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PDMS/PVDF hybrid electrospun membrane with superhydrophobic property and drop impact dynamics for dyeing wastewater treatment using membrane distillation

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Abstract

Fouling in membrane distillation (MD) results in an increase in operation costs and deterioration in a water quality. In this work, a poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) electrospun (E-PH) membrane was fabricated by hybridizing polydimethylsiloxane (PDMS) polymeric microspheres with superhydrophobicity onto the E-PH membrane via electrospinning. The resulting hybrid PDMS with E-PH (E-PDMS) membrane showed a significant enhancement in surface hydrophobicity (contact angle, CA = 155.4°) and roughness ($R_a = 1,285\text{nm}$). The zeta potential of E-PDMS membrane surface showed a higher negative value than that of a commercial PVDF (C-PVDF) membrane. These properties of E-PDMS membrane provided an antifouling in treating of differently-charged dyes and generated a flake-like dye-dye (loosely bound foulant) structure on the membrane surface rather than in the membrane pores. This also led to a high productivity of E-PDMS membrane ($34\text{ Lm}^{-2}\text{h}^{-1}$, 50% higher than that of C-PVDF membrane) without fouling or wetting. In addition, complete color removal and pure water production were achieved during a long-term operation. An application of intermittent water flushing (WF) in direct contact MD (DCMD) operation led to a 99% CA recovery of E-PDMS membrane indicating its sustainability. Therefore, the E-PDMS membrane is a promising candidate for MD application in dyeing wastewater treatment.

ABBREVIATIONS: AFM: Atomic force microscopy; AR18: Acid Red 18; ART: attenuated total reflectance; AY36: Acid Yellow 36; BOD: Biochemical oxygen demand; CA: Contact angle; CNTs: Carbon nanotubes; COD: Chemical oxygen demand; C-PVDF: Commercial PVDF membrane; CV: Crystal violet; DCMD: Direct-contact membrane distillation; DI: Deionized; ENMs: Electrospun nanofibrous membranes; E-PDMS: Hybrid PDMS/PH membrane; E-PH: PVDF-HFP electrospun membrane; FF: Fouling factor; FTIR: Fourier transform infrared

spectroscopy; LEP: Liquid entry pressure; MB: Methylene blue; MD: Membrane distillation; MW: Molecular weight; PVDF: Polyvinylidene fluoride; PVDF-HFP: Poly(vinylidene fluoride-co-hexafluoropropene); PDMS: Polydimethylsiloxane; SEM: Scanning electron microscopy; WF: Water flushing; XRD: X-ray diffraction; ZP: Zeta potential

Keywords: Direct contact membrane distillation; dyeing wastewater; electrospun membrane; fouling; polydimethylsiloxane; polyvinylidene fluoride

1. Introduction

MD has been broadly explored for wastewater treatment and resource recovery, such as treatment of colored wastewater, oil-water separation, produced water as well as recovery of valuable component by concentration feed solution (acid, fruit juices, sugar and alcohols etc) [1]. Compared to other membrane based treatment methods. MD can reject 100% (theoretically) of inorganic ions, macromolecules and other non-volatile compounds; requires relatively low operating temperatures and lower operating pressures than conventional pressure-driven membrane separation processes; has insensitivity to feed concentration and less requirements on membrane mechanical properties [2,3]. However, MD is still in its embryonic stage in terms of development due to membrane wetting and fouling issues that hinder the MD commercialization. The development of an ideal membrane, which is strong against wetting and fouling, will enable the MD to apply prominently in wastewater treatment [4]. Dyeing wastewater is produced in large amounts and its treatment is riddled with complexities due to the inherent coloring and the multitude of chemicals used during the textile process. Developing an ideal membrane that is capable of color rejection as well as purification is essential. Therefore, the technology to

produce high quality permeate water from dyeing wastewater, when achieved, will greatly further the application of MD to other areas of wastewater treatment.

The recent trend in the research on membranes for the MD process is hybrid, or composite using nano/micro particles or organic/inorganic materials in membrane fabrication to improve the membrane performance for selective separation and harsh water treatment [5]. Composite membranes have been gaining recognition due to their high functionality and selectivity for a variety of applications in the field of water treatment [6–9]. Methods for incorporating nanoparticles into organic polymer to fabricate the nanocomposite membranes have been largely investigated based on chemical approaches [10]. However, the complexity of chemical methods has been somewhat of deterrence for practical application. As an alternative method, electrospinning has been noted as a simple and versatile method that can enhance the properties of the membrane by direct application of nanomaterials, allowing a greater control over the structure of resultant membranes by changing the dope solution viscosity, voltage, flow-rate, and hybrid combination of materials [11]. This reliable technique also enables to constructing controllable interfacial surface with inorganic nanomaterials and polymer matrix [12]. The resulting electrospun nanofibrous membranes (ENMs) have high porosity and hydrophobicity, which translates to high permeability and rejection [13]. For this reason, ENMs have gained a great interest as emerging materials for advanced applications of membrane technology such as MD, which requires membranes with hydrophobic, anti-wetting/fouling, and chemically stable properties.

Since hydrophobicity is an essential requirement for MD membranes in most applications, the ENMs must be made from intrinsic or modified hydrophobic polymers with low

surface energy and good ability to electrospinning. For this reason, polyvinylidene fluoride (PVDF), a semi-crystalline polymer is the most commonly utilized. The surface energy and hydrophobicity (in terms of contact angle, CA) of PVDF electrospun membrane were reported 30.3×10^3 N/m and approximately $120 \sim 130^\circ$, respectively [5]. Recently, superhydrophobic (CA > 150°) membrane with low CA hysteresis (water bouncing dynamic) was proved to be effective for preventing fouling and wetting by giving water droplets the smallest contact surface with the solid [14]. Therefore, further application of the hybrid materials such as carbon nanotubes (CNTs), graphene, and inorganic nanoparticles to modify the surface morphology of PVDF is a subject of interest for achieving superhydrophobicity.

