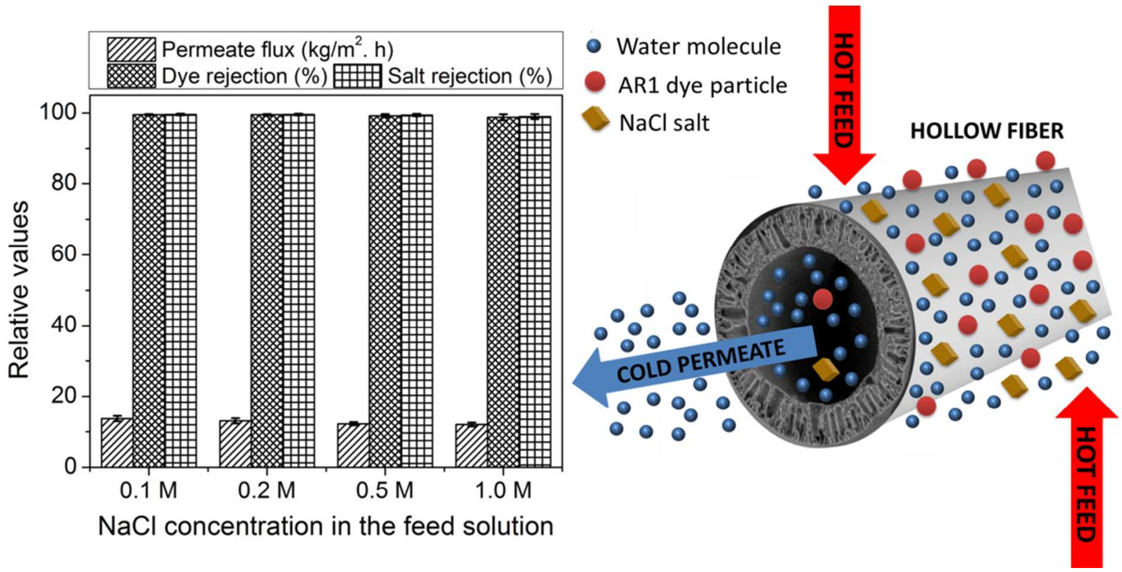
Graphical abstract



Performances of novel PVDF-Cloisite 15A hollow fiber composite membrane in treating dyeing solution containing 50 ppm AR1 and 0.1–1.0 M NaCl

Performance evaluation of novel PVDF-Cloisite 15A hollow fiber composite membranes for treatment of effluents containing dyes and salts using membrane distillation

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Abstract

The present study reports the performance of novel PVDF-Cloisite 15A hollow fiber composite membrane for the treatment of effluents containing dyes and salts through direct contact membrane distillation (DCMD) process. The performance of the membrane was evaluated by varying several important parameters during DCMD process which included feed properties (type of dyes, dye and salt concentration) and process conditions (feed temperature and flow rate). Experimental results showed that the in-house made membrane was able to achieve stable fluxes and excellent dye rejections (>97%) when tested with feed solutions containing dyes of different classes and molecular weights (MW), except crystal violet (CV) dye. The lower rejection resulted from CV-contained feed is likely due to its small MW coupled with high diffusion rate in aqueous solution. With respect to feed concentration, it is found that an increase in salt concentration in the feed solution had negligible effect on the membrane separation performance. Increasing dye concentration in the feed however led to lower membrane water flux owing to the deposition of dye particles on membrane surface which resulted in severe fouling. Meanwhile, increasing feed temperature and its flow rate could improve membrane flux without affecting the permeate quality. When tested using dyeing solution containing 50 ppm acid red and 1.0 M NaCl, the membrane flux was reported to enhance by 200% and 25% with increasing feed temperature from 50 to 90˚C and flow rate from 0.010 to 0.023 m/s, respectively.

Keywords: membrane distillation; composite membrane; textile wastewater; dye-salt mixtures; membrane fouling

1 Introduction

Wastewater treatment has been a challenge to the textile and dyestuff manufacturing industries due to the color exhibited by the effluents. Colored textile effluents usually represent severe environmental problems as they contain a mixture of chemicals, auxiliaries and dyestuffs of different classes and chemical constitutions with elevated organic and inorganic parameters [1–3]. The colored textile effluents often come from printing and dyeing processes that use high concentrations of dyes, additives and salts to produce high quality fabrics [4]. Synthetic dyes, which are the most common among all other dyes, are typically used in textile industries. They are generally derived from coal tar and petroleum based intermediates [5,6]. According to Sen and Demirer [6], more than 7×10^7 tons of synthetic dyes are produced and consumed worldwide annually. Of these synthetic dyes, azo dyes are the largest and the most common group of dyes used in textile industry [1,7]. However, it must be noted that azo dyes are highly toxic, mutagenic and carcinogenic in nature [8]. The presence of a small quantity (even at 1 ppm level) of azo dyes in water can be visible and results in acute effect to the aquatic system due to their high level of toxicity [2,9].

Owing to ecological factors, a new global trend on developing various sustainable technologies for removal of such colored agents from aqueous solutions is of significant environmental and technical importance. The technologies that have been employed for textile effluent treatment can be categorized based on chemical, physical and biological methods [10–12]. Some of the examples of physical-chemical treatment methods are membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, electrolysis, advanced oxidation and chemical reduction. With respect to biological methods, bacterial/fungal biosorption and biodegradation in aerobic, anaerobic, anoxic or combined aerobic/anaerobic conditions have been generally reported [10]. Although physical-chemical methods are a good option regarding high color and suspended substances removal, they are associated with some problems such as sludge generation, low chemical oxygen demand (COD) removal and high operating cost. Biological treatment process on the other hand experiences several technical challenges such as difficulty of maintaining bacterial growth, longer period of treatment cycle, etc [13].

To date, the importance of membrane technologies in textile wastewater treatment is continuously growing. Membrane separation processes have become the best alternative methods that can be adopted for large-scale treatment process owing to the advantages such as environmentally friendly, high removal efficiency, modest energy requirement, etc [14]. Among the membrane-based processes, membrane distillation (MD) has been seen as a potential candidate in treating textile effluents as this membrane process can be operated at very low pressure, thus minimizes fouling effect [15–23]. Furthermore, MD can exploite the free energy given by hot effluent discharged by textile industry [16,23]. In order to consistently maintain the effluent temperature during treatment process, low-grade waste and/or alternative energy sources such as solar and geothermal energy can be potentially integrated with MD process [24]. Another promising feature of MD is its ability to reject 100% (theoretically) ions, macromolecules, colloids, cells, and other non-volatile organic compounds from the wastewater as its separation mechanism is mainly governed by vapor-liquid equilibrium (VLE) [25].

