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High flux and antifouling properties of negatively charged membrane for dyeing wastewater treatment by membrane distillation

Alicia Kyoungjin An^{1*}, Jiaxin Guo¹, Sanghyun Jeong², Eui-Jong Lee¹, S. Assiyeh Alizadeh Tabatabai²,
TorOve Leiknes²

¹ School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue Kowloon, Hong Kong, China,

² King Abdullah University of Science and Technology (KAUST), Water Desalination and Reuse Center (WDRC),
Biological and Environmental Science & Engineering (BESE), Thuwal 23955-6900, Saudi Arabia

* Corresponding author: Tel: + (852)-3442-9626, Fax: + (852)-3442-0688, E-mail: alicia.kjan@cityu.edu.hk

Abstract

This study investigated the applicability of membrane distillation (MD) to treat dyeing wastewater discharged by the textile industry. Four different dyes containing methylene blue (MB), crystal violet (CV), acid red 18 (AR), and acid yellow 36 (AY) were tested. Two types of hydrophobic membranes made of polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) were used. The membranes were characterized by testing against each dye (foulant-foulant) and the membrane-dye (membrane-foulant) interfacial interactions and their mechanisms were identified. The MD membranes possessed negative charges, which facilitated the treatment of acid and azo dyes of the same charge and showed higher fluxes. In addition, PTFE membrane reduced the wettability with higher hydrophobicity of the membrane surface. The PTFE membrane evidenced especially its resistant to dye absorption, as

its strong negative charge and chemical structure caused a flake-like (loose) dye–dye structure to form on the membrane surface rather than in the membrane pores. This also enabled the recovery of flux and membrane properties by water flushing (WF), thereby direct-contact MD with PTFE membrane treating 100 mg/L of dye mixtures showed stable flux and superior color removal during five days operation. Thus, MD shows a potential for stable long-term operation in conjunction with a simple membrane cleaning process, and its suitability in dyeing wastewater treatment.

Keywords: Dyeing wastewater; hydrophobic membrane; membrane distillation; membrane fouling; water flushing

1. Introduction

Because of the increasing use of chemical synthetic textiles in recent years, dye wastewater has become one of the largest contributors to pollution (Hao et al., 2000; Rawlings and Samfield, 1979; Vanhulle et al., 2008). Textile production requires an extremely large amount of water, which is discharged as wastewater containing high concentrations of reactive dye, chemical residues and low-biodegradable materials, with high levels of chemical and biochemical oxygen demand (COD and BOD, respectively) (Basava Rao and Ram Mohan Rao, 2006; Hu and Wang, 1999; Lin and Chen, 1997). The composition of the discharge effluents and the complexity of contaminants in dyeing wastewater make it one of the most hard to treat forms of wastewater, and despite the development and application of various treatment methods, there is still much progress to be made. Conventional treatment methods have various drawbacks when applied to dyeing wastewater. For instance, traditional biological treatment methods do not completely mineralize the target dye contaminants and discharge effluents that are of great concern to human health (Chequer, F.M.D.; Dorta, D.J.; de Oliveira, 2011). Meanwhile,

physicochemical methods (such as coagulation, adsorption, radiation, oxidation, and photocatalysis) (Basava Rao and Ram Mohan Rao, 2006; Hu and Wang, 1999; K. Vinodgopal, D.E. Wynkoop, 1996; Kar et al., 2009; Lin and Chen, 1997) have a multitude of limitations, such as high cost, complexity (often necessitating hybrid processes that require highly skilled operators), and production of large amounts of sludge that requires secondary disposal (Garg et al., 2003; Ip et al., 2009; Robinson et al., 2001; Slokar and Marechal, 1998).

As an alternative to conventional dyeing wastewater treatment methods, membrane-based processes have attracted attention due to their inherent simplicity, scalable modular design, easy maintenance, and excellent rejection rate (Dasgupta et al., 2015; Tang and Chen, 2002). Continuous efforts by scientists and engineers have improved the effectiveness of membrane-based processes for the removal of color and toxicity (Alcaina-Miranda et al., 2009; Aouni et al., 2012; Han et al., 2009; Mo et al., 2008). In particular, membrane distillation (MD), an emerging membrane-based technology, has generated interest because it can achieve a high rejection rate under mild temperatures and normal atmospheric pressure (Alkhudhiri et al., 2012; Kezia et al., 2015; Liao et al., 2014; Mokhtar et al., 2015). MD uses a hydrophobic porous membrane to separate the hot feed stream and the cold stream (Elimelech, 2014), whose temperature difference creates a trans-membrane vapor pressure difference that drives the vapors from the hot side to the cold side through the membrane pores (Hassan and Fath, 2013; Woo et al., 2015). The application of MD for dyeing wastewater treatment has two particularly notable advantages. First, it can utilize the industrial waste heat already present in dyeing wastewater without requiring extra heating, as the wastewater discharged from the textile industry is generally above 80 °C (Criscuoli et al., 2008; Nadzirah M. Mokhtar et al., 2015). Second, the dye can potentially be recovered from the concentrate, which is attractive to the textile industry (Ge et al., 2012).