This study explored the use of poly(dimethylsiloxane) (PDMS), $-\text{Si}(\text{CH}_3)_2\text{O}-$, a polymeric organosilicon compound with high porosity and low surface energy (due to its very low cohesive energy density) [15], as a hybrid composite material to fabricate a superhydrophobic PDMS/PVDF ENM. Simple and easy electrospinning technology was employed to transform PDMS to a polymer state and then to composite emulsion droplets onto PVDF in polymeric microspheres. A versatile hybrid structure was formed through this process, in which the spherical PDMS polymeric microspheres are linked with each other, well-dispersed and firmly attached to the membrane surface. The shape and size of the particles can be controlled by changing the polymer concentration or the rate of solvent of evaporation. This study may be the first in engineering the membrane surface with tunable polymeric microspheres in the field of MD research.

The purpose of this study is to investigate how the hydrophobic PDMS microspheres coated on a basic electrospun poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) (E-PH) membrane does improve anti-wetting and antifouling property of the membrane. Dyeing

wastewater is chosen as a feed solution for MD since at present the amount of dyeing wastewater emitted is being increased and its complex composition has made it one of the largest contributors to water pollution [16–18]. To date, limited researches have been conducted on MD fouling in treating dyeing wastewater. Moreover, membrane development for MD applications in treating dyeing wastewater has yet not made. Existing researches have been limited only to short-term test operating times and used only a single dye at a low feed concentration [19–24], most likely due to fouling and wetting issues. This study applied the laboratory-fabricated hybrid PDMS/PH membrane (E-PDMS) to direct contact MD (DCMD) operation for treating dyeing wastewater containing a high concentration (up to 200 mg L⁻¹) of four different dyes, namely, methylene blue (MB), crystal violet (CV), acid red 18 (AR18), and acid yellow 36 (AY36). MD performances (i.e. flux and rejection) with the E-PDMS membrane is compared with the E-PH and commercial PVDF (C-PVDF) membranes and evaluated with various membrane characterization techniques. Possible mechanism of MD membrane fouling by dyes is also discussed.

2. Experimental

2.1. Materials

2.1.1. Membranes

To prepare the polymer solution for electrospinning membranes, polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP, hereinafter PH; $M_w = 455,000 \text{ g mol}^{-1}$), lithium chloride (LiCl) as additives, and N-dimethylformamide (DMF), tetrahydrofuran (THF), and acetone as solvents, were purchased from Sigma-Aldrich. For the preparation of PDMS solution, Sylgard® 184 (Dow Corning Corporation), which consists of silicone elastomer base and curing set (10:1

wt/wt), was used. The detailed fabrication procedure of E-PDMS is described in section 2.2. A commercial PVDF membrane (hereafter, C-PVDF membrane) with pore size of 0.45 μm , purchased from Millipore Company (Durapore® Membrane Filters, Merck Millipore Ltd), was used as a reference membrane to compare with the electrospun membranes on the MD performance.

2.1.2. Dyes

Different types of dyes are usually used in textile industries, among which are acid, basic, direct, reactive, sulfur, azoic, and vat dyes [17]. To find out how the dyes' complex structures work in dyeing wastewater treatment by MD, this study tested two basic and two acid dyes, namely methylene blue (MB), crystal violet (CV), acid red 18 (AR18), and acid yellow 36 (AY36). The four dyes were purchased from Shanghai Zhanyun Chemical Co., Ltd, Shanghai, China. The two basic dyes, MB and CV, are cationic or positively charged reacting with negatively charged material well, while the two acid dyes, AR18 and AY36, are negatively charged and typically a salt of sulphuric, carboxylic or phenolic organic acid. **Fig. S1** illustrates the chemical structures of the four dyes. The molecular weights (M_w) of the four dyes range from 300 to 600 g mol^{-1} and their pH values range from 5.2 to 9.1. The dye salts were dissolved in distilled water to make dye feed solutions at 20-200 mg L^{-1} of concentration for MD testing.

2.2. Fabrication of E-PDMS membrane

2.2.1. Solution preparation

The main dope solution for electrospinning of E-PH membrane was prepared by a mixture of PH and LiCl (as an additive), and DMF and acetone (as solvents) with the composition ratio of PH:DMF:acetone = 15:59.5:25.5. To prepare polymeric microspheres, a cured PDMS solution

(precursor and curing agent 10:1 wt%) and PVDF were dissolved in a blended solvent of DMF and THF (1:1 wt %) at 50°C, This ratio was selected to prevent nozzle blocking due to volatility of THF according to a previous study [25]. The final weight ratio of PDMS, PVDF and DMF/THF solvent was 2.5:2.5:95.

2.2.2. Electrospinning and PDMS hybridization

Fabrication of E-PDMS membrane is comprised of i) electrospinning for making E-PH membrane and ii) electrospraying for hybridizing PDMS microspheres onto E-PH membrane. Firstly, two E-PH membranes containing 15%PH were fabricated using the electrospinner by applying a positive voltage of 18kV over a distance of 15 cm between the nozzle and the collector at a flow rate of 0.7 mL/h. The electrospinner comprised of a plastic syringe combined with a metal nozzle mounted at pump and a grounded rotating collector covered with aluminum foil regulated by an electronic controller. Then, one of E-PH membranes was coated by emulsion droplet of PDMS. A high voltage of 30kV was applied at distance between nozzle and collector of 11 cm, and a flow rate of 2.0 mL/h.