In our previous work [21], we have investigated the effect of Cloisite 15A clay loadings (zero–10 wt%) on the properties of polyvinylidene-fluoride (PVDF)-based hollow fiber membranes for MD application. Of the PVDF-Cloisite 15A composite membranes studied, it is found that the incorporation of 3 wt% Cloisite 15A was the ideal loading to produce best performing composite membrane by taking into consideration the membrane structural properties and separation characteristics. In this work, we will further evaluate the potential of this membrane in treating feed solutions containing dyes and salts via direct contact membrane distillation (DCMD) system. The separation performances of this membrane will be studied under different conditions by varying the properties of feed solution as well as process conditions.

2 Experimental

2.1 Materials

Five synthetic dyes supplied by Sigma-Aldrich were used as received and their classification and chemical structure are shown in Figure 1 and Table 1, respectively. Salt, sodium chloride (NaCl, MW = 58.44 g/mol) supplied by Merck was added to the dyeing solution to simulate industrial textile wastewater which often contains dissolved salts in the effluent.

Table 1 Overview of dye classification used in this study [1,26]

Class	Principal substrates	Method of application	Chemical types	Dye fixation (%)	Dyes used in this study
Acid	Nylon, wool, silk, inks, leather	Usually from neutral to acidic dyebaths	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso	89-95	Acid red 1 (AR1), Congo red (CR)
Basic	Polyacrylonitrile, modified nylon, polyester, inks	Applied from acidic dyebaths	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine, anthraquinone	95-100	Crystal violet (CV)
Reactive	Cotton, wool, silk, nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	Azo, anthraquinone, phthalocyanine, formazan, oxazine, basic	50-90	Reactive orange 16 (RO16), Reactive black 5 (RB5)

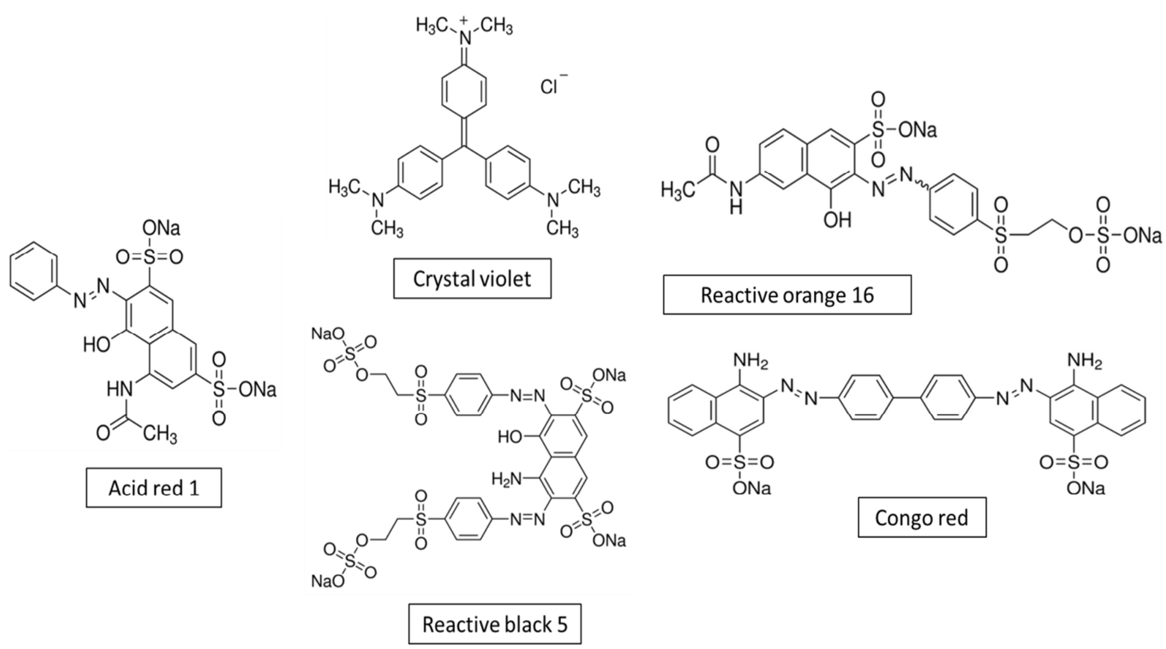


Figure 1 Chemical structure of the synthetic dyes used in this work

2.2 Stokes diameter of dye particle

The diameter, d_A (nm) of the dye particle was measured using Stokes-Einstein equation [27]:

$$d_A = \frac{kT}{3\pi \mu_B D_{AB}} \quad (3)$$

where k is the Boltzmann coefficient (J/K), T is temperature (K), μ_B is the water viscosity (Pa.s) and D_{AB} is the diffusion coefficient (m^2/s) of dye in water. The D_{AB} can be further defined according to the Wilke-Chang equation:

$$D_{AB} = 1.173 \times 10^{-16} \sqrt{\phi M_B} \frac{T}{\mu_B V_A^{0.6}} \quad (4)$$

where ϕ is the water association parameter, M_B is the MW of water (g/mol), μ_B is the water viscosity (Pa.s) and V_A is the molar volume of dye particle (m^3/kg.mol). The molar volume for each dye was calculated using a group contribution method [28].

2.3 Membrane fabrication

PVDF-Cloisite 15A dope solution consisted of 12 wt% PVDF and 3 wt% Cloisite 15A (i.e. clay concentration was determined based on the total weight of PVDF) was prepared by dissolving the PVDF pellets and clay powder in the NMP (80 wt%) and EG (8 wt%) mixture, while stirring at 60˚C, until the solution became homogeneous. After that, the PVDF-Cloisite 15A hollow fiber composite membrane was fabricated using dry-jet wet spinning technique in which the detailed fabrication procedure can be found in our previously published work [21]. After air-drying process, the membrane was subject to several characterizations to determine its structural properties.

