. PEG additions were probably more significant contributing to the membrane surface hydrophilicity compared to PAN. Increasing the membrane surface hydrophilicity leads to improvement in its performance and water permeability.

Figure 3 compares the obtained SEM top and cross-section images of the prepared membranes to investigate the effect of PAN and PEG additions on the morphology of PVDF membranes. The PVDF membranes with no PAN or PEG additions (M15,0,0) shows sponge-like structure (compact configuration) with small surface pores,  $\sim < 0.1 \mu\text{m}$ , indicating ultrafiltration membrane pore size. In addition, the pore distribution is not uniform and micro pores  $\sim 1 \mu\text{m}$  exist as shown in Figure 3 (a and b). PVDF is a hydrophobic polymer, and its solution has low affinity to water that slows down the phase inversion process. The slow phase inversion process produces pores with sponge-like structure and a narrow micro void on the

surface [20,13]. This morphology resulted in a small porosity and few effective micro pores as given in Table 3. It is observed that the addition of PAN and PEG to the casting solution greatly affects the morphology and porosity of the neat PVDF membrane as given in Table 3 and Figure 3- (c-h). The addition of hydrophilic polymers increases the dope solution affinity to the coagulation water path which results in improved speed of inversion producing asymmetric structure consisting of a dense top skin layer and porous fingerlike sub layer [13,18].

The addition of 1% PAN and 2% PEG to PVDF casting solution (M14,1,2) resulted in uniformly distributed micro-voids due to the addition PEG that acts as a pore former (Figure 3-c). The cross-section snapshot in Figure 3- d, shows slightly wide finger-like structure compared to PVDV. Increasing the content of PAN to 2% and decreasing the amount of PEG to 1% in the PVDF casting (M14,2,1) solution resulted in membranes with a dense surface layer and more sponge like structure compared to (M14,1,2) as presented in Figure 3 (e and f). The high molecular weight PAN polymer increases the casting solution viscosity and leads to a delay in the de-mixing process producing a spongy structure [21]. The decrease in PEG content influences the membrane porosity. Also, few micro-pores were noticed on the surface of M14,1,2.

M15,0,5,3 shows a denser thick top layer and a wider finger like sublayer structure with macro voids as given in Figure 3 (g and h). The fingerlike pores are changed in shape and their size also increases until they get closer to the bottom of the membrane. This could be attributed to the increase of the total hydrophilic content in the casting solution which result in increased affinity and inflow of water during the phase inversion process [21,18]. The enhanced demixing rate at the interface may result in rapid collapse of polymer chains and the formation of macro-voids between collapsed chains leading to the formation of surface voids as noticed for M15,0,5,3 [19]. However, the membrane surface exhibits smaller porosity probably due to the thicker top layer.

Table 1 Effect of PAN and PEG additions on the prepared PVDF membranes

Membrane symbol	Porosity	Water contact angle	Tensile Strength	Elongation at breakage,	Rejection	FRR	R <sub>t</sub>	R <sub>r</sub>	R <sub>ir</sub>
	%	°	N/cm <sup>2</sup>	%	%	%	%	%	%
M15,0,0	22.78	102.06	701	27.39	90.91	79.20	0.82	0.61	0.21
M14,1,2	51.26	91.26	774	27.36	97.62	85.59	0.80	0.66	0.14
M14,2,1	48.87	92.76	768	32.59	98.84	80.00	0.84	0.64	0.20
M15,0,5,3	42.62	89.84	793	31.04	99.21	74.72	0.90	0.65	0.25