Fig. 1 shows the procedure of fabrication of PDMS microspheres coated E-PH membrane (hybrid PDMS/PH membrane or E-PDMS membrane). Here, the topography of microspheres was determined by polymer concentration and solvent evaporation speed.

2.3. Membrane characterizations

2.3.1. Surface morphology, roughness, and fouling layer composition

The surface morphologies of both virgin and fouled (or tested) membranes were observed using scanning electron microscopy (SEM) (EVO MA10, ZEISS, Germany) after coating with gold by

sputtering for 80 s, to visualize the structure of nanofibers and foulants deposited on the membrane surface.

The surface roughness was measured by an atomic force microscopy (AFM) (Dimension Icon, Bruker Germany) with silicon tips (LTESP-V2, ca. 330 kHz) for tapping mode.

To obtain more specific information on the functional group of membrane or foulants on the membrane, Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were analyzed. IR spectra ($700\text{--}4000\text{ cm}^{-1}$) of each membrane were collected under the attenuated total reflectance (ATR) mode of FTIR spectrometer (Iraffinity-1, Shimadzu, Japan) with a 2 cm^{-1} resolution. An X-ray diffractometer (X'Pert³ Powder, PANalytical, Netherlands) using Cu K α radiation recorded the diffraction peaks with an experiment condition of 40 kV and 40 mA.

2.3.2. Hydrophobicity, wettability, and droplet bouncing effect

The wettability of membrane surface, which depends on its chemical composition and architecture, can be evaluated in terms of contact angle (CA). To prevent membrane pore wetting in MD, the membrane should be hydrophobic or better, i.e. superhydrophobic ($\text{CA} > 150^\circ$). A membrane with low CA hysteresis (water bouncing dynamic) can mitigate fouling by reducing water-membrane contact area [14].

CA and sliding angle of the liquid on the membranes was observed by the EASYDROP Contact Angle Measuring System (Kruss, Germany) and goniometer (G1-40R15, DPln, Korea), respectively. All measurements were repeated at least three times, and results are reported as mean value.

In order to monitor water droplet bouncing effect on the membrane surface, the water droplet was produced from a fine stainless steel needle connected to a syringe pump (KD Scientific) from a pre-determined height. The dynamics of the droplet effect were recorded using

a high-speed camera (Photron, Fastcam SA4) with a frame rate of 3,600 fps with 1/3,600 s shutter speed. Captured images were analyzed with software ImageJ (Version 1.46, National Institutes of Health). All the experiments were conducted in ambient environment with room temperature and relative humidity (~50%).

2.3.3. Pore size, liquid entry pressure, and porosity

The mean pore size was measured using a capillary porometer (PoroLux™ 1000, POROMETER, German) based on the gas-liquid displacement porometry method.

The liquid entry pressure (LEP) measurement was carried out using the same equipment by measuring the minimum pressure required to allow water to penetrate into the membrane pore.[26]

Membrane porosity was determined by a gravimetric method: (i) after measuring the weight of the dry membrane samples (3 cm × 3 cm), (ii) the samples were fully wetted with ethanol, and (iii) the weight of the wetted membrane was measured. Then, the porosity (ϵ) was determined by calculating the volume of ethanol in the membrane samples using the following equation (Eq. 1),

$$\epsilon = \frac{\frac{W_1 - W_2}{D_e}}{\left[\frac{W_1 - W_2}{D_e} \right] + \frac{W_2}{D_p}} \quad (1)$$

where, W_1 and W_2 are the weights (g) of wet and dry membrane, respectively, and D_e and D_p are the densities (g/m^3) of the ethanol (e) and the polymer (p), respectively.

2.3.4. Surface zeta potential measurement

The streaming current method using an electro kinetic analyzer (Surpass Anton Paar, Austria) was employed to measure the zeta potential (ZP) of the membrane surface. Generally, the

polymeric membranes can obtain a surface charge in the contact with an aqueous solution and during the zeta potential measurement, an electrolyte solution was passed through the membrane sample as a function of pH. The relative motion between the electrolyte solution and membrane surface resulted in an electro kinetic effect called streaming potential. During the measurement, streaming potential can quantify an electro kinetic effect, which reflects the charge properties of the membrane surface.

Membrane samples (2 cm × 1 cm) were mounted on sample holders and immobilized on an adjustable gap cell. Several KCl solutions (1.0 mmol L⁻¹) with different pH values were used as the background electrolyte and the pH was adjusted with hydrochloric acid (HCl) and potassium hydroxide (KOH). The charge densities (ZP) of the membrane surfaces were calculated using the Visolab for Surpass software.

2.4. MD test and performance evaluation

2.4.1. MD test set-up

The DCMD tests with dyeing wastewater as the feed solution were conducted using lab-scale equipment (**Fig. 2**). The initial volumes of the feed solution (dye: 100 mg L⁻¹) and the cooling water (or permeate) (deionized or DI water) were 2.0 and 0.5 L, respectively. A moderate feed temperature of 60 °C was used, while the permeate side was set at 20 °C. To minimize heat loss and temperature fluctuation, the temperature of each solution was maintained at ±2 °C for all experiments using a hotplate/stirrer and a heat exchanger equipped with a chiller, and all tubes were insulated. The feed and permeate solutions were channeled into the membrane cell containing the membrane (effective area = 9.8 cm²) at a same feed and permeate flow rate of 0.5 L min⁻¹ in a counter current mode. Membrane flushing with DI water (hereafter referred to as

water flushing, WF) was conducted by circulating the DI water in the feed channel for 10 min at a flow rate of 0.5 L min⁻¹. Water flux (Lm⁻²L⁻¹, LMH) was calculated by increasing the rate of the permeate container weight with a 10 min interval.