2.4 Direct contact membrane distillation (DCMD) experiments

A stainless steel module containing PVDF-Cloisite 15A hollow fiber composite membrane was prepared and used to determine the performances of the membranes during

DCMD process. Table 2 shows the details of the membrane properties and its module. The DCMD system that was used in this work is illustrated in Figure 2, together with SEM images of the hollow fiber composite membrane. The system was designed to have two circulating streams, i.e. hot stream also known as feed stream (circulated through the membrane shell-side) and cold stream (fed through the lumen-side of the hollow fiber membrane). Both solution temperatures were controlled using coiled heater (830, PROTECH) and chiller (F26-ED, JULABO), respectively. The change of feed concentration in the feed tank during experiment was assumed to be negligible as large feed volume (5 L) was used. In order to avoid membrane flux decline caused by dye deposition (fouling), a new membrane module was used whenever there was a change in the feed property and/or process condition.

Prior to the dyeing solution treatment process, the permeate flux, J_v of membrane ($kg/m^2.h$) was determined using Eq. 1.

$$J_v = \frac{\Delta W}{A \Delta t} \quad (1)$$

where ΔW (kg) is the weight of permeate collected over a predetermined time Δt (h) of process and A (m^2) is the effective membrane area. To determine the solute (dye or salt) rejection, R (%) of the membrane, Eq. 2 was employed.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where C_p and C_f stand for permeate and feed concentration (mg/L), respectively. The results of flux and rejection reported in this work were the average of three measurements.

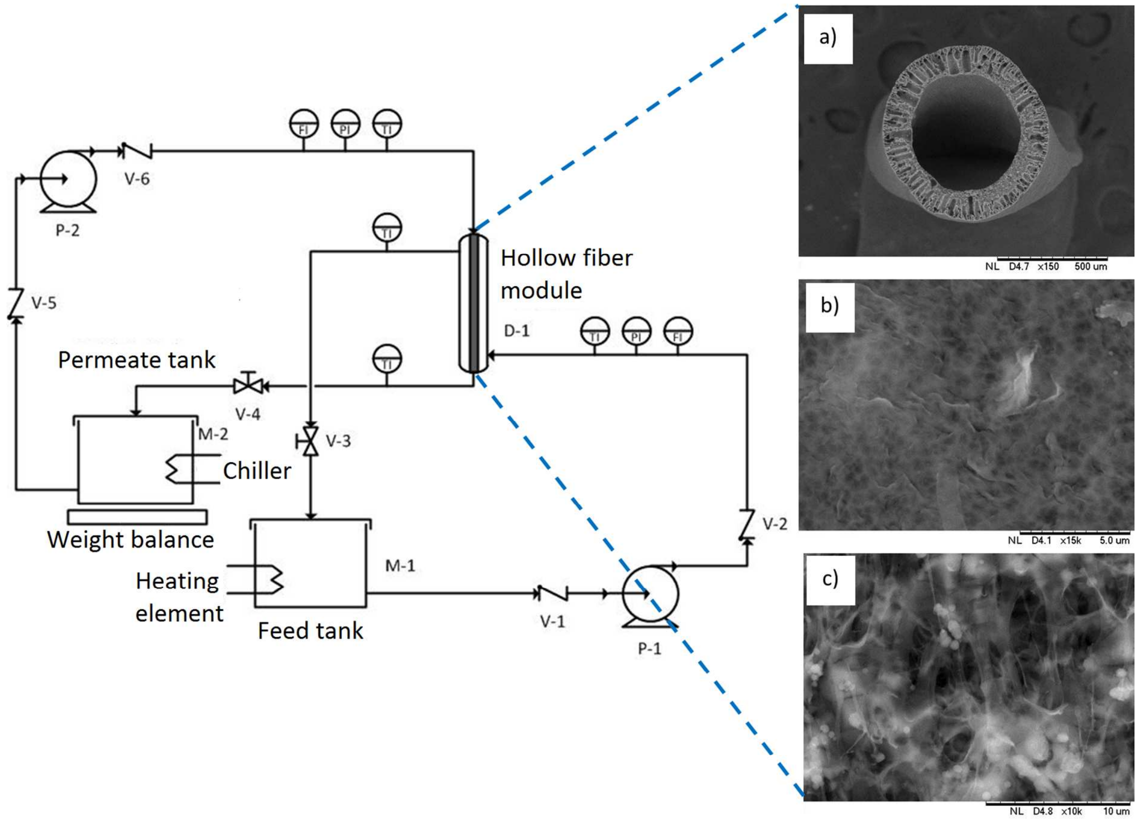


Figure 2 Schematic DCMD experimental setup and the SEM micrographs of PVDF-Cloisite 15A hollow fiber composite membrane, a) cross sectional view (magnification of 150×), b) outer surface (magnification of 15,000×) and c) inner surface (magnification of 10,000×)

Table 2 Membrane properties and module design

Membrane properties	
Average pore size (nm)	88
Porosity (%)	83.70 ± 0.67
Contact angle (˚)	97.72 ± 2.54
Fiber outer dia. (μm)	763 ± 19
Module design	
Module inner dia. (m)	0.01
Module length (m)	0.22
Number of fibers in module	20
Effective fiber length in module (m)	0.19
Effective membrane area in module (m^2)	0.01

2.5 Analytical methods

2.5.1 Dye and salt concentration determination

The dye concentration in the sample solutions was detected by a UV-vis spectrophotometer (DR5000, Hach) which measured at its maximum absorbance wavelength. Meanwhile, the ionic conductivity of the sample solutions was measured using a bench conductivity meter (4520, Jenway). Both sample absorbance and conductivity were later converted into concentration using a calibration curve.

2.5.2 SEM-EDX

The dry membrane samples were immersed in liquid nitrogen and fractured, followed by sputter-coating with platinum using a sputtering device. The cross-sections of the membrane samples were examined using scanning electron microscope (SEM) (TM-3000, Hitachi). Meanwhile, energy-dispersive X-ray (EDX) spectrometer (XFlash® 430H, Bruker) was used for elemental analysis in order to identify the elements caused by foulants that deposited on membrane surface.

3 Results and discussion

3.1 Effect of dye characteristics on DCMD performance

Figure 3 shows the effect of dye characteristics on the permeate flux and rejection of PVDF-Cloisite 15A hollow fiber composite membrane during DCMD process. The error bars indicate the standard deviations of the average measured values of both water flux and dye rejection. From the figure, it can be clearly seen that the in-house made membrane could achieve very similar permeate fluxes (around 10 $kg/m^2.h$) for all dyes studied, except for CV which showed >17 $kg/m^2.h$. With respect to separation characteristics, it is found that the membrane could potentially eliminate almost all types of dyes regardless of their MW and Stokes diameter. Although the membrane average pore size (d_p = 88 nm) is significantly larger than those of dyes' particle size (Table 3), its excellent separation performance is not compromised. This is because MD does not work according to the principle of size exclusion and/or Donnan exclusion as in ultrafiltration and nanofiltration [29–32]. It instead works as a physical barrier to hold the liquid–vapor interface at the entrance of the membrane pores. In view of this, the separation mechanism in MD is predominantly determined by the VLE principle [33].