While fouling mechanisms and cleaning issues have been heavily investigated for other membrane technologies (e.g., micro- and ultrafiltration (MF/UF), nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO)), significant advancements are required for MD to achieve cost competitiveness and market share growth (Hassan and Fath, 2013). Fouling in MD is of particular importance, as it results in higher energy consumption, longer downtimes, more frequent cleaning and membrane replacement, and deteriorates the product water quality due to pore wetting (Kim et al., 2015; Warsinger et al., 2014). Most likely due to these fouling and wetting issues, previous studies on dyeing wastewater treatment by MD have limited their tests to short operating times and have used only a single dye at a low feed concentration (Banat et al., 2005; Mokhtar et al., 2015, 2014; Mozia et al., 2010, 2009; Qu et al., 2014).

The main aim of this study is to demonstrate the possibility of incorporating water flushing (WF) as a means to control membrane fouling for long-term application of MD to dyeing wastewater treatment. Four different dye solutions were treated using various MD membranes to comprehensively examine the mechanisms of interaction between the dyeing wastewater and MD membranes and to improve the performance of MD for treating dyeing wastewater. The MD membranes studied included two commercial membranes. Then, for the first time in this field, a mixed dye solution was treated in a bench-scale direct-contact MD (DCMD) test unit, which incorporated simple membrane cleaning by WF for five days to demonstrate the long-term performance of the MD membranes. These promising results open the application of MD with antifouling characteristics to textile wastewater treatment and provide an avenue for the scale-up of MD in commercial applications.

2. Material and Methods

2.1 Dyes

The dyes commonly used in textile industries include acid, basic, direct, reactive, sulfur, azoic, and vat dyes (Hao et al., 2000). To enhance the understanding of the complex structure of dyes in terms of their treatment efficiency, two basic and two acid dyes were tested in this study. The four tested dyes – methylene blue (MB), crystal violet (CV), acid red 18 (AR18), and acid yellow 36 (AY36) – were purchased from Shanghai Zhanyun Chemical Co., Ltd, Shanghai, China. MB and CV are basic dyes (cationic or positively charged) that react with negatively charged material. AR18 and AY36 are acid dyes (negatively charged) that are typically a salt of sulphuric, carboxylic or phenolic organic acid (More details in supplementary information, **Table S1**). The dyes used in this study have a molecular weight (M_w) and pH ranging from 300 to 600 g mol⁻¹ and 5.2 to 9.1, respectively. The dye feed solutions were prepared at a concentration of 100 mg/L by dissolving appropriate amounts of the dye salts in distilled water. **Fig. S1** presents the chemical structures of the dyes (illustrated using ChemBioDraw Ultra software).

(**TABLE S1**)

(**FIGURE S1**)

2.2 Membranes

Two types of hydrophobic flat sheet membrane made of PVDF and PTFE were used in this study. The PVDF membrane with pore size of 0.22 μ m (GVHP) and 0.45 μ m (HVHP) were purchased from Millipore (Durapore® Membrane Filters, Merck Millipore Ltd, USA). The PTFE membrane used was TF-200 with 0.20 μ m pore size and was purchased from Pall Gelman (USA). **Table 1** summarizes the characteristics of the membranes used in this study.

(**TABLE 1**)

110

111 **2.3 DCMD setup for dye wastewater treatment**

112 A schematic diagram of the DCMD test unit for dyeing wastewater treatment is shown in **Fig. 1**. The hot
 113 feed and cold permeate solutions were circulated in opposite directions across the membrane (effective
 114 area: 9.8 cm²), which was mounted in a custom-made membrane module. The feed and permeate water
 115 (cooling water) were maintained at 60 °C using a hotplate/stirrer and 20 °C using a heat exchanger
 116 equipped with a chiller, respectively. Synthetic dye wastewaters with an initial volume of 2.2 L (feed)
 117 and the deionized (DI) water with an initial volume of 0.5 L (permeate) were circulated continuously at
 118 the same flow rate (0.5 L min⁻¹) by a gear pump. To minimize the heat loss, insulated rubber tubes were
 119 used because of their low heat conductivity. Membrane permeability was calculated by measuring the
 120 weight changes of the permeate container placed on a digital balance connected to a computer. To
 121 control fouling, the membranes were flushed by circulating DI water (hereafter referred to as water
 122 flushing, WF) for a duration of 10 min, every 3 hours, at a flow rate of 0.5 L min⁻¹. Each test was
 123 repeated at least three times to guarantee the reproducibility of the results.

