Direct Contact Membrane Distillation for Treatment of Mixed Wastewater of Humic Acid and Reactive Dye: Membrane Flux Decline and Fouling Analysis

Pyae Phyo Kywe and Chavalit Ratanatamskul*

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ABSTRACT: The main waste stream from the textile industry is its wastewater with high color, organic matters, and other contaminants. This study aims to investigate the effect of humic acid in mixed wastewater of humic acid and reactive dye on the treatment performance and permeate flux of a direct contact membrane distillation (DCMD) system. In this research, feed temperature and humic acid concentration were the main input parameters for the analysis of DCMD system operation. The fouling resistances significantly increased with higher humic acid concentrations in the mixed wastewater. As compared with the DI water test, 23% of flux decline occurred when the humic concentration in the wastewater was increased up to 20 mg/L. After the DCMD treatment, the 25 ADMI residual color was detected in the permeate when the mixed wastewater contained 20 mg/L humic acid. The mathematical model, based on the Antione equation, was proposed to predict the membrane flux decline of the DCMD system. The reduced pore size of the cake layer by a dimensionless constant β from the Kelvin equation was also considered for the fouling calculation to describe the transport mechanism.
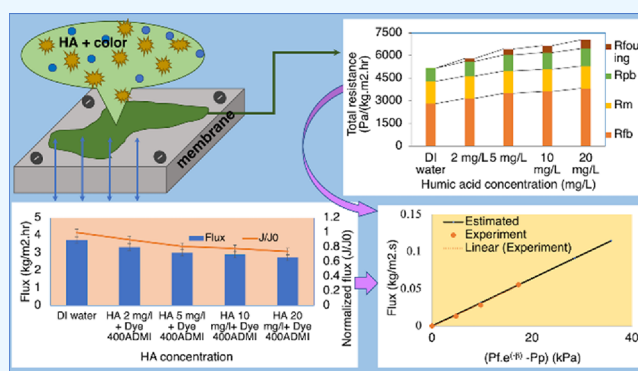
1. INTRODUCTION

Nowadays, the increased demand and growing scarcity of fresh water have been recognized to have significant impacts around the world. According to the United Nations data, more than two billion people have faced the problem of freshwater resource reduction. Worsening hunger and malnutrition may be caused by drought.[1] As with the blooming of industries, appropriate water management in industrial sectors is one of the main concerns to conserve water resources and to prevent water pollution. The textile industry has been recognized as a water intensive industry that uses a large amount of water in the wet processing stage such as sizing, desizing, scouring, bleaching, mercerizing, and dyeing. The main waste stream from the textile industry is its wastewater with color and other contaminants. The wastewater contains complex mixtures of chemicals from various processes, acids, bases, dissolved solids, toxic compounds, and color as the main contaminants. Color is one of the prominent characteristics of this wastewater even at low concentrations of reactive dye substances. Natural and synthetic dyes are used in the dyeing industry. Nowadays, synthetic dyes are also used in textile, rubber, paper, plastic, and leather industries. Salt is also another problem of the textile wastewater. It is used to aid the exhaustion of ionic dyes, especially for anionic dyes like reactive and direct dyes on

cotton.[2] Therefore, further development of appropriate textile wastewater treatment is still needed to safely dispose the treated effluent to natural bodies of water to reuse and to get clean water for communities. Different amounts of dyes are required per unit of fabric. Color and salts in wastewater are the major pollutants that are of environmental concerns. The use of dyes is dependent on the required dyebath ratio, which is the ratio of the units of dye required per unit of fabric and typically ranges from 5 to 50 depending on the type of dye, dyeing system, and affinity of the dyes for the fibers.[3]

Among the developed treatment methods, membrane processes are becoming popular. These processes have been applied for wastewater treatment, water treatment, and desalination processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED), etc. Most of these membrane systems utilize transmembrane pressure as the main driving force.

Some of the other driving forces for membrane filtration are concentration, electric potential, or chemical potential. As a recent development in membrane technology, another type, which is membrane distillation (MD), is driven by temperature difference through a microporous hydrophobic membrane unlike the other types of former membrane technologies. Because of its hydrophobic property, only vapor can pass through the membrane and can be distilled. The vapor from the hot feed side can permeate through the pores of the membrane to the permeate side because of the temperature difference between these two sides. Hydrophobic membranes can be made from different polymers such as polytetrafluoroethylene (PTFE), polyethylene (PE), polypropylene (PP), or polyvinylidene fluoride (PVDF). The preparation methods may be different depending on the polymer types. The PTFE membrane has good thermal and chemical stability with low surface energy. This membrane has good hydrophobicity and wetting resistance. Also, it can be prepared by extrusion, rolling, stretching, sintering, or in some instances by melting processing techniques.[4] The PTFE membrane can produce a higher flux than the PVDF membrane for the DCMD operation.[5] Nonsolvent or thermally induced phase separation is also used for PVDF soluble polymers.[6] It has moderate thermal stability and good chemical resistance.[7] Moreover, development of material technology on nanocomposite polymeric membranes has been reported to achieve a higher organic removal and membrane permeate flux through surface modification. Common procedures to modify membrane surfaces include nanoparticle coating and deposition, chemical bonding, and grafting methods.[8,9]

Membrane distillation has been tested and researched in different fields such as desalination, food production, brine concentration, and others. Nevertheless, fouling deposition is one of the major problems for the application of membrane distillation. It can reduce the hydrophobicity of membranes as well as the pore size distribution of the MD membrane. According to membrane wettability, liquid better penetrates the membrane pores and can pass through the membrane with the feed wastewater during the process. The efficiency of membrane distillation can be reduced depending on the extent of membrane fouling, which can cause the flux decline and the membrane wettability. Operating conditions for fouling minimization have been discussed. Increased feed velocity could reduce the amount of scaling, whereas increased feed temperature results in a higher fouling.[10] The most common organic fouling is natural organic matter or NOM such as humic substances in raw water that is used for manufacturing processes.[11] Fouling in MD occurs in the form of inorganic scaling, particulate or colloidal fouling, natural organic matter (NOM) fouling, and biofouling.[12] Natural organic matter (NOM) is also a critical issue for fouling of membrane processes.[13,14] NOM can be in the form of humic acid, amino acid, sugars, polysaccharides, and polyhydroxyaromatics.[15] In surface water, ground water, and seawater, humic substances are the major constituents of NOM.[13] Humic acid production during seasonal changes may be caused by tree leaf decomposition in large quantities, leaching to rivers and lakes. Therefore, bacteria are nourished and this can result in bacterial fouling of the membrane system.[16]