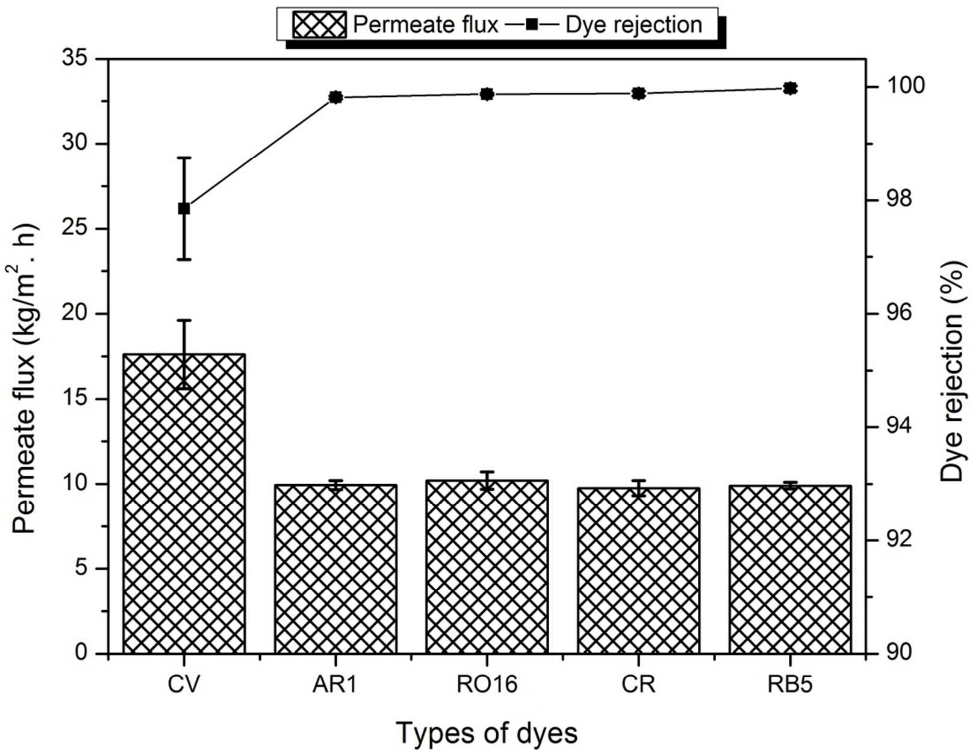


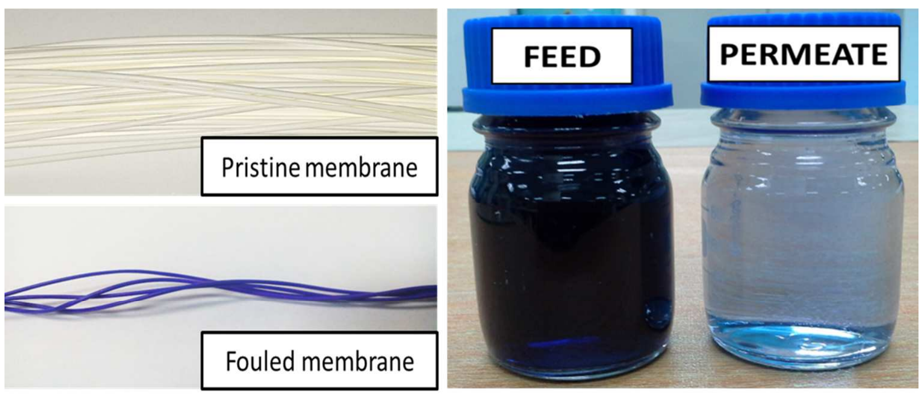
Figure 3 Effect of dye components on the permeate flux and dye rejection of membrane during DCMD process (Conditions = hot stream: 50 ppm dyeing solution, 70˚C at flow rate of 0.023 m/s; cold stream: distilled water, 20˚C at flow rate of 0.010 m/s)

Table 3 Properties of synthetic dyes used in this work

Dye	$^a\lambda_{max}$ (nm)	^{b}MW (g/mol)	$^cD_{AB}$ (10^{-10} m^2/s)	^dd_A (nm)
CV	590	407.98	3.99	1.23
AR1	506	509.42	4.25	1.15
RO16	493	617.54	3.81	1.29
CR	498	696.66	3.24	1.52
RB5	597	991.82	3.01	1.63

$^a\lambda_{max}$= Maximum absorbance wavelength
^{b}MW= Molecular weight
$^cD_{AB}$ = Diffusion coefficient of dye in water
^dd_A = Stokes diameter of dye in water

Unlike other dye components which displayed very similar flux and rejection results, the CV dye seemed to have different interaction with the membrane matrix, leading to relatively higher permeate flux but lower removal rate. This can be possibly due to the high "affinity" of this particular dye towards the membrane matrix. The high adsorption rate of CV towards PVDF-based membrane is believed to be the main factor changing the color of membrane after treatment process (see Figure 4(a)). Furthermore, the high diffussivity of CV in aqueous solution could be another reason causing less promising dye removal (<98%) as evidenced from the permeate sample collected (Figure 4(b)). The detection of nitrogen (N) and chlorine (Cl) element on the composite membrane surface as shown in Figure 5 strongly indicates the presence of dye component on the membrane surface, owing to the possible interaction between the aromatic rings of the dye molecule and the membrane via Van der Waals [22].