124 **(FIGURE 1)**125 **2.4 Permeate flux and dye rejection efficiency**

126 In the MD process, the water (or permeate) flux J , in units of L m⁻² h⁻¹ (LMH) can be expressed as
 127 follows:

$$128 \quad J = \frac{\Delta W}{\Delta t \times A} \quad (1)$$

129 where ΔW is the change in the mass of the permeate collected, Δt is the permeate collection time, and A
 130 is the active membrane surface area, which is 9.8 cm².

In the MD test, the dye concentration in the permeate (distillate) tank was measured using an ultraviolet-visible (UV-vis) spectrophotometer (UV-2600, SHIMADZU, Japan). This apparatus detects the light absorbed at the maximum wavelength, which can then be used to calculate the dye concentration, as dyes are chromatic and highly visible even at very low concentrations. The dye rejection efficiency R (%) was determined by the following equation (Lu et al., 2016):

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

where C_f (mg/L) is the initial dye concentration in the feed and C_p (mg/L) is the final dye concentration on the permeate (distillate) side calculated taking the dilution factor into account. Each MD test for flux and color rejection was repeated at least three times to guarantee the reproducibility of the results.

2.5 Membrane analyses

2.5.1 Pore size, liquid entry pressure, and contact angle

A capillary porometer (PoroLuxTM 1000, POROMETER, German) was employed using the gas-liquid displacement porometry method to measure the mean pore size and liquid entry pressure (LEP) of the membranes. The EASYDROP Contact Angle Measuring System (Kruss, Germany) was used to determine the contact angle (CA) of the liquid on the membranes. This measurement was conducted by dropping a 5- μ L droplet of DI water on a membrane specimen placed on a sample board using a syringe equipped with a thin needle. A computer featuring a video-digitizer board was used to capture an image of the water drop on the membrane, which was displayed on a monitor. DSA1 software was used to analyze the image and calculate the CA by a geometrical method (sessile drop). In this analysis, the liquid drop is assumed to be part of a sphere. Geometrically, the contact angle can be calculated by

measuring the drop diameter and the height of the apex. All measurement were made in triplicate, results were presented as mean $\pm$ standard deviation.

2.5.2 Porosity and tensile strength

The void volume of the membrane (porosity) was measured by means of a gravimetric method. Membrane samples (3 cm $\times$ 3 cm) were fully wetted with ethanol for 30 min. Porosity was measured by calculating the volume of ethanol based on weight difference between dry and wet membrane samples, and the material densities of ethanol and the PH polymer (Lee et al., 2016; Tijing et al., 2016) (Lee et al., 2016) The tensile strength of the membranes was determined using a material testing instrument (Lloyd LS1, AMETEK, U.S.).

2.5.3 Surface morphology and fouling layer composition

The morphology of the fouling layer formed or deposited on the membrane surfaces was observed before and after the MD tests using scanning electron microscopy (SEM) (EVO MA10, ZEISS, Germany). To further investigate and compare the chemical bonds in the virgin and used membranes, Fourier transform infrared spectroscopy (FTIR) analysis was conducted using an IRAffinity-1 FTIR spectrometer (Shimadzu, Japan). The IR spectra of the membranes were acquired in attenuated total reflectance (ATR) mode and included 16 scans in the range of 400 to 4000 cm^{-1} with a 2- cm^{-1} resolution.

2.5.4 Surface zeta potential measurement

The zeta potential of the membrane surfaces was measured via a streaming current method using an electrokinetic analyzer (Surpass Anton Paar, Austria). The membrane samples were cut into 0.2 cm $\times$

0.1 cm pieces and then immobilized on an adjustable gap cell. KCl solution (1.0 mmol L^{-1}) was used for the determination of zeta potential, and several solutions were prepared to study the effect of solution pH on the charge density of the membrane surfaces. Hydrochloric acid (HCl) and potassium hydroxide (KOH) were used to adjust the pH value. The calculations were performed using the Visolab for Surpass software.