Humic acid fouling in membrane distillation may vary based on feed composition, membrane hydrophobicity, temperature, membrane pore characteristics, and pH.[17,18] The fouling layer can also affect the thermal and hydraulic resistances of the membrane system and the temperature polarization effect. Humic acid may cause another type of scaling, and it can be significant on calcium carbonate scaling.[19] The scale deposit on the membrane surface can result in complete or partial blocking phenomena. The formation of a fouling layer could reduce water recovery and vapor passage. Scaling may increase temperature and concentration polarization by creating a hydrodynamically stagnant or slow-moving layer of water at the membrane surface.[20] According to Agashichev and Sivakov,[21] scaling could affect the flow velocity and a slower velocity could increase the temperature polarization. Schofield et al.[22] introduced the membrane distillation transport model by taking into account the influence of temperature polarization. The membrane mass transfer coefficient was estimated by measurement of flux and temperatures at both the inlet and outlet of the membrane distillation.[23,24] Tan et al.[25] hypothesized the Kelvin effect for the study on fouling of the PVDF membrane from using a very high concentration of humic acid (160 mg/L) and calcium chloride (3.775 mM) solutions. A larger vapor pressure declination was highlighted because of the temperature polarization effect in the feed side. Vapor pressure declination and fouling analysis by the changes in both humic acid and color concentrations with different temperature effects have yet to be further explored for future studies.

At present, there is little information on the treatment performance and the permeate flux of direct contact membrane distillation systems for mixed wastewater of humic acid and reactive dye. In this work, humic acid was selected as the simulated dissolved organic matter in this mixed wastewater. Humic acid is a major species of natural organic matters in raw water supply. Boggs et al.[26] reported that the amount of humic acid concentration in the natural water was in the range of 0.1−20 mg/L. The proportion of humic acid-like substances in the bio-treated textile wastewater was also reported to be up to 31.46%.[27] Indeed, humic acid also causes color in the treated effluent. Therefore, the effect of humic acid on the color removal and the permeate flux of MD membrane under different feed temperatures and humic acid concentrations was investigated in this research. This study aims to investigate the mass transfer resistance by the fouling effect, the vapor pressure depression due to the contaminants in the wastewater for the flux prediction, and the mitigation of the contaminants from the feed solution to the permeate side. This work focused on simultaneous treatment of humic acid and color in the mixed wastewater of reactive dye and humic acid by the hydrophobic PTFE membrane. Moreover, the mathematical model for this membrane fouling and flux decline analysis was developed by considering the fouling resistance and the interaction of humic acid and color on the hydrophobic PTFE membrane material. The influence of different operating temperatures and concentrations of humic contaminants was analyzed for the membrane fouling phenomena. The fouling resistance, the permeate flux, and the reduced pore size of the cake layer were also predicted using a dimensionless constant (β) from the Kelvin equation in this research.

2. MATERIALS AND METHODS

2.1. Experimental Setup. The MD membrane used in this research was a flat-sheet hydrophobic membrane. The membrane was a negatively charged polytetrafluoroethylene (PTFE) membrane, manufactured by Sterlitech Corporation. This membrane is a microfiltration membrane, having a pore
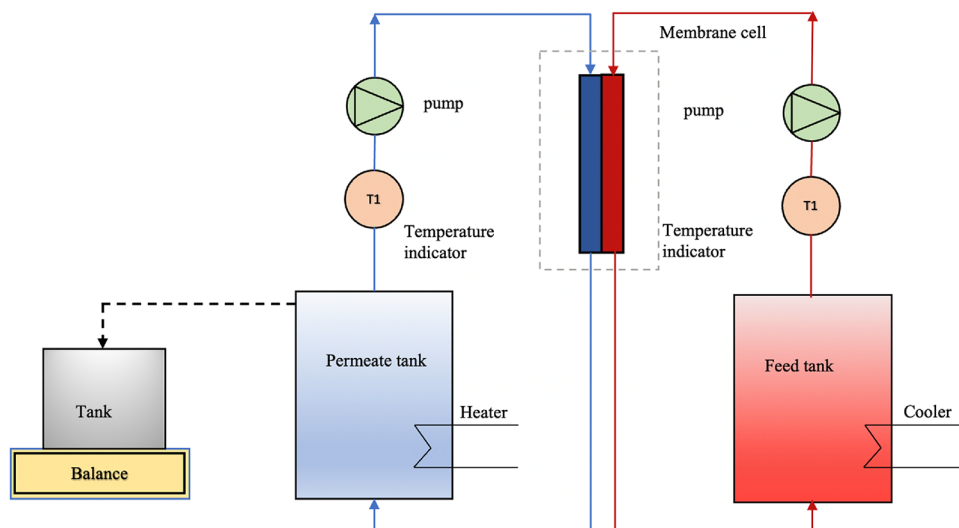
Figure 1. Schematic diagram of the DCMD experimental setup.

Table 1. Characteristics of the Reactive Blue Dye Used in This Study

molecular formula	molecular weight (g mol^{-1})	color index number	molecular structure	maximum wavelength (nm)
$C_{22}H_{16}N_2Na_2O_{11}S_3$	626.54	61,200	anthraquinone	590

size of 0.1 μm, thickness of 45 μm, and membrane area of 140 cm^2. The feed wastewater was heated using a hot water bulk (WNB-7 from Memmert) and the permeate water was cooled down using a chiller (Xi'an Heb Biotechnology Co., Ltd. (CCA-420)) as a closed loop system. The membrane sheet was sandwiched between the hot and cold water compartments in the membrane cell.