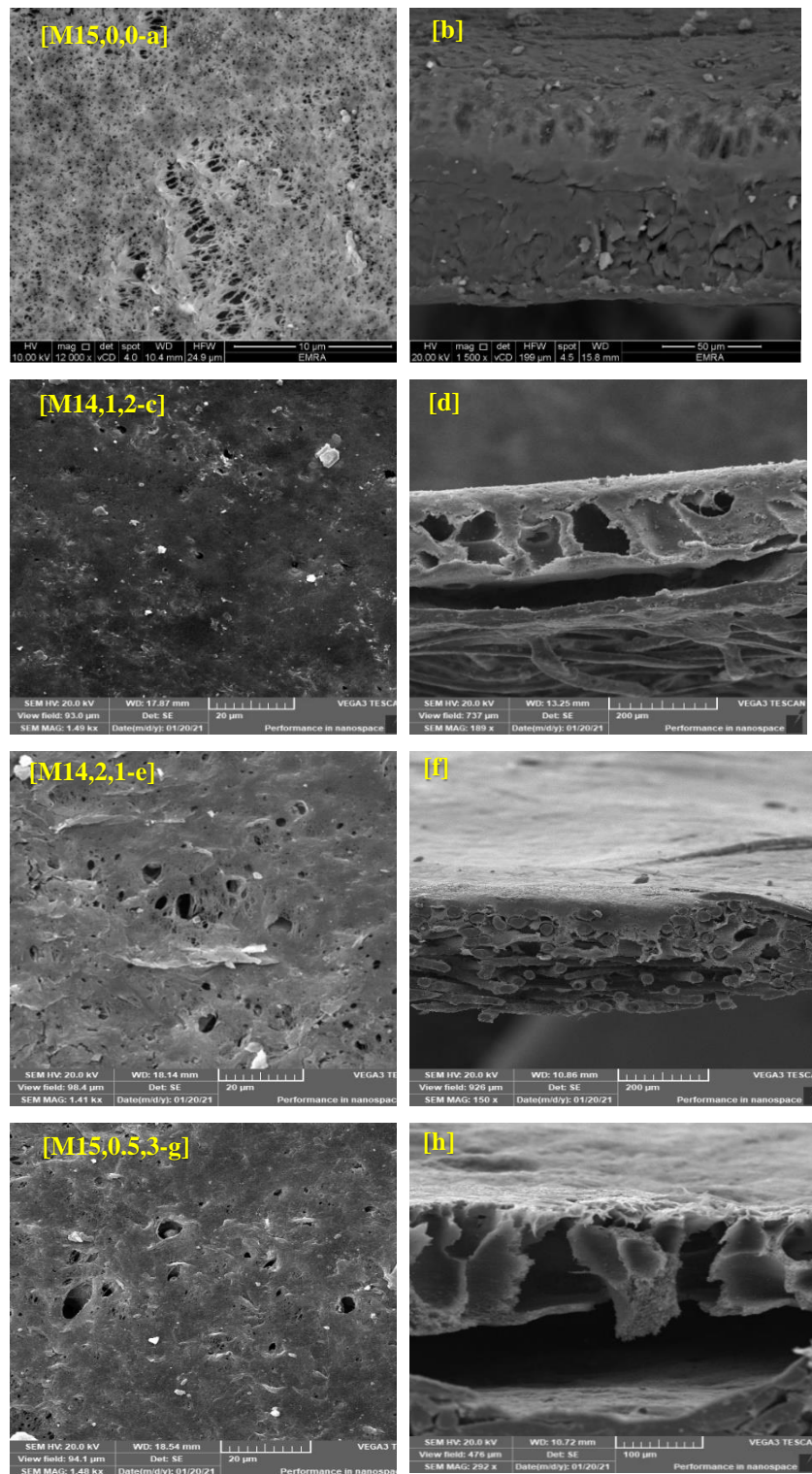


Figure 3 Surface and cross-section SEM images for the blended PVDF membranes prepared in this work.

### 3.3. Permeation and antifouling characteristics of the synthesized membranes

Permeations tests were conducted to study the performance and anti-fouling characteristics of the PVDF/PAN/PEG blend membranes. Figure 4 shows

three permeation stages for all tested membranes as flux normalized per operating pressure. The first stage is for pure water permeation for the fresh membranes. Stage 2 shows the flux of the membranes for the amine solution while stage 3 shows the pure water flux for

the membranes after the physical cleaning of the membranes. The pure water flux, first stage, sharply declined during the first 60 min for all tested membranes (data are not shown) and then reached a plateau after 120 min of permeation. The pure water flux of the membranes was in the order  $M15,0.5,3 > M14,1,2 > M15,0,0 > M14,2,1$  indicating the effect of PEG and PAN additions on the pure water permeation properties of the membranes in comparison to the pristine PVDF.  $M15,0.5,3$  showed the highest pure water flux although the membrane porosity is lower compared to the other membranes. This can be attributed to the significant reduction in the contact angle with increasing the content of hydrophilic polymers in the casting solutions. Also, the micro voids found in the surface of the membrane contributes to the fast permeation of pure water through the membrane. The improved water flux for  $M14,1,2$  is mainly attributed to the large porosity and open structure of the sub layer with more uniform distribution of ultrafiltration pores on the membrane surface.  $M14,2,1$  showed the lowest water flux compared to the pristine PVDF membrane although the membrane has more open structure and lower contact angle compared to PVDF. This indeed is related to the formation of a dense layer on the top of the membrane that hinder the transport of water through the membrane.