3. Results and Discussion

3.1 Characterization of membranes for dyeing wastewater treatment

As a barrier, an ideal porous MD membrane should only allow the transport of vapor and/or non-condensable gases through the membrane pores (El-Bourawi et al., 2006), creating a liquid/vapor interface between the membrane surface and the feed stream. To reduce pore wetting, membranes for MD applications should be hydrophobic with a high CA. However, due to the complex composition of dyeing wastewater, in addition to the nature of the membrane material, the dye type and concentration are also important parameters for the efficiency of MD treatment. At present, MD processes still suffer from the key limitations of low flux, wetting, and gradual deterioration during long-term operation. Thus, before investigating the incorporation of membrane cleaning to improve the long-term applicability of MD for dyeing wastewater treatment, the flux and color removal efficiency (without wetting) of the three membranes were tested to unveil the removal mechanisms of various dyes by MD treatment.

3.1.1 MD flux and pure water flux

First, the MD fluxes achieved with different membranes to treat the four dyes were monitored, as shown in **Fig. 2**. As expected, the higher porosity of the PTFE membrane compared to the PVDF membrane, (Refer to Table 1), resulted in a higher flux than that of PVDF, in the following trend for all dyes: PTFE >> PVDF-0.45 > PVDF-0.22 (Fig. 2). The highest initial water flux of the PTFE membrane was approximately 34 LMH, while the PVDF produced permeate at a lower initial flux of 21-23 LMH. Furthermore, for all the membranes studied, the highest water flux was observed for the MD treatment of AY36, whereas the lowest water flux was found for that of CV. Different initial fluxes and flux declines were observed for the different dye solutions. However, both initial flux and flux decline followed the order: AY36 > AR18 > MB > CV

(FIGURE 2)

Rapid decline in permeate flux was observed for the first 7-8 h of MD operation for all membranes. After the initial flux decline, the membranes reached the critical flux, after which the permeate fluxes for all membranes remained stable for the rest of the operation as shown in **Fig. 2**. This clearly showed that the PTFE achieved greater water production than the PVDF membranes in the MD process for dye treatment. In particular, the PTFE membrane shows not only higher water CA but also dye CA compared to PVDF, as shown in **Fig. 3**. These findings showed that the PTFE membrane had the lowest wettability.

(FIGURE 3)

The membranes were subjected to pure water flux to determine the cause of this initial flux drop. The membrane fluxes for the dyes were lower than those for pure water, with the pure water fluxes being 23.9-25.2 LMH for the PVDF membranes and 39.2 LMH for PTFE membranes, respectively, as shown

in **Table 1**. In addition, as shown in **Table S2**, the CAs of dyes were slightly lower than the CAs of water for all membranes. Thus, the flux drop can be attributed to the high loading of organic foulant (dyes) on the virgin membranes, as the retention of organic solutes on the membrane surface partially blocks the membrane pores and induces concentration polarization. Organic fouling by the dyes on the membrane is a complicated phenomenon with multiple causes and whose mechanism in the MD process is poorly understood. It is believed that this phenomenon is primarily the result of the interaction between the chemical characteristics of the organic fouling materials (dye molecules) and the membranes, which is explained in the following section.

(TABLE S2)

3.1.2 Color removal and membrane zeta potential

During 24 h of MD operation, a complete color removal and pure water recovery at the permeate side of PTFE and PVDF-0.22 was achieved. (**Table 2**). However, the color removal efficiency was lower for the PVDF-0.45 than the PVDF-0.22 due to the slightly higher flux and larger pore size of the former by dye passage through partially wetted pores. The PVDF-0.45 membrane showed the lowest color removal efficiency ($AY36, 100\% = AR18, 100\% > MB, 98.29\% > CV, 96.54\%$), while the PTFE membrane showed excellent color removal efficiencies despite having the highest flux. This may be attributed to the higher hydrophobicity (as measured by contact angle), higher zeta potential and small pore size.

Interestingly, the color removal efficiency by dye type corresponded exactly to the dye flux efficiency for all the membranes. This phenomenon can be explained by considering the characteristics of each dye and their effect on adsorption onto the membrane surface.

(TABLE 2)

As shown in **Fig. S1**, AR18 and AY36, which were most efficiently removed, are azo dyes and are adsorbed to the membrane via their sulfonate groups. The sulfonate group is strongly adsorbed by positively charged surfaces, but the membranes tested in this study were mainly negatively charged at equilibrium pH ranges. The pH values of AR18 and AY36 were 9.1 and 7.2, respectively. At these pH values the surface charges of PVDF and PTFE membranes were highly negative (in the range of -40 mV to -60 mV), as shown in **Fig. 4**. Thus, relatively few molecules of these two dyes adsorbed onto the membrane surface, as the sulfonate groups were repelled by the highly negative membrane surfaces. AR18 and AY36 solutions have pH values of 9.1 and 7.2, respectively. At pH 9.1 of AR18, higher repulsive forces may increase the resistance of vapor mass transportation.