The schematic diagram of the DCMD experimental setup is shown in Figure 1. Two peristaltic pumps were used to transport the water, and the accumulated permeate water was measured by an electronic balance from A&D Company (GX-6100) within the time interval. The flowrates were set up at 0.5 L/min for both feed and permeate sides.

2.2. Chemicals, Synthetic Wastewater, and Analytical Methods. *2.2.1. Reactive Dye.* The color substance used in this study was a reactive blue dye as a main component of the synthetic textile wastewater. This reactive blue dye is an anionic dye with high-water solubility and strong covalent bonds. Reactive Blue 19 dye was purchased from SIGMA-ALDRICH Company. The characteristics of the reactive blue dye are shown in Table 1 and Figure 2.

2.2.2. Humic Acid. Humic acid (HA) is a typical chemical widely used for the organic foulant, and it is commonly found in natural water and wastewater. Sodium salt humic acid ($C_9H_8Na_2O_4$) was used in this research. HA from SIGMA-ALDRICH Company was used for the preparation of the mixed wastewater.
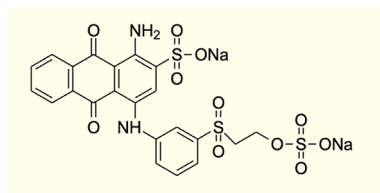

Figure 2. Structure of the reactive blue dye used in this study (MW = 626.54 g mol^{-1}).

2.2.3. Wastewater Preparation and Analytical Methods. In this research, the mixed wastewater was prepared in the laboratory as synthetic wastewater using Reactive Blue 19 dye and sodium salt humic acid. The reactive blue dye was prepared to have the required concentration of 400 ADMI, which is a high range of color concentration found in textile wastewater in Thailand. A Spectroquant Prove Spectrophotometer 100 was used to measure the color concentration in ADMI unit. Humic acid (HA) concentrations were prepared at different concentrations of 2, 5, 10, and 20 mg/L as a mixture of simulated NOM in the mixed wastewater for experimental investigation. Humic acid concentration was also measured using a UV spectrophotometer at a wavelength of 280 nm.

2.3. Experimental Procedure. During the DCMD experiments, the negatively charged PTFE membrane sheet was used for treatment of the mixed wastewater containing humic acid and reactive dye. The permeate temperature was kept constant at 20 °C, while the feed wastewater temperatures were varied to 40, 50, and 60 °C to investigate the effect of feed temperature on the DCMD permeate flux and treatment performance. At first, DI water was initially tested with the DCMD system to obtain the clean water flux of the DCMD system as the baseline water flux before testing with the mixed wastewater of humic acid and reactive dye. The membrane resistance was also calculated from the DI water test. To know the fouling propensity and the fouling resistance, the synthetic mixed wastewater prepared from humic acid (2 mg/L) and reactive dye (400 ADMI) was initially treated by the DCMD system under the same temperature and flow rate condition as in the DI water test. The permeate flux was calculated by the experimental mass difference that was measured using the balance. Then, humic acid (HA) concentrations were varied to 5, 10, and 20 mg/L while maintaining the reactive dye concentration of 400 ADMI to investigate the fouling effect of humic acid foulant in the mixed wastewater of the DCMD system at a feed temperature at 60 °C and a permeate temperature at 20 °C, which was the optimal temperature

operating condition of the DCMD system. Total resistance and fouling resistance were calculated by the mathematical model in Section 2.4.

2.4. Theoretical Model Calculation. The removal efficiency can be calculated by the below equations:

$$\text{rejection} = \left(1 - \frac{C_\text{p}}{C_\text{f}}\right) \times 100 \tag{1}$$

where C_f is the initial concentration and C_p is the permeate concentration after treatment.

The permeate flux of the DCMD membrane can be calculated using eq 2, where J is the flux ($\text{kg/(m}^2\cdot\text{h)}$), ΔW is the weight difference of permeate water at a time interval (kg), t (h) is the time that is accumulated by the permeate water, and A is the membrane area (m^2).

$$J = \frac{\Delta W}{(t_2 - t_1) \times A} \tag{2}$$

The driving force for DCMD is the partial vapor pressures through the membrane. The mass flux J ($\text{kg/(m}^2\cdot\text{h)}$) is directly proportional to the vapor pressure difference through the membrane material, and it also has a relationship with the membrane coefficient. The vapor pressure can be calculated by the Antoine equation with the temperature difference. Hence, the driving temperature can govern the flux.[28] The vapor pressure for pure water can be calculated by the Antoine equation as below:

$$P = \exp\left(23.238 - \frac{3841}{T - 45}\right) \tag{3}$$

The resistances of membrane distillation are calculated by eqs 4−6. The resistances R_fb, R_m, and R_pb are the feed boundary layer, membrane, and permeate boundary layer resistances, respectively. P_mf and P_mp are the vapor pressures at the membrane surface at the feed and permeate sides. P_f and P_p represent the feed bulk vapor pressure and the permeate bulk vapor pressure.

$$R_\text{fb} = \frac{P_\text{f} - P_\text{mf}}{J} \tag{4}$$

$$R_\text{m} = \frac{P_\text{mf} - P_\text{mp}}{J} \tag{5}$$

$$R_\text{pb} = \frac{P_\text{mp} - P_p}{J} \tag{6}$$

Pressures are calculated by eq 3. To get pressure, temperatures at membrane surfaces (T_mf and T_mp) are estimated by eqs 7 and 8

$$T_\text{mf} = \frac{h_\text{m}\left(T_\text{p} + \left(\frac{h_\text{f}}{h_\text{p}}\right)T_\text{f}\right) + h_\text{f}T_\text{f} - J\Delta H_\text{v}}{h_\text{m} + h_\text{f}\left(1 + \left(\frac{h_\text{m}}{h_\text{p}}\right)\right)} \tag{7}$$

$$T_\text{mp} = \frac{h_\text{m}\left(T_\text{f} + \left(\frac{h_\text{p}}{h_\text{f}}\right)T_\text{p}\right) + h_\text{p}T_\text{p} + J\Delta H_\text{v}}{h_\text{m} + h_\text{p}\left(1 + \left(\frac{h_\text{m}}{h_\text{f}}\right)\right)} \tag{8}$$

where h_m, h_f, and h_p are the heat transfer coefficients of the membrane, feed, and permeate, respectively. ΔH_v stands for the latent heat of vaporization.