2.4.2. Dye rejection, fouling factor, and adsorption rate

The dye concentration was measured using an ultraviolet-visible (UV-vis) spectrophotometer (UV-2600, SHIMADZU, Japan) based on different wavelengths. To plot the calibration curve, the absorbances of the four standard solutions with different concentrations were measured at wavelengths of 430nm (for AY36), 506nm (for AR18), 590nm (for CV) and 664 nm (for MB).

The dye rejection efficiency R (%) was determined by the following equation:

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

where, C_f (mg L⁻¹) is the initial dye concentration in the feed and C_p (mg L⁻¹) is the final dye concentration in the permeate container taking the dilution factor into account.

Membrane performance as a function of the dye concentration was evaluated in terms of the membrane fouling factor (FF), as presented in the following equation:

$$FF = \left(1 - \left(\frac{J}{J_0}\right)\right) \times 100 \quad (3)$$

where, the normalized flux $(J/J_0) = \frac{\text{Membrane flux at 24 h}}{\text{Pure water flux}}$.

The level of dye adsorption was also calculated using the adsorption isotherm indicator, R_L [27]:

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

where, b is the Langmuir constant and C_0 is the initial dye concentration.

The relationship between the FF and initial dye concentration (C_0) was then used to determine b and maximum FF ($FF_{\max}$) based on the following equation:

$$\frac{C}{FF} = \frac{1}{FF_{\max}} \times C_0 + \frac{1}{FF_{\max} \times b} \quad (5)$$

Here, the rejection of dye was almost 100% and concentration in feed was maintained. Thus, it assumed that $C_e \approx C_0$.

3. Results and Discussion

3.1. Characteristics of E-PDMS membrane

3.1.1. Morphology of polymer microspheres with engineering a convoluted surface

Monodispersed microspheres were obtained on the surface of E-PDMS membrane as shown in **Fig. 3a**. Closer examination showed wrinkling patterns (or small bumps) on the particle surface. The layer of numerous polymeric particles exhibits a sufficient thickness (around 8 μm), a three dimensional hydrophobic barrier (Fig. 3b), which can be contributed to providing a high surface-to-volume ratio (specific surface area) having a potential of the improvement in flux. The microsphere with unique surface morphology is likely due to the interfacial behavior, which is caused by solvent evaporation rate and polymer viscosity. At high evaporation rate of THF solvent, PDMS molecules were not able to neither diffuse back to inside microspheres nor approach each other during the shrinkage of the droplet. If the PDMS concentration or their entanglement (molecular weight) is high, the polymer molecules are able to link together more easily [15].

Compared to a previous study [28], much smaller hydrophobic microporous polymers with tunable sizes of 2 to 5 μm were generated in this study by controlling polymer viscosity and the rate of solvent evaporating. As the present study is focused on dye treatment by MD using E-PDMS membrane, anti-fouling properties, method of roughness formation and its controlling, and phenomena of the optimized roughened PDMS microspheres will be dealt with in a future paper.

3.1.2. Chemical structure

PVDF as well as PH for its larger fluoride (F) ratio, which further enhances the hydrophobicity of fabricated membrane, have particularly attracted an attention in membrane fabrication by electrospinning. The hydrophobic property of the membranes could clearly be explained by the FTIR analysis (**Fig. 4a**). The three hydrophobic membranes (C-PVDF, E-PH and E-PDMS) with a base of PVDF, had multiple repetitions of small molecules (bonding of CH_2 and CF_2), the absorption peaks for the CH_2 bonds were observed at 1400, 1178 and 877 cm^{-1} corresponding to the stretching vibration of C-H bonds, the symmetrical stretching of C-F bonds and the skeletal vibration of C-C bond, respectively [29–31]. In the E-PDMS membrane surface coated with functionalized PDMS microspheres, a multi-component peaks at between 1000 cm^{-1} and 1100 cm^{-1} were attributed to Si-O-Si stretching and the peak at around 800 cm^{-1} represented $\text{Si}(\text{CH}_3)_2$ rocking [32,33]. With regard to crystalline phase, in IR absorption band spectra of E-PDMS, the peak at 840 cm^{-1} corresponding to β phase of the PVDF crystal was enhanced comparing to that of C-PVDF and E-PH. This result indicates the formation of β phase induced by crystallization

occurred in electrospinning with PDMS and was consistent with the membrane property shown in **Table 1**, in which a much porous and high LEP were found.

This result is in line with the XRD test, where the E-PDMS membrane showed a new peak at 2θ value of 11.8° corresponding to the tetragonal crystal lattice of PDMS. However, diffraction peaks were found weakened or disappeared at 18.4° and 39.2° in the E-PDMS compared to C-PVDF membrane which indicates the α -phase [34,35]. This indicates that PDMS was successfully coated and embedded on the E-PDMS membrane, which resulted in a hybrid (PDMS/PH) membrane.

3.1.3. Hydrophobicity and surface roughness

The E-PDMS membrane showed favorable properties (e.g., higher porosity and higher LEP: see **Table 1**) for (i) higher water production in MD compared to the commercial membranes, and for maintaining high resistance to water intruding into membrane pore (i.e. pre wetting) due to its higher hydrophobicity and lower wettability. The PDMS microspheres significantly improved surface hydrophobicity on the E-PH membrane, as confirmed by the increase in CA value from 137.2° (E-PH) to 155.4° (here, $>150^\circ$ referred to as a superhydrophobic) [26]. However, the C-PVDF membrane showed only 118.3° of CA. Higher CA values in the order of E-PDMS > E-PH > C-PVDF was consistent even with CA of dye droplets. (**Fig. 5a**).