In the second stage, i.e. the amine solution filtration, the flux has decreased significantly for all membranes. The decline in the amine solution flux could be due to several factors such as fouling of the membrane surface and concentration polarization on the surface that consequently imposed more resistance to the flow of the solution [24]. The steady state flux order was different from the flux in the case of pure water ( $M14,1,2 > M15,0,0 > M15,0.5,3 > M14,2,1$ ). The ratios of the flux of the fouled membranes to their initial fluxes were 31.1, 42.2, 23.3, 16.0 % for the membranes  $M15,0,0$ ,  $M14,1,2$ ,  $M14,2,1$  and  $M15,0.5,3$  respectively. After one hour for amine solution filtration, these ratios reach plateau values of 17.6, 19.9, 15.8, and 10.0 % respectively.

$M15,0.5,3$ 's flux was significantly reduced during amine solution filtration compared to its pure water flux. This could indicate that the large pores found on the membrane surface contribute the water flux of the membrane. In case of amine solution, those large pores are closed so fast with the solid particles in the amine solution and the dense surface of the membrane only allows slow flow of the amine solution and thus the current flux depends more on the denseness of the skin layer than the porosity of the membrane [14]. The rejection data for the prepared membrane are given in Table 3. All the modified membranes exhibited excellent solid rejection compared to the bare PVDF membrane. Even the membranes with large micro pores show excellent rejection because these large pores will be filled with the solid particles that will be

entrapped in the membrane structure leading to rejection of the particles through the remaining exposed surface of the membrane. A good compromise between the flux and rejection can be attained using  $M14,1,2$  membrane.

The third stage of permeation starts after the physical cleaning of the membranes with deionized water. The water flux of all membranes was partially restored as shown in Figure 4. The pure water permeance of the membranes was in the order  $M15,0.5,3 > M14,1,2 > M15,0,0 > M14,2,1$  similar to the order in stage 1. However, the effect of cleaning on flux recovery is more effective for the blend membrane  $M14,1,2$ . The other membranes with relatively big surface pores showed less flux recovery. This could be attributed to the fact that the entrapped particles in those big pores are difficult to remove by physical cleaning.

To further assess the membrane fouling properties the values of  $FRR$ ,  $R_t$ ,  $R_{rev}$  and  $R_{ir}$  are calculated and presented in Table 3. Higher values of  $FRR$  (>50%) reflect lower permanent adsorption to the membrane surface [13]. The pristine PVDF membrane is more prone to fouling caused by organic molecules, and the foulants firmly stick to the surface of the membrane, which is challenging for cleaning and long-term operation [25]. As noticed from Table 3, the  $FRR$  was the lowest in case of  $M15,0.5,3$  and then the bare PVDF membrane suggesting much fouling occurring on their surfaces. This could be due to large pore blockage. The trapped particles in the pores of the membranes cannot be washed out by the physical cleaning causing lower flux recovery [13].  $M14,1,2$  shows the highest  $FRR$  and the lowest  $R_{ir}$  value suggesting that the addition of 1 wt.% PAN and 2 wt. PEG to PVDF casting solution enhances the anti-fouling properties of the membrane. This can be attributed to enhancement of the membrane hydrophilicity as confirmed by the decrease of the contact angle value and the production of a membrane with less large surface pores.

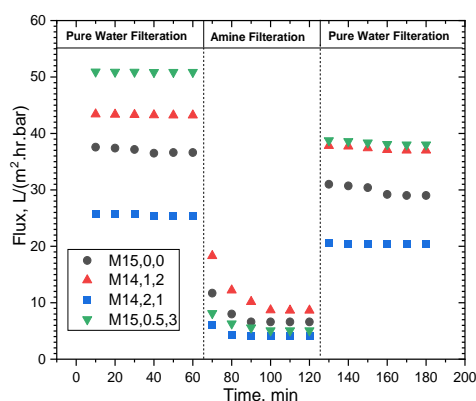


Figure 4 Permeation characteristics of the synthesized membranes for deionized water and amine solution.

## Conclusions

Ultrafiltration membranes were successfully synthesized using poly(vinylidene fluoride) blended with polyethylene glycol and polyacrylonitrile using the phase inversion method. The application of the right amounts of PAN and PEG400 to the casting solution can be conducive in increasing PVDF membrane water flux and enhancing its mechanical and antifouling properties. This can be attributed to the morphological changes (the increase in porosity and fingerlike pores) of the membranes as well as the improvement in wettability by the addition of PAN and PEG400 to the membrane casting solution. The addition of 1 wt. % PAN and 2 wt. % PEG400 to the casting solution of PVDF membranes results in 18% increase pure water flux and ~97% rejection of the solids in the amine solution. The membrane showed improved surface anti-fouling properties with a high flux recovery ratio of 85.6% and a low irreversible resistance of 0.14 and hence, improved long-term performance.

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