The fouling condition of solution (R_fouling) is considered by the comparison with the distillate water test (R_water)

$$R_\text{total} = R_\text{fb} + R_\text{m} + R_\text{fouling} + R_\text{pb} \tag{9}$$

The transport of water vapor through the membrane is driven by the temperature difference between the feed and permeate temperatures. Tan et al.[25] proposed the mass transfer flux equation as shown below. The vapor pressure force can be calculated by the temperature across the membrane

$$J = C\cdot(e^{-\beta}\cdot P_\text{mf} - P_\text{mp}) \tag{10}$$

where J is the flux and C is the overall mass transfer coefficient. The vapor pressures P_mf and P_mp can be calculated from the temperature on the membrane surface for each side. $e^{-\beta}$ is considered for the flux reduction by the fouling layer that can reduce the temperature curvature at the water interface at the feed side. The dimensionless constant β is derived from the vapor pressure decrease from the Kelvin equation[29]

$$\beta = \frac{4\gamma V_w}{RdT_\text{mf}} \tag{11}$$

where V_w is the molar volume of the liquid, d is the characteristic pore diameter in the fouling layer, and R is the universal gas constant.

3. RESULTS AND DISCUSSION

3.1. Surface Morphology of the Negatively Charged PTFE Membrane. SEM imaging and surface analysis of the negatively charged PTFE membrane in this study were performed by SEM (S-3400N, Hitachi, Japan) in conjunction with energy dispersive X-ray spectroscopy (EDX, Apollo X, EDAX, USA). The surface morphology of this PTFE membrane is illustrated in Figure 3. The major elements of this membrane surface were C (41.39%), O (6.76%), Si (14.53%), and F (37.34%). For other surface morphology parameters, our previous work reported that the original PTFE membrane used in this study has a zeta potential of −23.18 mV (negatively charged surface) with a contact angle of 99.83° as a hydrophobic surface.[30]

3.2. Effect of Feed Temperature on the Permeate Flux of the DCMD System in Treating the Mixed Wastewater of Humic Acid (HA) and Reactive Blue Dye. By the Antoine equation, the vapor pressure is increased by an increase in the temperature difference as a driving force. From Figure 4, the permeate flux of the DCMD system could be significantly enhanced by an increase in the feed temperature from 40 to 50 and 60 °C while the permeate temperature was maintained at 20 °C. The steady-state flux could be obtained within 7 h, as can be seen in Figure 4a. There is no significant reduction of flux at the end of the experiment after a filtration time of 7 h. The increased flux resulted from the temperature difference between the feed side and permeate side of the DCMD system. The permeate flux from the DI water test increased from 1.04 to 3.74 $\text{kg/m}^2\cdot\text{h}$ with the increased feed temperature, as shown in Figure 4b.

The membrane resistance was decreased by an increase in the feed temperature. The increased temperature can result in the increased vapor pressure and can drive the vapor to pass through the membrane pores. Therefore, the membrane
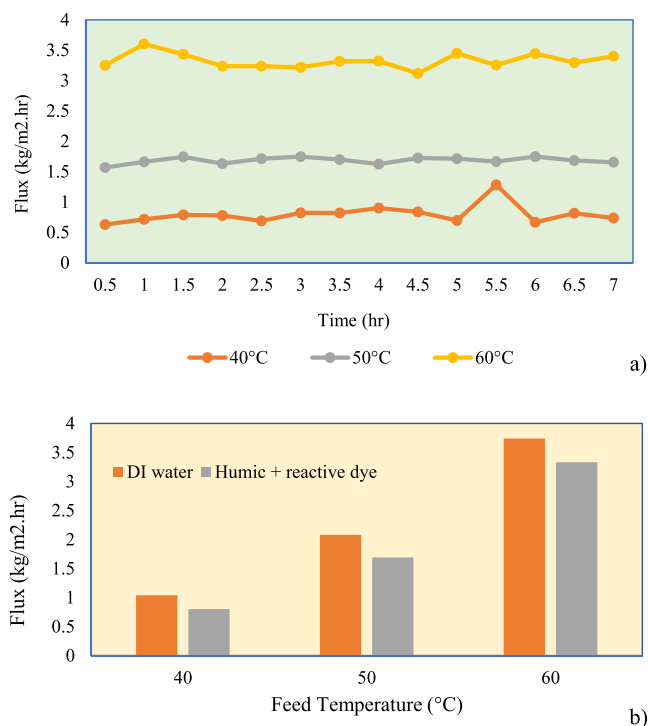
a)