All membranes were less effective at treating MB and CV than AR 18 and AY36. In the case of MB, higher adsorption of the dye onto the membranes was observed, which can be attributed to the fact that it is a basic cationic dye that dissociates in aqueous solution into a cation (the chromophore) and an anion, Cl^- . Accordingly, MB can be represented as Dye^+Cl^- (Liu et al., 2010), and the electrostatic attraction between the Dye^+ and the negatively charged membranes facilitates the adsorption of MB. Similarly, CV is a direct dye that is water-soluble and charged with organic compounds that can bond to ionic and polar sites on the membrane. This dye contains both positively and negatively charged groups and is easily adsorbed onto the membrane molecules through hydrogen bonding between the negative functional group of the membrane (the zeta potential of the membranes was -50 mV at pH 6.8, see **Fig. 4**) and the electron-donating nitrogen atoms ($-\text{N}:)$ of the dye. CV is a basic dye that contains positive charge and higher pH (6.8) than that of MB (5.2). The higher zeta potential of the membrane at pH 6.8 will have a stronger attraction for CV, resulting in attachment to the membrane surface and lower flux than MB.

(FIGURE 4)

3.2 Membrane fouling during dye treatment

As described above, dye molecules can be absorbed onto the membrane surface due to physicochemical interactions, i.e., hydrophobic interactions (dispersion forces), polar interactions (dipole forces), and charge transfer (hydrogen bonding), and their absorption onto the membrane may affect the permeate flux. The affinity between the dye and the membrane depends on their chemical structures and their interactions; thus, chemical bonding plays an important role in the mechanism behind dye fouling in the MD process. Further investigation was conducted to determine how dyes with different chemical structures, properties, and concentrations affect the MD performance.

3.2.1 Dye adsorption on membrane surface

To examine membrane fouling during dye treatment, the membranes were removed and studied after 24 h of MD operation. It was expected that the dye would aggregate into multiple sub-layers over time, causing the bulk concentration of the dye to increase as compacted sublayers are formed and resulting in concentration polarization. As expected, dye adsorption was evident, showing that the dye formed a sublayer on the membrane surfaces. However, when membrane fouling was further analyzed using SEM, while dye molecules entered the pores of the PVDF membranes, flake-type crystals covered the surface of the PTFE membrane. The SEM images of membranes before and after being used for CV treatment are shown in **Fig. 5**.

(FIGURE 5)

This unique feature of the PTFE membrane can be explained by its strong negative charge. Dye molecules block the pores of the MD membrane (which is hydrophobic and negatively charged) due to the association and dissociation of the functional groups on the membrane surface. These processes

result from the formation of charges during the ionization that occurs when the membrane is placed in contact with an ionic solution (dye solution). However, the negative charges generated repulse the negative ions of the dye. The PTFE membrane has a zeta potential of -70 mV (negative) at pH 9. Thus, the strong repulsive force between the PTFE membrane and the negative ions of the dye leads to a formation of a dye–dye (foulant-foulant) structure on the membrane surface instead of within the membrane pores (membrane-foulant) (Hadi et al., 2016). This difference has a significant effect on the long-term applicability of MD, as will be elaborated below.

3.3 Viability of long-term MD operation with membrane cleaning

The applicability of MD to the treatment of dyeing wastewater and the potential for long-term MD operation with membrane cleaning (or water flushing; WF) was investigated. The four dyes were mixed and treated by MD for five days using three different membranes (PVDF-0.22, PVDF-0.45, and PTFE) and WF for 10 min every 3 h to examine the cleaning efficiency on flux recovery for MD.

(TABLE 3)

3.3.1 *In-situ* membrane fouling control for long-term operation with water flushing

A mixture of the four dyes was processed using three membranes (PVDF-0.22, PVDF-0.45, and PTFE) for 5 d of MD treatment with WF for 10 min every 3 h to study the applicability of long-term MD operation with WF to the treatment of complex dyes. **Fig. 6** shows the flux pattern during 5 d MD operation of PTFE and PVDF membranes with WF. The PTFE membrane showed much higher permeate flux and flux recovery with WF than PVDF membrane and permeate flux. However, WF did

not help the recovery of permeate flux in DCMD filtration with the PVDF membrane. After 30 h of operation, flux of PVDF membrane reduced to around 15 LMH. On the other hand, the flux of the PTFE membrane was maintained at between 28 and 33 LMH during 5 d of operation.