(a) (b)

Figure 4 Direct comparisons between (a) pristine membrane and fouled membrane and (b) 50 ppm CV dyeing solution (feed) and permeate produced by the composite membrane

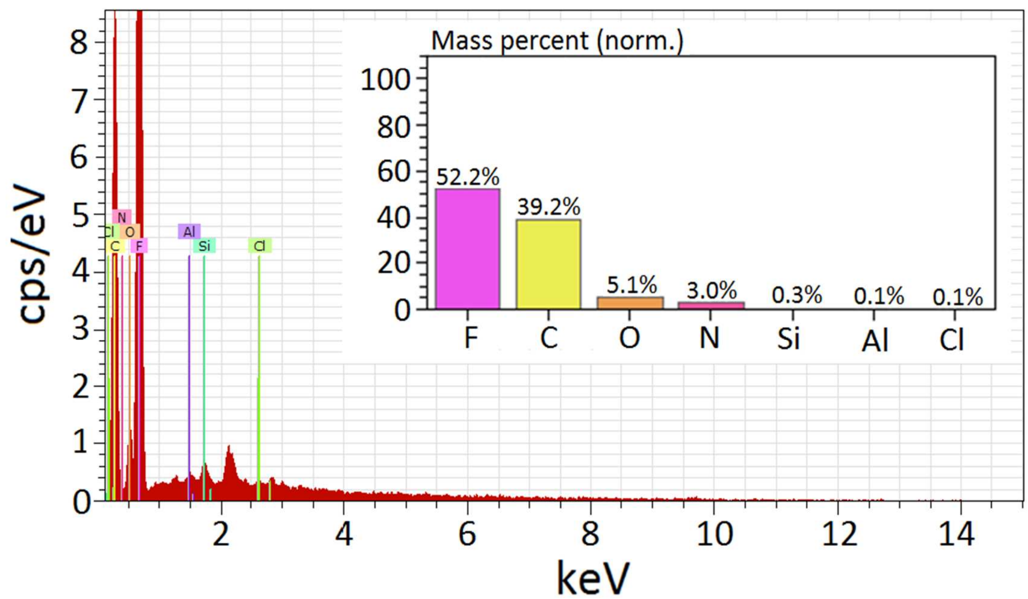


Figure 5 EDX results on the membrane surface after treating CV dyeing solution

3.2 Effect of dye concentrations on DCMD performance

In general, approximately 10–20% of textile dyes are lost during dyeing process and as a consequence, the effluent discharged typically contains between 10 and 1000 ppm of dye components [34,35]. To evaluate the effect of dye concentration on the DCMD performance, a series of experiments were carried out and the results are shown in Figure 6. Results showed that both permeate flux and dye rejection tended to decrease with increasing dye concentration from 50 to 1000 ppm. The permeate flux decline at high solute concentration can be caused by the lower water vapor transport rate. This phenomenon is common in MD process as higher solute concentration could lead to lower activity coefficient of water vapor pressure [33,36].

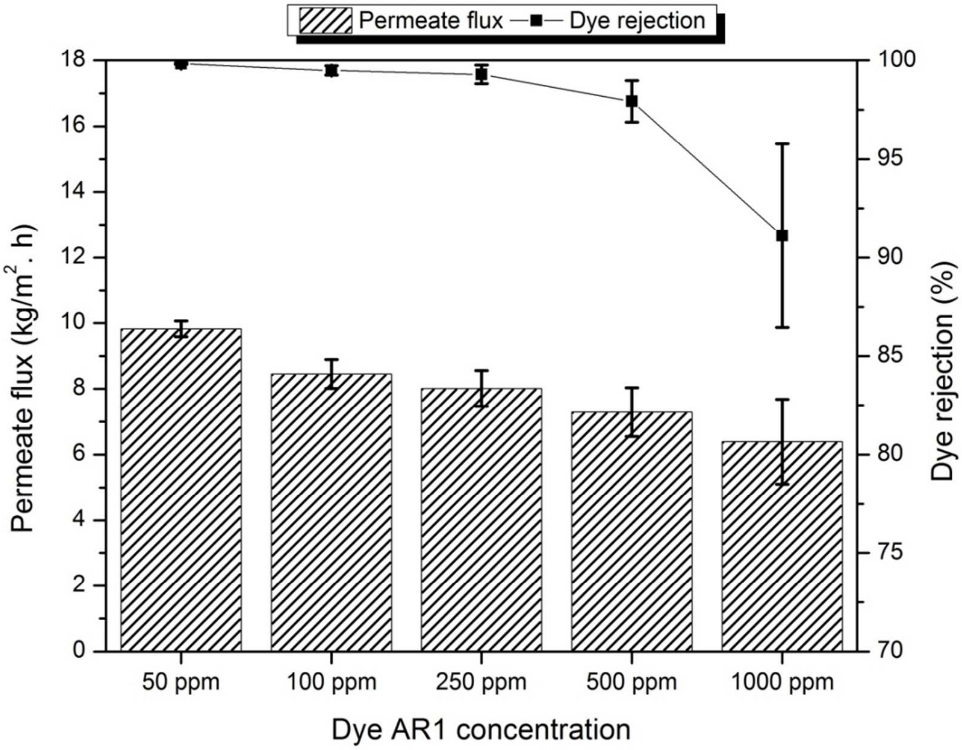


Figure 6 Permeate flux and dye rejection as a function of dye concentration (Conditions = hot stream: 70˚C at flow rate of 0.023 m/s; cold stream: distilled water, 20˚C at flow rate of 0.010 m/s)

In addition to activity coefficient of water vapor pressure, the reduction of permeate flux and dye rejection at high concentration of dye solution is also possibly due to the attachment of dye particles on the membrane surface which leads to either partially or fully pore blockage. Additional fouling layer could be developed which further reduces the evaporation area and affects permeate quantity. As reported by Yarlagadda *et al.* [37], severe fouling caused by high feed concentration may damage the membrane surface and allow the passage of small quantities of non-volatile solutes through the membrane. In addition, increasing feed concentration will also increase feed viscosity and boundary layer thickness, which enhances the mass transfer resistances [33]. Even though MD experienced lower permeate flux at high dye concentration, its degree of flux decline was still much lower compared to pressure-driven membrane process, e.g. nanofiltration. Comparing the results obtained from lowest and highest dye concentration, it is found that the flux of MD was only reduced by 12.4% with dye rejection maintained at > 90%.

3.3 Effect of salt concentrations on DCMD performance

Cotton is the most important and widely used textile fiber in the world which consists around 88-96% of pure cellulose [38]. However, natural cellulose fibers commonly carry negative charge, which create repulsion with anioic dyes. In order to promote dye-fiber fixation, high amount of NaCl is needed to suppress the fiber surface charge. This as a consequence has led the effluent to have high NaCl concentration (0.7–1.4 M) [39]. In this section, the effect of feed salt concentration on the performance of DCMD process was investigated and the results are shown in Figure 7. It can be seen from the figure that the variation in NaCl concentration in the feed solution has very little impact on the performance of membrane with respect to permeate flux and separation characteristics. The findings from this work were consistent with Banat *et al.* [15] in which they also reported that salt concentration (0.05–1.0 M) has negligible effect on the driving force for the vapor flux.