b)
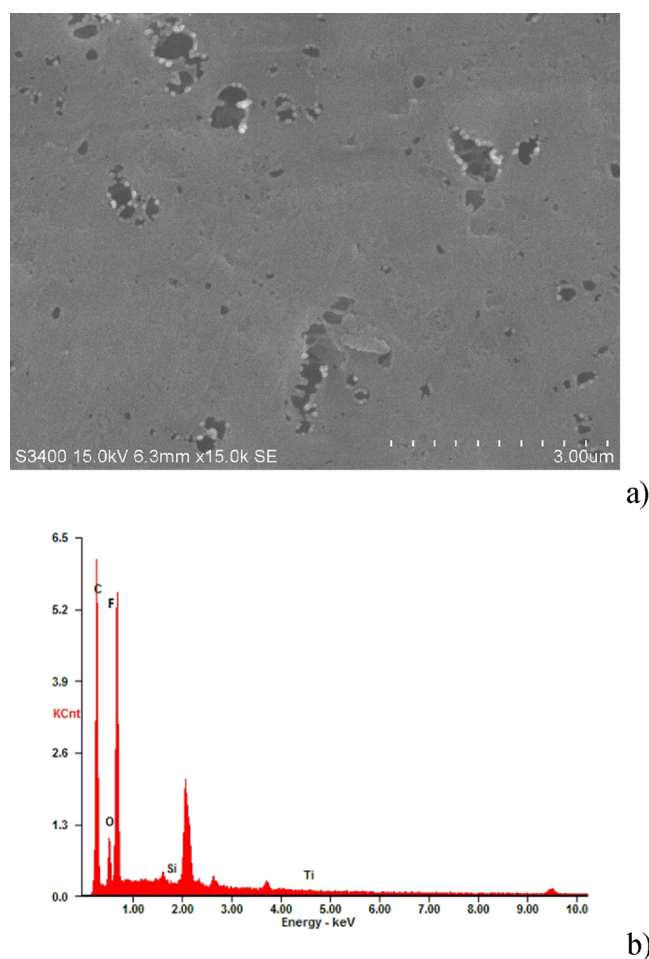
Figure 3. SEM−EDX measurement of the PTFE membrane surface. (a) SEM image. (b) EDX analysis.

a)

b)

Figure 4. Permeate flux of the DCMD system in treating the mixed wastewater. (a) Permeate flux at different feed temperatures. (b) Permeate flux comparison between DI water and the mixed wastewater.

a)

b)

Figure 5. Normalized flux (J/J_0) as a function of feed temperature and humic acid concentration. (a) Normalized flux (J/J_0) of DI water at different feed temperatures. (b) Normalized flux (J/J_0) at different humic acid concentrations (feed temperature: 60 °C).
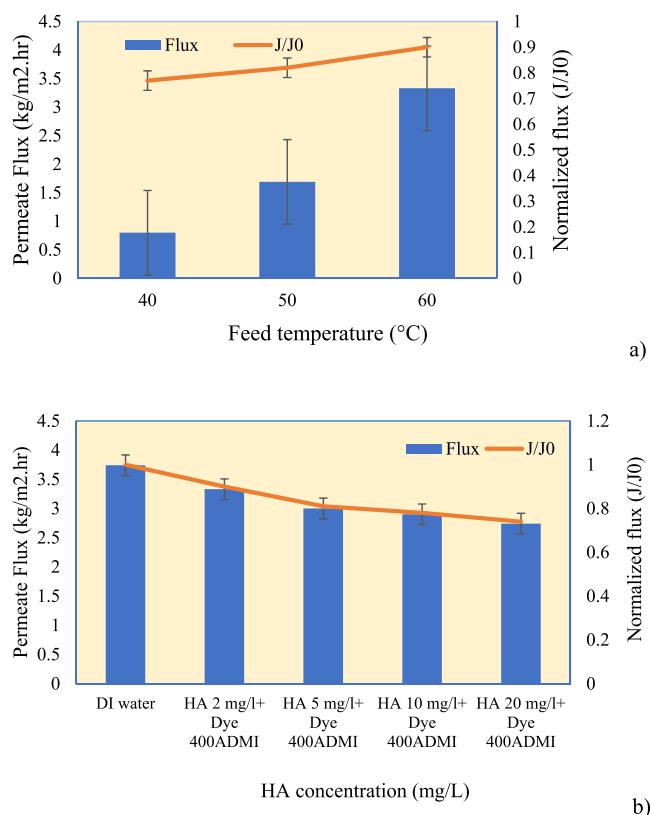
resistance was reduced, resulting in the increased flux. Permeate fluxes of 0.8, 1.69, and 3.33 kg/m^2·h were observed in treating the mixed wastewater having 400 ADMI color and 2 mg/L humic acid at 40, 50, and 60 °C, respectively, as shown in Figure 4b. The obtained fluxes were reduced by 23, 18, and 10% of the DI water fluxes from the DCMD system at the same feed temperatures, respectively. The permeate flux of the DCMD system in treating the mixed reactive dye wastewater was lower than the permeate flux of DI water due to membrane fouling, filtration resistance, and temperature polarization coefficient. The permeate flux of the DCMD in treating the mixed wastewater of HA and reactive dye is also relevant to the Antoine equation.