The color rejection results are illustrated in **Table 3**. With WF, MD with the PTFE membrane showed 100% dye rejection efficiency, as shown in **Fig. 7**. After 5d of treating the mixed dye solution (100 mg/L; 25 mg/L of each dye) with WF, blue color was detected in the distillate of the other membranes, while the PTFE membrane continued to produce a high-quality and colorless distillate. Two possible reasons for this efficient color rejection can be given: i) the dye molecules could not enter the membrane pores due to the formation of the dye–dye flake-type foulant (foulant-foulant) on the membrane surface, and ii) this loosely bound dye foulant and high fraction of water had a repulsion effect to the hydrophobic membrane surface. As a result, the PTFE membrane did not suffer from membrane wetting, and its properties could be recovered. In comparison, the PVDF-0.22 and PVDF-0.45 membranes may have undergone partial wetting, resulting in less color rejection (75.7 to 88.2%).

(FIGURE 6)

(FIGURE 7)

3.3.2 Membrane cleaning after MD operation

Electrostatic and hydrophobic/hydrophilic interactions between membranes and fouling materials have a significant effect on membrane fouling (Zamani et al., 2016). This is particularly true for the more complex fouling problems caused by the adsorption of dyes onto a membrane. The balance between the forces of electrostatic repulsion and hydrophobic adhesion determines the outcomes of membrane fouling as well as the efficiency of WF or operation with pure water (or cleaning) in MD. Therefore, this

study conducted MD cleaning with WF to investigate membrane cleaning efficiency in terms of the CA and LEP of the membranes before and after cleaning.

The CA is a semi-quantitative index associated with the hydrophilicity/hydrophobicity of a membrane surface, with higher CA values representing higher hydrophobicity. The LEP indicates the minimum pressure at which water flux occurs and is often called the “wetting pressure.” Because these two indicators reveal how well the membrane surface can process water flux, they are the most important determinants of the performance of an MD membrane. As shown in **Fig. 8a** and **b**, the CA and LEP of the PTFE membrane decreased over 24 h of MD operation but were then recovered by 10 min of cleaning. Meanwhile, for the other membranes the reductions in the CA and LEP after MD operation could not be recovered by cleaning. After 24 h of MD treatment of CV with WF, the surface of the PTFE membrane was much cleaner than that of the PVDF-0.45 membrane, which exhibited severe dye adsorption (dark-purple areas), as shown in **Fig. 8c**. This result shows that the use of WF in PTFE MD operation has the potential to prevent fouling and enable long-term operation.

(FIGURE 8)

3.3.3 Foulant membrane analysis

ATR-FTIR studies of the membranes after the MD tests with WF further support the above observations. **Fig. 9** shows the differences in the functional groups on the virgin PVDF and virgin PTFE membranes (a and c) and after (b and d) dye treatment. The observed vibrational band at 1396 cm^{-1} corresponds to the deformation vibration of the CH_2 group (CH_2 wagging and scissoring vibrations of vinylidene). The peak at 1166 cm^{-1} corresponds to CF_2 stretching. The band at 1062 cm^{-1} is due to the β crystalline phase of PVDF. The peaks at 873 and 837 cm^{-1} correspond to the rocking mode of the vinylidene group of the polymer. The bending vibration of CF_2 is observed at 578 cm^{-1} . The bands at 527 and 480 cm^{-1} may be assigned to the wagging and bending vibrations of CF_2 , respectively. Thus, the

PVDF membrane is composed of multiple repeating units of small molecules (CH_2 and CF_2 bonds). In the FTIR spectrum of the PTFE membrane, C-F bonds are stretching at 1205 and 1159 cm^{-1} , which is corresponding to its monomer of C-F bond. Several new peaks were observed for the PVDF membrane upon dye treatment (c). For instance, CF_3 symmetric deformation and CF_3 asymmetric deformation were observed at 760 cm^{-1} and 579 cm^{-1} , respectively, which may be due to hydrogen bonding between the dye and CF_3 of PVDF (Mohamed and Arof, 2004). Meanwhile, the functional groups of the PTFE membrane did not exhibit any changes, indicating that the interaction between the dye and PTFE was restricted during the dye treatment by the PTFE coated membrane.

(FIGURE 9)

4. Conclusions

This study tested hydrophobic membranes in an MD process for dyeing wastewater treatment. It also demonstrated the feasibility of MD coupled with water flushing (WF) as a means to control membrane fouling by dye adsorption and regaining water flux for long-term application of MD to dyeing wastewater treatment. Four different dye solutions and one mixed dye solution at a high concentration of 100 mg/L were treated using three different MD membranes made of PVDF and PTFE. The following results were obtained from this study,

- The PTFE membranes had higher porosity and hydrophobicity than the PVDF membranes tested. These characteristics resulted in higher flux and prevented permanent fouling.
- Membranes showed a high negative zeta potential in the tested pH ranges. AR18 and AY36 are negatively charged and had a low adsorption affinity for the negatively charged membranes. These dyes were repulsed from the membrane and formed aggregated flake type

foulants (foulant-foulant) away from the membrane interface. However MB and CV had more fouling and wetting potential due to the higher positive charge of these dyes (membrane-foulant).