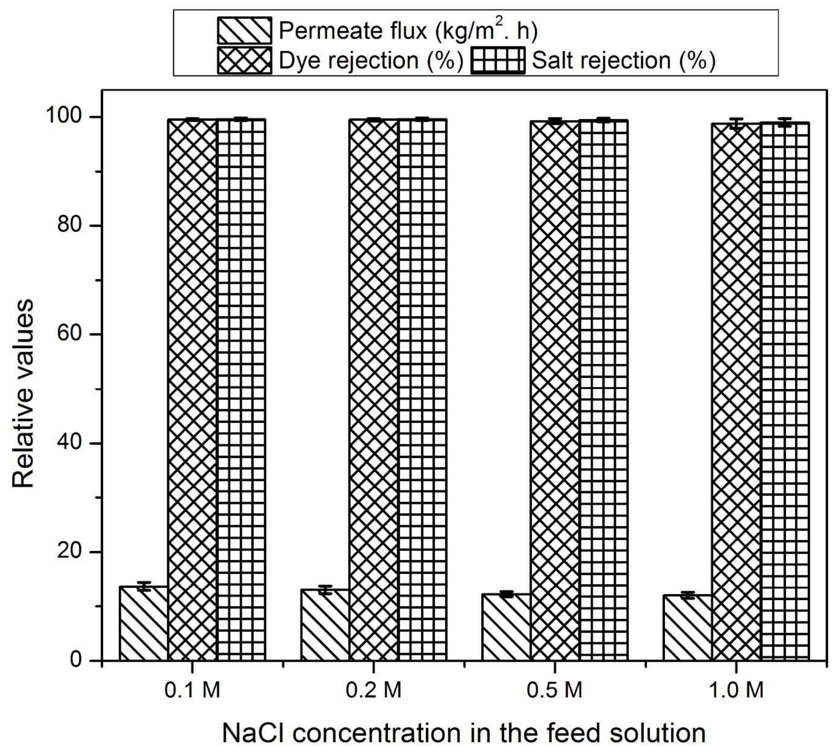


Figure 7 Permeate flux and solute rejection as a function of salt concentration in the dyeing solution containing 50 ppm ARI (Conditions = hot stream: 70˚C at flow rate of 0.023 m/s, cold stream: 20˚C at flow rate of 0.010 m/s)

Although the salt concentration has negligible effect on membrane permeate flux, it does have huge impact on membrane scaling when it is present at high concentration. Figure 8 shows the SEM images of the membranes after testing with two different salt concentrations (0.1 and 1.0 M). Crystallized salts were found within the structure of the fouled membrane after treating 1.0 M NaCl feed solution. This observation could be directly related to membrane scaling [40]. Generally, the scaling occurs when the salt concentration in the feed solution reaches supersaturation due to high product water recovery. Concentration and temperature polarizations are the major causes for the salt solution to become supersaturated and crystallize directly on the membrane surface or crystallize in the bulk solution and deposit on the membrane surface. The presence of salt on the composite membrane was further analysed based on EDX results shown in Figure 9. As can be seen, Na and Cl elements corresponded to salt were detected, in addition to the elements (F, C, O, Si and Al) belonging to the PVDF-Cloisite 15A membrane. Furthermore, the amounts of Na and Cl detected are consistent with the SEM images shown. Since the fouling scaling is hydrophilic, there is a high tendency for the membrane to have pore wetting problems. The membrane scaling however has no obvious influence on the permeate flux because the evaporation area at the feed side did not decrease significantly. In all cases, the solute rejections are still promising, recording >98%. Nevertheless, more research is still needed to examine the long-term effect of crystallized salts (within membrane matrix) on separation performance.

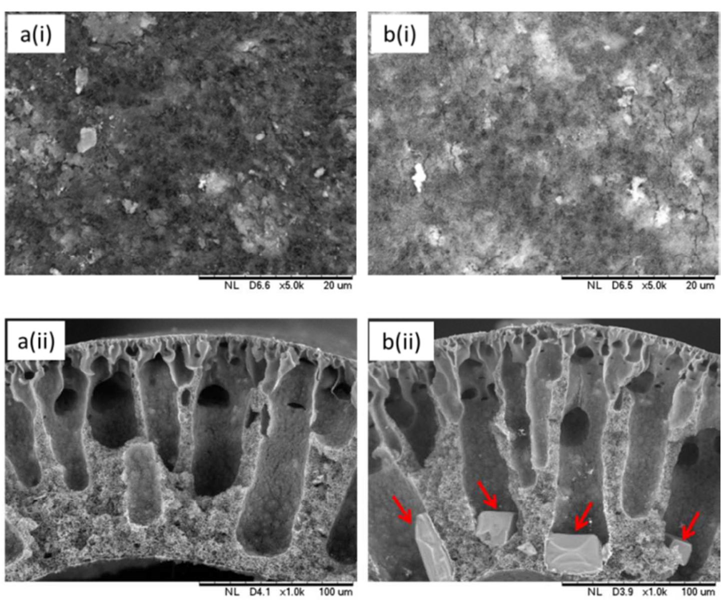


Figure 8 SEM images of the i) outer surface and ii) cross-section of the composite membrane after testing with 50 ppm ARI solution containing a) 0.1 M and b) 1.0 M NaCl