This result can be explained by unique surface morphologies of the membranes as exhibited in the AFM images of C-PVDF (**Fig. 6b**) and E-PDMS membranes (**Fig. 5c**). The surface topography of the C-PVDF showed smooth hills and shallow valleys due to the structure

formed by phase inversion. Electrospinning can inherently bestow the Wenzel wetting state[36], the state in which a higher CA than original value of the material can be gained, on membrane surface by interconnecting nanofibers. In the case of E-PDMS, particularly, a large amount of air pockets in the hierarchical structures generates the convoluted interface. This engineered surface of bumps and deep valleys enables the water and dye droplet to be suspended on the membrane surface without water infiltration to increase the CA based on the Cassie-Baxter equation which refers to the roughness factor and fraction of the drop's contact area with the solid [37,38].

The calculated roughness (R_a) values of the C-PVDF, E-PH, and E-PDMS membranes were 133, 358 and 1,285 nm, respectively. This shows that PDMS microspheres resulted in a highly rough E-PDMS membrane surface.

3.1.4. Droplet bouncing behavior on the superhydrophobic surface of the E-PDMS membrane

The effect of the unique surface structure was confirmed in the water droplet (radius $r \sim 1.45$ mm) bouncing impact test with an impinging velocity $v_0 = 0.39$ m/s (see the supporting **Video S1**). As shown in **Fig. 6**, the water droplet first spread over the membrane surface uniformly driven by the inertia. After complete spreading, the droplet retracted and departed from the surface within 15.8 ms. Due to the superhydrophobic property of the as-prepared membrane, the adhesion between the liquid and substrate is negligible during the impact processes short contact. The water droplet would not have bounced off the surface if there is still an adhesive force amounting to the difference between “Lotus effect” and “Petal effect” [39,40]. Recently, Shen et

al.[41,42] reported that the short contact time and well rebounding were accomplished by low CA hysteresis in the water droplet impacting test. The well-rebounding indicates that a large amount of tiny air pockets prevent the membrane surface from being impregnated with the water droplet despite the pressure of the falling water. The trapped air pockets under the water droplet can play a role as a barrier for anti-wetting and anti-fouling in the hydrophobic membranes of the MD process.

3.1.5. Surface zeta potential

The relationship between the ZP and ambient conditions surrounding the nanoparticles remains a largely unexplored area, which necessitates researchers from many scientific disciplines to fully explore. The ZP is the charge of nanoparticles in relation to the surrounding conditions, however, it is not an actual measurement of the individual molecular surface charge; rather, it is a measurement of the electric double layer produced by the surrounding ions in solution (i.e., counter ions). As can be seen from **Fig. 8**, all tested membranes showed negative ZPs at tested pH ranges. At around pH 7.0, E-PDMS membrane possessed -70 mV of super negative ZP.

3.2. MD performance in treating synthetic dye solution

An ideal porous MD membrane should only allow the transport of vapor and/or non-condensable gases through the membrane pores [43] where the MD membrane serves as a barrier and a liquid/vapor interface is formed between the membrane surface and the feed stream. Thus, to prevent membranes from pore wetting, it should be hydrophobic with a high CA, and in this

regard the E-PDMS membrane (CA was measured up to 155.4°) had the lowest wettability, which indicates the suitability to MD. DCMD tests using three different membranes for the treatment of four different dyes were evaluated in terms of initial water flux, average water flux, and color removal efficiency in conditions of feed temperature = 60 °C, flow rate = 0.5 L min⁻¹, and C₀ = 100 mg L⁻¹. **Table 1** represents the characteristics of the three membranes used in this study.

3.2.1 MD water flux

The mechanism of water vapor transport across the membrane and water flux in DCMD can be explained by molecular diffusion [44]. Thus, water flux is proportional to the pore size (D) and the porosity (ε) of the membrane. Although pore size and membrane thickness of three membranes were quite similar, compared to the C-PVDF (fabricated by phase inversion), the electrospun membranes (E-PH and E-PDMS) have higher porosity and better hydrophobicity (see **Table 1**), which resulted in a higher flux. As shown in **Fig. 8**, the initial flux of the laboratory-fabricated E-PH and E-PDMS membranes was 1.5 times greater than that of the C-PVDF. The initial water flux of electrospun membranes (E-PH and E-PDMS) was approximately 34 LMH, while the C-PVDF produced the permeate at a lower initial flux of 21-23 LMH. In addition, among the four dyes, the highest water flux in MD for all membranes tested was observed in AY36 treatment while MD in CV treatment showed the lowest water flux. Overall, the initial water fluxes and flux decline patterns by the type of dye were in the following order: AY36 > AR18 > MB > CV. The result of water flux as a function of MD operation time for the treatment of mixed dye solution using three different membranes (C-PVDF, E-PH, and E-

PDMS) can be found in **Fig. S2**. In addition, Table S1 compared the MD membrane performance for the treatment of dyeing solutions for the literature.