3.3. Effects of Feed Temperature and Humic Acid Concentration on the Normalized Flux of the DCMD System in Treating the Mixed Wastewater of HA and Reactive Dye. The mass transfer is influenced by the feed temperature. The temperature difference between both sides of the hydrophobic PTFE membrane is the driving force for the DCMD system. In this experiment, the permeate temperature was kept constant at 20 °C and the feed temperatures were increased to 40, 50, and 60 °C to know the influence of temperature on the performance of the DCMD system in treating humic acid and reactive dye in the mixed wastewater. Larger permeate fluxes resulted from higher feed temperatures.
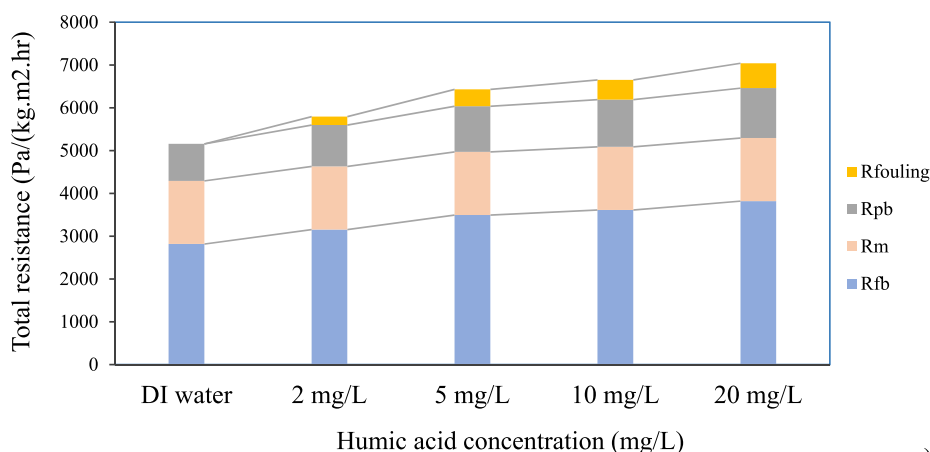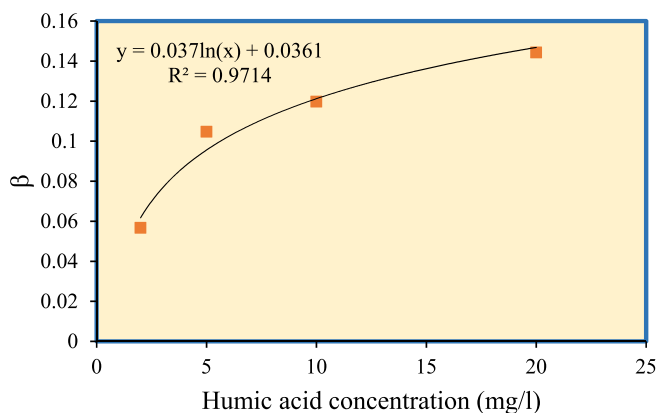
The normalized flux (J/J_0) that refers to the DI water flux can be seen in Figure 5a. When the temperature as the driving

Figure 6. Fouling of the DCMD system for treatment of the mixed wastewater. (a) Classification of DCMD resistances from the treatment of the mixed wastewater. (b) Obtained β values at different humic acid concentrations.

force is higher, the normalized flux could increase from 10 to 23% with feed temperatures of 50 and 60 °C. Therefore, the feed temperature is one of the essential influencing parameters of the DCMD system that can significantly drive the water flux. The permeate flux at 60 °C was higher than that at a lower feed temperature range.

Amaya-Vías et al.[31] and Naidu et al.[32] also reported an increased flux at higher operating temperatures. However, organic deposition on the membrane surface occurred due to the migration of organic substances in their experiments. The additional fouling layer could reduce the permeate flux. In this work, an MD membrane flux decline was observed with an increase in humic acid concentration at the feed temperature of 60 °C, as shown in Figure 5b. To know the effect of humic acid concentration on the DCMD permeate flux, the humic acid concentrations in the mixed wastewater were varied from 2 to 5, 10, and 20 mg/L while keeping the same reactive dye concentration of 400 ADMI. The feed and permeate temperatures were kept at 60 and 20 °C, respectively. The normalized flux decreased from 10 to 26% with the increased humic acid concentration from 2 to 20 mg/L. As compared with the previous study by Srisurichan et al.,[33] humic acid fouling could cause flux reduction of the membrane distillation by up to 35% after 9 h operation time. This might be due to an increase in fouling resistance from humic acid deposition on the membrane surface. The obtained fouling resistances were expected to be higher with higher humic acid concentrations in the feed mixed wastewater. The additional fouling layer can

cause a decrease in heat transfer resistance. The hydraulic resistance of the water vapor that passed through the membrane can cause the reduction of the vapor pressure through the membrane. As can be seen from Figure 5b, the obtained permeate fluxes varied from 3.33 to 2.74 kg/m^2·h with humic acid concentrations in the range of 2 to 20 mg/L due to the natural organic fouling problem. The deposition of organic matter on the membrane surface was increased by higher humic acid concentrations. This could increase the total filtration resistance.[34] Therefore, the normalized flux significantly decreased with the treatment of the mixed wastewater containing 20 mg/L humic acid.

The resulting thick membrane fouling layer could increase the heat transfer resistance and reduce the pore size for the passage of vapor. Khayet et al.[17] tested the feed humic acid solution and reported that the fouling layer could cause the reduction of vapor pressure. Flux reduction was observed for the PVDF membranes due to humic acid fouling. According to data analysis, a significant hydraulic resistance was caused by the thickness of the fouling layer with millimeter or subnanometer pore diameters.

3.4. Fouling Characteristics of the DCMD System in Treating the Mixed Reactive Dye Solution. The accumulation of the foulant layer of humic acid and reactive dye substances increased the total filtration resistance that reduced the DCMD permeate flux. The vapor pressure reduction and the increased temperature polarization can reduce the flux. The increased total resistances are shown in

Figure 6a by the increased temperature polarization conditions. Higher humic acid concentrations could significantly affect the flux resistances. As compared with the DI water test, the fouling resistance was calculated by eq 9. The increased feed boundary resistance was observed at higher humic acid concentrations. This resulted in the increase of the filtration rate and the mass transfer in the membrane pore. The fouling layer was also increased more and more by the increased humic acid concentration. The increased fouling resistance values are presented in Figure 6b.

The resistance could reduce the vapor curvature by organic fouling from humic acid when humic acid concentrations were increased in the mixed wastewater. The fouling resistance was derived from the resistance from the DI water test and the mixed reactive dye wastewater test. It can be seen from Figure 6a that the fouling resistance increased from 196 to 581 Pa/(kg·m²·h) for HA concentrations from 2 to 20 mg/L. The value of fouling resistance tends to increase with the increased humic acid concentration.

As explained in eq 10, $e^{-\beta}$ is the coefficient of fouling that can reduce the vapor pressure from the feed side. The calculated coefficient and experimental flux from the treatment of the mixed reactive dye wastewater were taken for the calculation of the vapor reduction coefficient β. The resulting values are presented in Figure 6b. The β value represents the condition of vapor pressure reduction of the feed side by feed solution and the pore size for the fouling layer. According to the Antione equation, the different vapor pressure can drive the flux of the DCMD system. Therefore, the reduction of flux is considered for the low vapor pressure difference. The feed solution may change the feed vapor pressure and the diffusion of the vapor in the membrane pore. The diffusion model for organic filtration was suggested by Amaya-Vías et al.[31] Diffusion is the temperature function by the Fick's law that could affect the fate of humic substance within the membrane surface. The adsorption of humic substance on the membrane surface can be increased by the increased temperature and the diffusivity of humic substance.