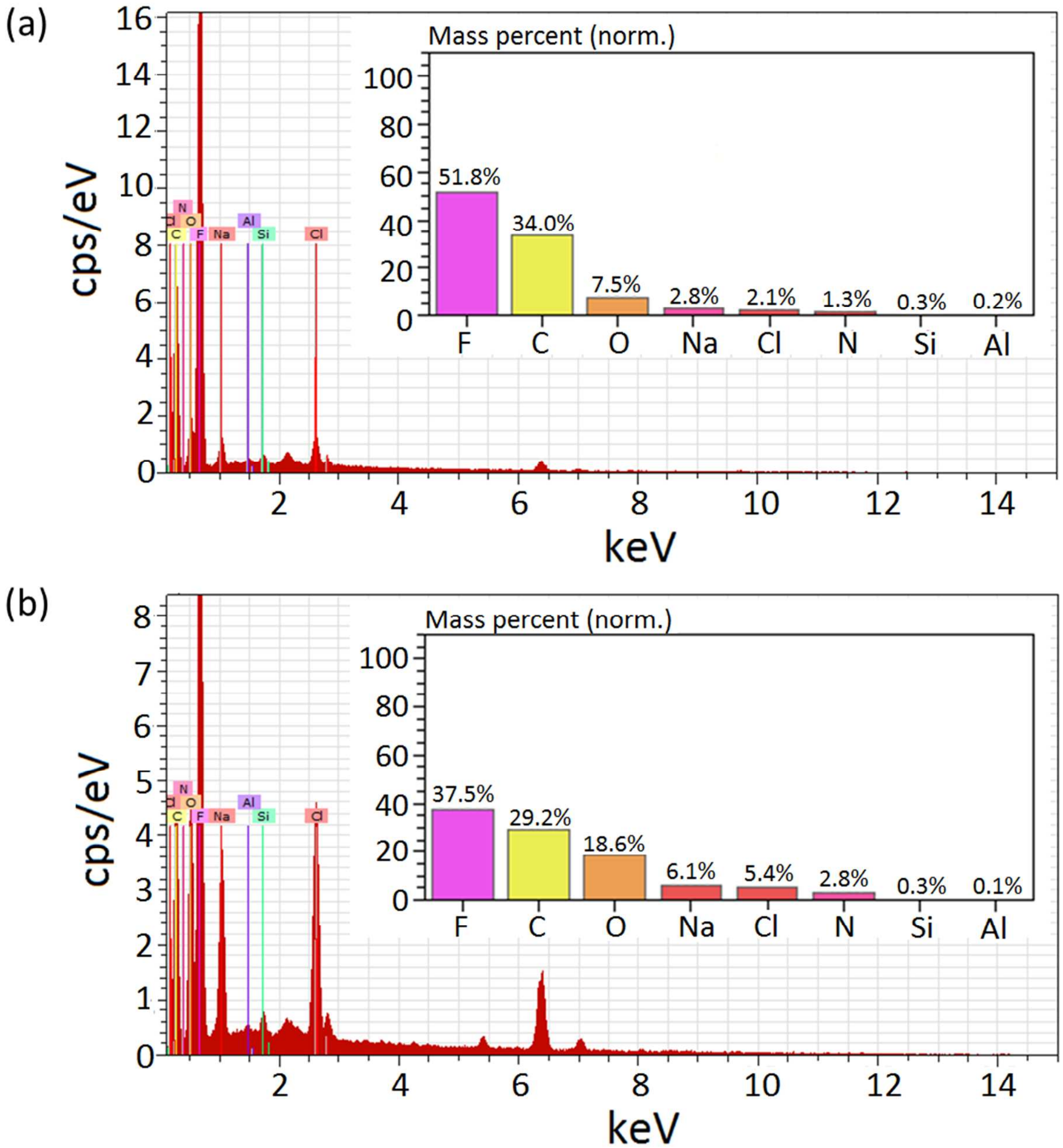


Figure 9 EDX analysis results of the membranes after testing with different salt concentrations, a) 0.1 M and b) 1.0 M NaCl

3.4 Effect of feed temperature and feed flow rate on DCMD performance

Figure 10 shows the effect of feed temperature on the permeate flux of PVDF-Cloisite 15A hollow fiber composite membrane in the feed solution composed of 50 ppm AR1 and 1 M NaCl. As expected, an exponential relation between permeate flux and feed temperature was observed. This trend could be explained by the Antoine equation which predicts an exponential relationship between the vapor pressure difference and temperature [15,33]. At low feed temperature, heat is likely to be wasted through conduction across both the membrane material and the gas-filled membrane pores, rather than to be used for water evaporation [41]. However, when the feed temperature is further increased, the latent heat of water evaporization is the main contribution to the total heat transfer which result in significant improvement in permeate flux as evidenced in this work. Although heat loss through conduction still occurs at high feed temperature, the impact can be minimized due to the higher partial vapor pressure at the feed side [42].

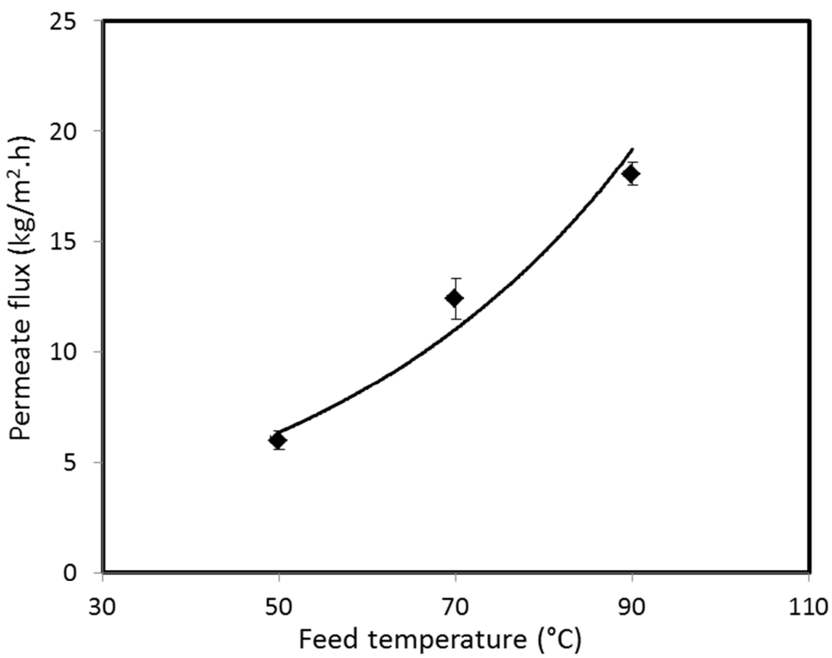


Figure 10 Permeate flux as a function of feed temperature (Conditions = hot stream: 50–90˚C at flow rate of 0.023 m/s, cold stream: 20˚C at flow rate of 0.010 m/s)

Figure 11 shows the permeate flux of PVDF-Cloisite 15A composite membrane as a function of feed flow rate using feed solution composed of 50 ppm AR1 and 1 M NaCl. It it noticed that the effect of feed flow rate is less significant compared to feed temperature in enhancing permeate flux of membrane. The permeate flux was reported to increase by only 25% even though the feed flow rate was greatly increased by more than 100%. The slight enhancement of permeate flux at higher flow rate can be attributed to the decrease in the temperature polarization effect between the membrane surface and the bulk streams [16,43–45]. Although the flux increases with increasing feed flow rate, it is important to ensure that the hydraulic pressure is lower than the wetting pressure while controlling the feed flow rate. This precaution is needed in order to prevent wetting problem during MD process.