3.2.2 Dye rejection and possible mechanisms

Despite the higher flux of the E-PDMS membrane compared to the C-PVDF as shown in **Fig. 8**, the color removal of E-PDMS membrane during 24 h of MD operation was superior to those of the other membranes. All membranes seemed to favor the color removal of AR18 and AR36 (100%) while the complete color removal of MB and CV proved to be difficult for the membranes except the E-PDMS (see **Table 2**). The removal efficiency of MB was slightly higher than that of CV in MD treatments using C-PVDF and E-PH membranes. Interestingly, the color removal efficiency followed the flux patterns, in other words, the higher flux membrane showed the higher color removal efficiency. For example, the average flux and color removal efficiency of MB and CV in MD treatment using E-PH membrane were 25.24 LMH (98.74%) and 24.02 LMH (97.62%), respectively. In this study, all the experiments were conducted in triplicate and the results were presented as mean value $\pm$ standard deviation to ensure the reproducibility.

The possible causes of this phenomenon can be explained by the dyes' chemical characteristics and their effects and extents on membrane adsorption. MB and CV contain both positively and negatively charged groups. MB is a basic cation dye that dissociates in an aqueous solution into a cation (the chromophore) and an anion, Cl^- (**Fig. S1a**). Accordingly, MB can be represented as Dye^+Cl^- [45]. Similarly, CV is a direct dye that is water-soluble and charged with organic compounds (**Fig. S1b**) that can bond to ionic and polar sites on the membrane. These

two dyes showed a high membrane adsorption property because of the electrostatic attraction between the Dye^+ in MB and the negatively charged membranes in the case of MB, and the hydrogen bonding between the negative functional group of the membrane ($\text{ZP} = 20 \text{ mV}$ at pH 4.9, see **Fig. 7**) and the electron-donating nitrogen atoms ($-\text{N}:)$ in the case of CV.

On the other hand, as can be seen in **Table 2** above, AR18 and AY36 (**Fig. S1c and d**) were most efficiently removed as they are negatively charged acid dyes that approach the membrane via their sulfonate groups. As the sulfonate groups were repelled by the highly negative membrane surfaces, relatively few molecules of these two dyes were adsorbed onto the membrane surface. In general, the sulfonate group (R-SO_3^-) has strong adsorption affinity toward positively charged surfaces, but the membranes tested in this study were mainly negatively charged at equilibrium pH ranges in the solution. The pH values of AR18 and AY36 are 9.1 and 6.4, respectively, and in these pH ranges, the surface charges of the C-PVDF and E-PDMS membranes are highly negative (in the ZP range of -40mV to -70 mV), as shown in **Fig. 6**. Thus, when dyes are closed to the membrane surface, the sulfonate groups of the dyes were repelled by the highly negative membrane surfaces [46].

The dyes' colors strongly depends on the chromogene–chromophore structure (electron acceptors) and their dyeing capacities (or binding energies) depend on auxochrome groups (electron donor) [47]. Hence, the chemical bonds between the dye molecules and the membrane are based on an attraction between the atoms within the chemical compounds. These bonds may result from electrostatic attraction between atoms with opposite charges or the sharing of electrons, as in covalent bonds. The strength of chemical bonds varies considerably; covalent or ionic bonds are "strong bonds," and dipole-dipole interactions and hydrogen bonding are "weak bonds" [48].

Dye molecules adsorbed onto/into the pores of the MD membrane (which is superhydrophobic and negatively charged) subsequently block the pores 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 (here, dye solution). However, the negative charges on the membranes generated repulsion to the negative ions of the dye. The E-PDMS membrane showed the highest flux and the most superior color removal efficiency in dye treating by MD. As observed earlier, attraction between the E-PDMS membrane and the negative ions of the dye led to a formation of a dye–dye structure on membrane surface instead of within the membrane pores. The stronger repulsive force between dye and the membrane can be formed by higher hydrophobicity of membrane. In this regard, the superhydrophobicity of the E-PDMS membrane facilitated this phenomenon. Moreover, the droplet bouncing effect of the E-PDMS membrane minimized the contact of dyes with the membrane while potentially increasing the chance of dye–dye binding, which hindered the penetration of dyes through the membrane pores and thus, led to higher color (or dye) rejection.

3.3. Fouling factor and dye adsorption

Fouling in MD is of particular importance, as it increases the costs of energy consumption, downtime, cleaning, and membrane replacement, and deteriorates product water quality due to pore wetting. As described above, dye rejection, and attraction, and repulsion between the dye and the membrane depend on their chemical structures and interactions, indicating that chemical bonding plays important role for dye fouling in the MD process.

To elucidate the fouling phenomena during dye treatment in MD, the membranes were taken out after 24 h of operation for CV (which showed the lowest flux dye) treatment and their

fouled surfaces were analyzed using SEM. Based on the blocking filtration laws which are generally applied in membrane fouling processes, it was anticipated that the dye will aggregate into the pore and surface of the membranes over time. As presented in **Fig. 9**, flake-type crystals covered the surface of the E-PDMS membrane but the pores remained open, while dye molecules blocked significant numbers of the pores of the C-PVDF and E-PH membranes. Closer examination showed that the loosely bound dye-dye (foulant-foulant) structure on E-PDMS membrane roughened surface to stimulate droplet bouncing with negative charge, and resulted in an effective antifouling and self-cleaning effect.

To extend the understanding to the effect of the dye concentration on the membrane-fouling mechanism during MD operation, different MB concentrations (20-200 ppm) were tested using DCMD with the three different membranes (C-PVDF, E-PH and E-PDMS). Interestingly, the flux at the very beginning of operational period was the same regardless of the dye concentration, but soon after, a greater flux drop was observed at higher dye concentrations. For all membranes, the fluxes were mostly stable over 24 h of operation when the dye concentration was low (20-40 ppm). In contrast, at dye concentrations above 60 ppm (up to 200 ppm), a rapid flux drop occurred during the first 4-8 h of operation. **Fig. 10(a)** shows the fouling factors (FFs) of the three membranes (C-PVDF, E-PH and E-PDMS) over 24 h of DCMD operation for MB treatment. With increasing dye concentration, the FFs remained constant up to 40 ppm, increased rapidly from 40 ppm to 100 ppm, and then stabilized above 100ppm. The rapid increase found for dye concentrations between 40 to 100 ppm can be attributed primarily to pore blocking and concentration polarization by dye adsorption.