- The aggregated flake type foulants could not enter the membrane pores and was therefore easily removed by WF. In the mixed dye solution test using a bench-scale direct-contact MD (DCMD) test unit for 5 days, the PTFE membrane showed a high resistance to dye-induced fouling, and was able to produce high flux and water quality with simple WF.
- These results show promise for the application of MD in textile wastewater treatment, using membranes with high flux and antifouling properties.

Supporting Information.

The following files are available free of charge.

Chemical structures of dyes tested in this study (Figure S1), properties of four dyes used in the DCMD experiments (Table S1), and water and dye contact angles of different membranes (Table S2).

■ AUTHOR INFORMATION

Corresponding Author

* Tel: + (852)-3442-9626, Fax: + (852)-3442-0688, E-mail: alicia.kjan@cityu.edu.hk

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ABBREVIATIONS

AR18: Acid Red 18; AY36: Acid Yellow 36; BOD: Biochemical oxygen demand; CA: Contact angle; COD: Chemical oxygen demand; CV: Crystal violet; DCMD: Direct-contact membrane distillation; DI: Deionized; LEP: Liquid entry pressure; MB: Methylene blue; MD: Membrane distillation; MW: Molecular weight; NF: Nanofiltration; PTFE: Polytetrafluoroethylene; PVDF: Polyvinylidene fluoride; RO: Reverse osmosis; SEM: Scanning electron microscopy; UF: Ultrafiltration

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Membrane	PVDF-0.22	PVDF-0.45	PTFE
Material	Polyvinylidene Fluoride (PVDF)	Polyvinylidene Fluoride (PVDF)	Polytetrafluoroethylen (PTFE) /laminated polypropylene (PP) support
Mean pore size (μm)	0.22	0.45	0.20
Porosity (%)	69.24	72.11	84.32
Tensile strength (MPa)	6.35	5.34	21.75
Contact angle ($^{\circ}$)	120.2	117.9	137.9
Wettability	Hydrophobic	Hydrophobic	Hydrophobic
LEP* of water (bar)	1.95	1.17	2.68
Pure water flux** (LMH***)	23.9 ± 0.41	25.2 ± 0.27	37.9 ± 0.55

Table 1. Characteristics of the membranes used in this study.

*LEP: liquid entry pressure. ** The temperature of feed and permeate water (cooling water) were 60 °C and 20 °C, respectively. ***LMH: $\text{L m}^{-2} \text{h}^{-1}$.

Table 2. Initial water flux, average water flux, and color removal efficiency achieved by DCMD treatment of four dyes using the studied membranes (Conditions: 60 °C, flow rate = 0.5 L min⁻¹, and C₀=100 mg/L).

Membrane	Dye	MB	CV	AR18	AY36
PVDF-0.22	Initial flux (LMH)	20.84 ±0.34	20.62±0.35	21.21±0.37	21.59±0.22
	Ave. flux (LMH)	17.45±1.18	16.15±1.58	18.36±1.01	19.09±1.13
	Color removal (%)	100	100	100	100
PVDF-0.45	Initial flux (LMH)	22.24±0.18	21.72±0.54	22.44±0.27	22.95±0.39
	Ave. flux (LMH)	17.80±1.47	16.98±1.69	18.69±1.39	19.53±1.46
	Color removal (%)	98.29±0.23	96.54±0.19	100	100
PTFE	Initial flux (LMH)	31.32±0.44	30.96±0.65	30.88±0.38	33.85±0.24
	Ave. flux (LMH)	26.83±1.24	25.26±1.71	29.32±1.26	30.33±1.06
	Color removal (%)	100	100	100	100

Table 3. Color removal by MD operation using PVDF and PTFE WF for 10 min every 3 h for 5 d.

Membrane	Dye	Feed concentration (mg L ⁻¹)	Permeate concentration (mg L ⁻¹)	Rejection (%)
PVDF-0.22 (with WF)	MB	25	4.3	82.8
	CV	25	2.5	90.0
	AR18	25	1.7	93.2
	AY36	25	3.3	86.8
	Mixed	100 (25 each)	11.8	88.2
PVDF-0.45 (with WF)	MB	25	8.6	65.6
	CV	25	4.5	82.0
	AR18	25	4.7	81.2
	AY36	25	6.5	74.0
	Mixed	100 (25 each)	24.3	75.7
PTFE (with WF)	MB	25	0	100
	CV	25	0	100
	AR18	25	0	100
	AY36	25	0	100
	Mixed	100 (25 each)	0	100

Table S1. Properties of four dyes used in the DCMD experiments.