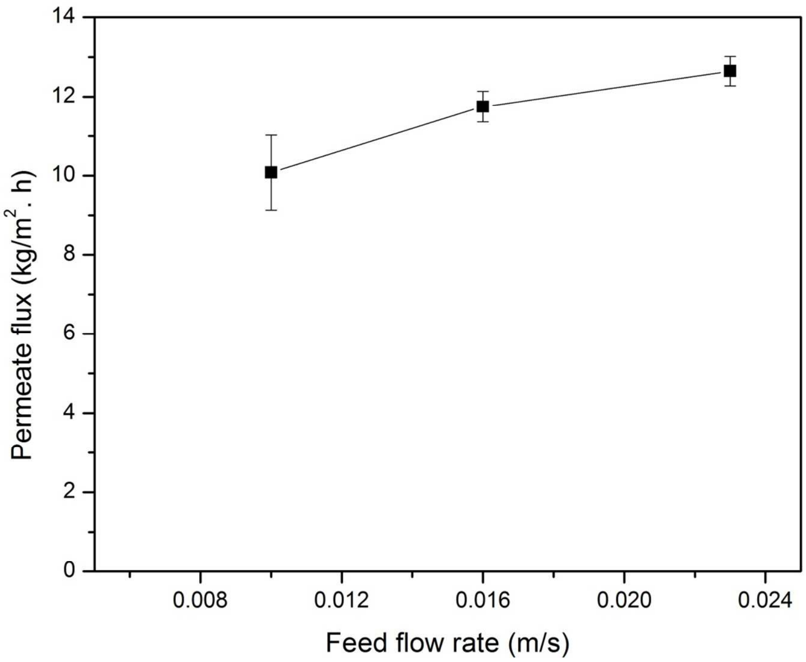


Figure 11 Permeate flux as a function of feed flow rate (Conditions = hot stream: 70˚C at flow rate of 0.010–0.023 m/s, cold stream: 20˚C at flow rate of 0.010 m/s)

3.5 Performance comparison of membrane distillation

Table 4 compares the performance of the self-made membrane studied in this work with previously published works for the treatment of dyeing solutions. Although other factors such as MD configuration, operating temperatures and feed properties might also affect the MD performance, in addition to the membrane property itself, the results shown in this work have revealed that the performance of the self-made PVDF-Cloisite 15A hollow fiber composite membrane is comparable or even better than the commercial membranes for textile wastewater treatment process. The results proved the in-house made membrane can be a reliable material for the DCMD process, particularly in treating effluents containing dyes and salts. Although VMD in general shows higher flux than DCMD, the objective of using DCMD in this study is due to its relatively simple operation mode and low maintenance cost. For DCMD configuration, both evaporation and condensation processes can occur simultaneously inside the membrane module and it requires no external vacuum pump. Thus, it is more cost-effective to implement.

Table 4 Comparison of the membrane performance obtained in this study with the literature in the MD process for the treatment of dyeing solutions

Membrane material	Membrane configuration	MD configuration	Type of dye (concentration)	Jv (kg/m^2.h)	^aT_f (˚C)	^bT_p (˚C)	$^cR_{,color}$ (%)	References
PP (commercial membrane module)	Hollow fiber	DCMD	Blue E-G (5,000 ppm)	1.62	50	35	100	[46]
PP (Enka Microdyn, USA)	Capillary	VMD	MB (18.5 ppm)	6.3	70	N/A	100	[15]
PP (Membrana GmbH, Germany)	Capillary	VMD	Blue R (50 ppm)	57	60	N/A	> 90	[16]
PP (Membrana GmbH, Germany)	Capillary	Hybrid photocatalysis -DCMD	AR18 (30 ppm)	3.5×10^{-3}	65	20	100	[17]
PP (Hangzhou Kaijie Membrane Company, China)	Hollow fiber	SPMDR	RB5 (400 ppm)	4.56	65	-	100	[18]
PVDF (fabricated)	Hollow fiber	DCMD	RB5 (50 ppm)	5.64±0.10	80	20	99.83±0.01	[19]
PVDF (fabricated)	Hollow fiber	DCMD	RB5 (500 ppm)	9.82±0.52	60	20	99.86±0.04	[20]
PVDF-Cloisite 15A (fabricated)	Hollow fiber	DCMD	RB5 (50 ppm)	10.13±0.18	70	20	99.98±0.01	[21]
PVDF-Cloisite 15A (fabricated)	Hollow fiber	DCMD	AR1 (50 ppm) and NaCl (1 M)	12.42±0.93	70	20	99.92±0.07	This study

^aT_f = feed temperature, ^bT_p = permeate temperature, $^cR_{,color}$ = color rejection

4 Conclusion

In the present work, the application of DCMD using PVDF-Cloisite 15A hollow fiber composite membrane for dye and salt removal was investigated systematically. Results showed that the in-house made composite membrane demonstrated excellent results in eliminating almost all dye components (except CV dye) with consistent permeate flux recorded irrespective of dye properties. Since CV dye has high affinity towards PVDF-based membrane material and exhibits lowest MW, it can be easily absorbed to membrane matrix, altering membrane color and affecting permeate quality. With respect to dye concentration, it is found that both permeate flux and solute rejection was slightly affected with increasing dye concentration in the feed solution. Reduced permeate flux as a result of increased dye concentration can be attributed to the membrane fouling which increases mass transport resistance. Although salt concentration has no significant effect on membrane performance, the presence of crystallized salts within membrane matrix when the membrane was subject to high concentration of salt solution might need to further analyze, in particular on its effect on membrane long-term performance. In terms of process conditions, it is reported that the increase in both feed temperature and feed flow rate could enhance membrane permeate flux owing to higher latent heat of water evaporation and higher heat transfer coefficient. While this work has focused exclusively on the separation of dyes and salts in aqueous solutions, the effect of surfactants on the activity of the dyes-salts aqueous solution and the performance of membrane is recommended for future work to better examine the potential of MD for industrial wastewater. Besides, effect of solution pH and co-existing ions are also necessary to take into account to better model the textile effluent.

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