The relationship between FF and initial dye concentration (C_0) was used to determine b and FF_{max} , to find that the values of FF_{max} and b were 40.82% and 0.021 mg L^{-1} for the C-PVDF

membrane, 45.66% and 0.019 mg L^{-1} for the E-PH membrane and 46.08% and 0.036 mg L^{-1} for the E-PDMS membrane, respectively. The R_L values ranged from 0.71 to 0.19 for the C-PVDF membrane, from 0.73 to 0.21 for the E-PH membrane and from 0.58 to 0.12 for the E-PDMS membrane. According to specification by Lee and Lueptow [49] that absorption is favorable at $0 < R_L < 1$, it can be said that all membranes exhibit favorable absorption by dye.

3.4 Effect of self-cleaning on the superhydrophobic surface and improved anti-fouling property of the membranes

This section ascribed how superhydrophobic surfaces shaped with bumps and valleys decorated with convoluted microspheres improved antifouling property by generating a bouncing regime between liquid dye droplet and membrane surface, which induced dyes to roll off rather than adhered on the surface. Inspired by “Lotus effect” which is the self-cleaning property of the membranes, therefore, this study conducted MD cleaning with simple water flushing (WF) to demonstrate the membrane cleaning efficiency by comparing the CA and LEP values of the membranes before and after DI water cleaning (WF). WF process was conducted by circulating DI water for 10 min every 3 h at a flow rate of 0.5 L min^{-1} . After MD operation, the E-PDMS membrane’s CA and LEP were reduced but they recovered with only for 10 min of the WF as shown in **Fig. 11**. However, in the C-PVDF and E-PH membranes, the reduced CA and LEP after MD operation could not fully be recovered with WF, because membranes had a stronger adhesive force with water droplets on the surface compared to E-PDMS membrane.[50] This result shows that the application of WF during MD operation using E-PDMS membrane holds potential to prevent fouling for a long-term operation.

Additionally, the effect of WF was tested for foulant removal and flux recovery using the single dye (CV) during 24h of MD operation, as it was the most difficult one among the four dyes in terms of color removal. The E-PDMS showed a high flux recovery with WF during MD operation as shown in **Fig. 12**. This is probably due to CA recovery of E-PDMS membrane with WF.

In summary, in the case of the E-PDMS membrane, flux was mostly recovered by intermediate WF. The droplet-bouncing regime of the E-PDMS membrane attributed by superhydrophobicity and featured morphology of PDMS microspheres prevented the dye particles from entering the pore to accumulate on the surface. The loose fouling layer formed on the E-PDMS membrane, which can be attributed to i) the weak bonding between the dye and the membrane, ii) the repulsion strength between the dye molecules and functional group on the E-PDMS membrane, and iii) the fluffy dye-dye structure formed before the dye molecules entered into the pores. As a result, it was possible to remove the dye-fouling layer on the E-PDMS membrane easily by simple WF. This result confirms that the superhydrophobicity of the membrane is one of the most critical factors determining its anti-wetting and anti-fouling properties, and subsequently removal efficiency. In other words, membrane's superhydrophobic layer affected the fouling mechanism to form loose fouling structures to be easily washed out. After 24 h of MD operation with WF in treating CV, much cleaner surface was observed on the E-PDMS membrane while the C-PVDF membrane showed severe dye adsorption and became dark purple colored membrane surface (**Fig. 13**).

The E-PDMS membrane showed quite low fouling tendency in the long-term operation with high dye rejection efficiency. Therefore, the E-PDMS membrane points to the potential for

possible dye recovery through WF without severe membrane fouling. The dye recovery will result in the consequent reduction of pollution as another advantage of utilizing the MD process for dyeing wastewater treatment.

4. Conclusions

PDMS polymeric microspheres were successfully coated and embedded on the E-PH membrane via simple and versatile electrospinning, which resulted in a hybrid PDMS/PH membrane (E-PDMS). The resultant E-PDMS membrane was tested to study for dyeing wastewater treatment by MD. The E-PDMS membrane showed favorable properties for a high water production and a high resistance to wetting due to its surface superhydrophobicity (contact angle: 155.4°) and roughness ($R_a = 1.285\mu\text{m}$). The zeta potential of E-PDMS membrane surface showed a negative value at neutral and acidic conditions, thus sulfonate groups of the dyes were easily repelled by the highly negative membrane surfaces. The negative ions of the dye led to a formation of a dye-dye structure on the E-PDMS membrane surface instead of within the membrane pores. It was found that higher hydrophobicity of membrane formed a stronger repulsive force between dye and the membrane. In addition, the unique surface structure was confirmed through the water droplet bouncing impact test that the droplet bouncing effect of the E-PDMS membrane minimized the contact of dyes with the membrane. This was potentially increased the chance of dye-dye binding, which hindered the penetration of dyes through the membrane pores and thus, led to higher color (or dye) rejection. In other words, the superhydrophobic layer of E-PDMS membrane affected the fouling mechanism to form loose fouling structures to be easily washed out by simply WF used in the present study.