Figure 6b shows that the β value increased from 0.06 to 0.14 when humic acid concentrations were increased from 2 to 20 mg/L. This means that the feed vapor pressure was reduced and the driving force was also decreased. Temperature polarization caused the vapor pressure reduction of about 5.8 to 13% on the feed side when the humic acid concentrations were increased in this range. Therefore, the concentration of humic acid in the mixed wastewater can seriously change the pore diameter of the fouling layer or cake layer on the membrane surface. This means that the flux can be reduced by the fouling condition on the membrane surface. The calculated pore diameter in the cake layer is illustrated in Figure 7. The pore diameter of the cake layer was significantly reduced from about 3.5 to 1.5 nm when humic acid concentrations were increased from 2 to 20 mg/L. The small pore size of the cake layer from the fouling effect can cause a reduction of the DCMD permeate flux by the reduced vapor pressure with the Kelvin effect. The temperature curvature can be influenced by the feed humic acid concentration. The vapor pressure depression and heat resistance that deals with the fouling layer having very small pores were also reported by Chew et al.[34]

3.5. Mathematical Model for Prediction of the Permeate Flux of the DCMD System in Treating the Mixed Wastewater of HA and Reactive Dye. As described
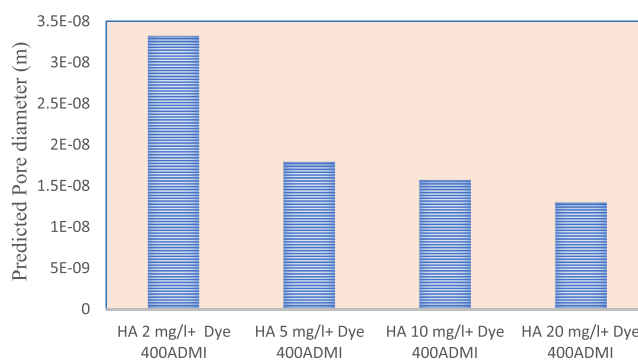

Figure 7. Predicted pore size diameter of the cake layer by the mathematical model.

in eq 10, the overall mass transfer coefficient can be derived from the flux and the pressure difference of the feed and permeate sides. For the DI water test, $\beta = 0$ for the no fouling condition. Therefore, the overall mass transfer coefficient was obtained from the DI water test. The value was calculated for each feed temperature from the experimental flux values on the same membrane type. The linear relationship between the DI water flux and the pressure difference $(P_f - P_p)$ between the feed and permeate sides is illustrated in Figure 8a. The overall mass transfer coefficient of 0.0032 kg/m²·s·kPa was calculated from this relationship. The β value is considered for the experiment using the mixed wastewater containing humic acid and reactive dye. This value shows a lower reduction of the feed vapor pressure with a high temperature under the same feed concentration. The relationship between the DCMD permeate fluxes of the mixed wastewater test and the DI water test is plotted in Figure 8b.

The two equations were solved to obtain the $e^{-\beta}$ value, and the resulting value was 0.9, which was further used for the prediction of DCMD permeate flux in treating the mixed wastewater as a function of vapor pressure difference, as shown in Figure 8c. The mathematical model could accurately predict the experimental DCMD permeate fluxes, obtained from the treatment of the mixed wastewater. The β value deals with the pore diameter in the fouling layer. The vapor pressure by the temperature polarization tends to reduce the DCMD flux due to the fouling condition. Tan et al.[25] also reported that 12.4% reduction of vapor pressure of the feed side was caused by the Kelvin effect. Hence, the temperature polarization could reduce the pore size of the cake layer on the membrane surface.

3.6. Investigation on Color and Humic Acid (HA) Removal Performances of the DCMD System for the Mixed Wastewater. The permeate of the DCMD system was analyzed in terms of color and residual humic acid concentration. The organic matter and ions could not reach the volatile points with the feed temperature of the DCMD. A high removal efficiency for humic acid over 99% could be achieved with the negatively charged PTFE membrane in DCMD operation under the operating feed temperature conditions of 40, 50, and 60 °C, as shown in Figure 9. Although the humic acid concentration was increased up to 20 mg/L in the feed wastewater, the removal efficiency of the DCMD system for humic acid still achieved over 99%. Moreover, the color removal efficiency of the DCMD for the mixed wastewater was higher than 93% for all operating conditions under different feed temperatures and humic acid

(a)

(b)