Dye name	Formula*	MW** (g mol ⁻¹)	Chemical Types	Charge	$\lambda_{\max}$ (nm)	pH** *	Company
Methylene Blue (MB)	$C_{16}H_{18}N_3SCl$	319.85	Basic	+1	664	5.2	Shanghai Zhanyun Chemical Co., Ltd
Crystal Violet (CV)	$C_{25}H_{48}N_3Cl$	407.99	Basic	+1	590	6.8	Shanghai Zhanyun Chemical Co., Ltd
Acid Red 18 (AR18)	$C_{20}H_{11}N_2Na_3O_{10}S$ 3	604.46	Acid, Anionic	-3	507	9.1	Shanghai Zhanyun Chemical Co., Ltd
Acid Yellow 36 (AY36)	$C_{18}H_{14}N_3NaO_3S$	375.38	Acid, Azo- dye	-1	527	7.2	Shanghai Zhanyun Chemical Co., Ltd

* Structures of dyes used in this study are presented in **Fig. S1** (Supplementary data); **MW: molecular weight; and *** Measured with 100 mg/L of each dye.

Table S2. Water (DI) and dye contact angles (CAs) of different membranes (°).

Membrane	DI	MB	CV	AR18	AY36
PVDF-0.22	120.2 ± 0.3	117.2 ± 2.3	117.0 ± 0.4	120.0 ± 1.1	118.2 ± 1.5
PVDF-0.45	117.9 ± 1.0	116.2 ± 1.7	114.7 ± 0.8	118.2 ± 0.4	117.4 ± 1.7
PTFE	137.9 ± 1.0	135.3 ± 1.8	136.6 ± 0.3	135.4 ± 2.2	135.7 ± 2.0

Figure 1. Schematic diagram of the DCMD test unit (1: Permeate tank, 2: Digital balance connected to a computer, 3: Thermometers, 4: Cooling unit, 5: Pumps, 6: Flat sheet membrane module, 7: Flow meters, 8: Feed reservoir, 9: Hotplate).

Figure 2. Water flux as a function of MD operation time for the treatment of four different dyes using the studied membranes (60 °C, flow rate = 0.5 L min⁻¹, C₀ = 100 mg/L).

Figure 3. Images of dye droplets on the surface of (a) PVDF and (b) PTFE membranes used in this study.

Figure 4. Zeta potentials of the membrane surfaces (PVDF-0.45 and PTFE) as a function of pH.

Figure 5. SEM images of 6 different membranes: (a) virgin PVDF-0.22 membrane, (b) fouling PVDF-0.22 after MD in the CV treatment; (c) virgin PVDF-0.45 membrane, (d) fouling PVDF-0.45 after MD in the CV treatment; (e) virgin C-PTFE membrane, and (f) fouling C-PTFE after MD in the CV treatment.

Figure 6. Flux patterns of PVDF-0.22, PVDF-0.45 and C-PTFE membrane during 5 d (120 h) operation with water flushing (WF).

Figure 7. Photograph of the distillate collected after 5 d of MD operation (with WF) after treating the mixed dye solution using the (a) PVDF-0.22, (b) PVDF-0.45, and (c) PTFE membranes (Conditions: 60 °C, flow rate = 0.5 L min⁻¹, C₀=100 mg/L).

(a) CA

(b) LEP

(c) Water-flushed membrane

Figure 8. Changes in the (a) contact angle (CA) and (b) liquid entry pressure (LEP) of the membranes (virgin, before DI cleaning, and after DI cleaning), and (c) image of the surface membrane (after DI cleaning).

Figure 9. ATR-FTIR spectra (1600-400 cm^{-1}) of (a) virgin PVDF, (b) tested PVDF, (c) virgin PTFE, and (d) tested PTFE.

Fig. S1. Chemical structures of dyes tested in this study (illustrated using ChemBioDraw Ultra software)

Research highlights

- Direct contact membrane distillation (DCMD) was tested with different dye solutions.
- MD showed a high potential for treating of dyeing wastewater.
- The high membrane porosity and hydrophobicity lead to high flux and low fouling.
- Negatively charged dyes showed a low fouling on negative zeta potential MD membranes.
- Water flushing enabled a long-term application of DCMD by removing dye foulant.