Supplementary material

The following files are available free of charge. Supporting Video S1: Superhydrophobic-like drop impact dynamics on the superhydrophobic surface of E-PDMS membrane; Table S1; and Figure S1, 2.

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Fig 1. Schematic illustration of hybrid PDMS/PH membrane (E-PDMS) fabrication.

Fig 2. 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).

Fig 3. SEM images of the of E-PDMS membrane laboratory-fabricated (top right of b: cross-sectional SEM image).

Fig 4 (A). FTIR spectra of (a) the C-PVDF membrane, (b) the feed side of E-PDMS membrane (surface coated layer) and (c) the permeate side of E-PDMS membrane (it can be considered as E-PH membrane); and **(B).** XRD patterns of (a) C-PVDF, (b) E-PDMS and (c) E-PH membranes.

Fig 5. (a) Pure water and dye droplets on the surfaces of the three different membranes (C-PVDF, E-PH and E-PDMS) and (b) C-PVDF and (c) E-PDMS membranes' roughness analyzed using AFM.

Fig 6. Superhydrophobic-like drop impact dynamics on the superhydrophobic surface of E-PDMS membrane: The selected snapshots show the complete rebounding of the droplet after impact on the hybrid superhydrophobic interface.

Fig 7. Zeta potentials of the membranes (C-PVDF, E-PH and E-PDMS) as a function of pH.

Fig 8. Water flux as a function of MD operation time for the treatment of four different dyes using three different membranes (C-PVDF, E-PH, and E-PDMS) (feed temperature = 60 °C, flow rate = 0.5 L min⁻¹, and C₀ = 100 mg L⁻¹).

Fig. 9 SEM images (X2,000 and X15,000) of (a) the virgin C-PVDF membrane, (b) the C-PVDF membrane after MD, (c) the virgin E-PH membrane, (d) the E-PH membrane after MD, (e) the virgin E-PDMS membrane, and (f) the E-PDMS membrane after MD in CV treatment.

Fig 10. Water flux as a function of MD operation time for (a) fouling factor (FF) vs. dye concentration (C) and (b) C/FF vs. C for crystal violet (CV) treatment at different initial concentrations ($C_0 = 20 - 200 \text{ mg L}^{-1}$) (feed temperature = 60°C , and flow rate = 0.5 L min^{-1}).

Fig 11. Behavior of a water droplet on the surface of the E-PDMS membrane (a) virgin membrane, (b) after 24 h of MD operation, at which point the CA dropped from 155.4 to 87.1°, and (c) after WF for 10 min, in this case the CA was 99% recovered to 154.9°.

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Fig 12. Water flux as a function of MD operation time for C-PVDF, E-PF and E-PDMS membranes for CV treatment ($C_0 = 100 \text{ mg L}^{-1}$). WF was conducted for 10 min every 3 h at 0.5 L min^{-1} of flow rate.

Fig 13. The surface picture of (a) C-PVDF and (b) E-PDMS membranes after 24 h MD operation with WF for CV treatment.

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

Parameter	C-PVDF Commercial	E-PH Electrospinning	E-PDMS PDMS on E-PH
Material	PVDF	PH	PDMS/PH
Mean pore size (μm)	0.45	0.52	0.49
Porosity (%)	72.11	87.28	87.84
Membrane thickness (μm)	105	98	102
CA ($^{\circ}$)	118.3	137.2	155.4
Sliding angle ($^{\circ}$)	-	-	18.4
LEP* (bar)	1.17	0.92	1.26
Pure water flux** (LMH)	25.2	36.2	37.6

* LEP: liquid entry pressure. ** Pure water flux was measured in DCMD at 0.5 L min^{-1} of flow rate. Temperatures of feed and permeate were 60°C and 20°C , respectively.

Table 2. Initial fluxes, average fluxes, and color removal efficiencies in DCMD operation using three membranes in treating four different dyes during 24h.

Membrane	Dye	MB	CV	AR18	AY36
C-PVDF	Initial flux (LMH)	23.24 $\pm$ 0.58	22.17 $\pm$ 1.09	22.44 $\pm$ 0.22	22.95 $\pm$ 0.68
	Ave. flux (LMH)	17.75 $\pm$ 1.24	16.61 $\pm$ 0.96	19.31 $\pm$ 1.33	19.82 $\pm$ 1.82
	Color removal (%)	98.29 $\pm$ 0.42	96.54 $\pm$ 0.37	100	100
E-PH	Initial flux (LMH)	31.67 $\pm$ 0.29	32.06 $\pm$ 0.57	32.79 $\pm$ 0.43	32.93 $\pm$ 0.71
	Ave. flux (LMH)	25.24 $\pm$ 1.47	24.02 $\pm$ 0.87	28.16 $\pm$ 1.02	29.06 $\pm$ 0.74
	Color removal (%)	98.74 $\pm$ 0.31	97.62 $\pm$ 0.92	100	100
E-PDMS	Initial flux (LMH)	32.58 $\pm$ 0.59	33.02 $\pm$ 0.26	33.63 $\pm$ 0.46	33.19 $\pm$ 0.81
	Ave. flux (LMH)	25.23 $\pm$ 1.62	24.14 $\pm$ 1.35	29.5 $\pm$ 1.04	28.81 $\pm$ 1.11
	Color removal (%)	100	100	100	100

Highlights

- A PDMS /PVDF hybrid membrane was tested to study its antifouling property in MD.
- Polymeric PDMS microspheres showed a superhydrophobicity to suppress fouling.
- Anti-wetting properties enhanced with hybridizing of PDMS.
- Zeta potential of E-PDMS membrane surface showed a high negative value.
- Complete color removal and high quality water production were achieved.