(c)
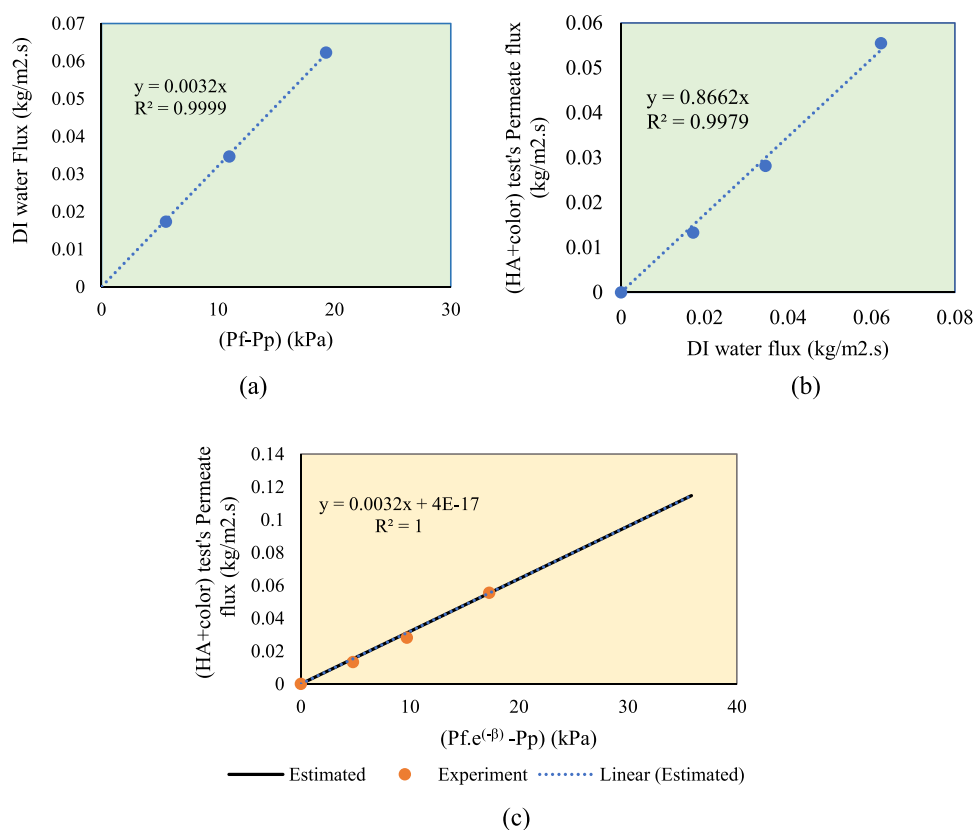
Figure 8. Calculated permeate fluxes of the DCMD system from the mathematical model. (a) Flux and pressure difference by the different temperatures from the DI test. (b) Plotting of DCMD permeate fluxes of the mixed wastewater test and the DI water test. (c) Calculated DCMD permeate fluxes of the mixed wastewater filtration from the mathematical model.

a)

b)
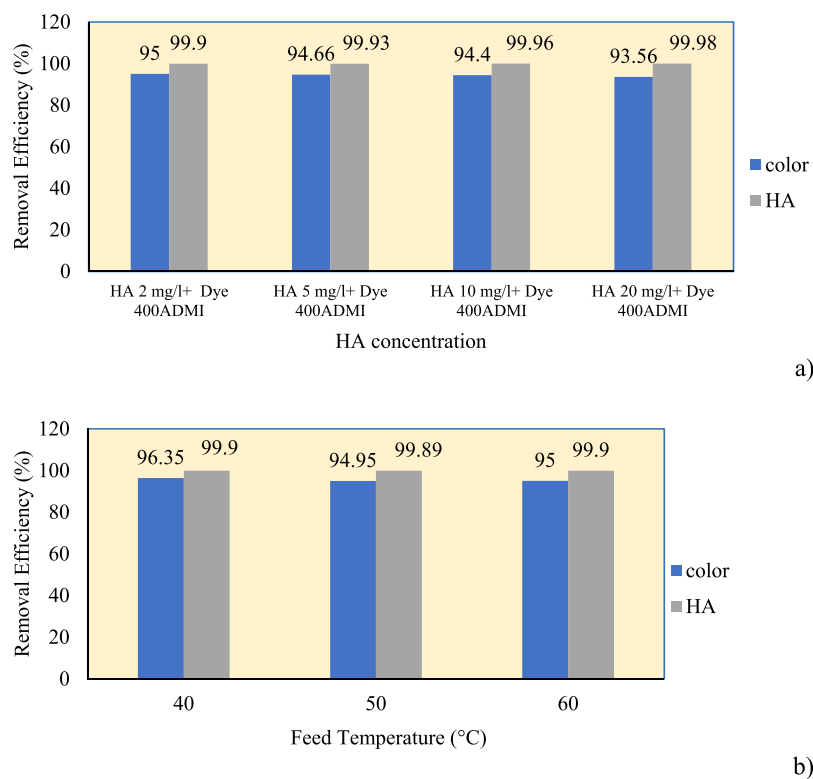
Figure 9. Color and humic acid removal as a function of HA concentration and feed temperature. (a) Effect of HA concentration. (b) Effect of feed temperature.

concentrations in this study. Couto et al.[35] also reported a high humic acid removal for sole humic acid wastewater with the DCMD system.

Although the feed temperature does not result in volatilization of humic acid, migration of humic acid on the membrane surface was discussed in some experiments. The migration of humic substances could occur by hydrogen bonding between the loose carboxylic or phenolic groups on the molecule and water vapor. Also, humic acid at the edge of the pores may be desorbed to the permeate side. Meng et al.[18] suggested that humic acid might absorb on the membrane surface and desorb to the distillate side. The organic compound was detected in the distillate flux. This may be due to the reduction of membrane roughness and adsorption ability since there was no wetting in the membrane from the unchanged conductivity of the permeate side.

The temperature difference is the main driving force for membrane distillation operation. Vapor can only pass through the membrane pore. Smaller molecular sizes can make a fouling layer by an adsorption mechanism. Over 90% removal efficiency for humic acid can be seen in Figure 9b. However, some research works detected humic acid concentration in the distillate side. Amaya-Vías et al.[31] detected an HA flux from 15.6 to 37.1 mg h-L m^{-2} for the AGMD system at higher feed temperatures. The deposition of humic acid on the membrane surface and the disaggregation of HA could occur by higher temperatures and migration of dissolved organic matters to the permeate side. However, the color value of the permeate side in this study did not change with the temperature difference. This means that the DCMD system could highly retain the reactive blue dye in the feed side.

3.7. Interaction of the Reactive Blue Dye, Humic Acid, and Hydrophobic PTFE Membrane. The possible mechanisms for color and humic acid removal by the negatively charged PTFE membrane in DCMD operation are discussed. The melting points of Reactive Blue 19 and humic acid (>300 °C) are higher than the operating temperature (60 °C). This suggested that the DCMD system could retain the reactive blue dye and humic acid in the feed side. Since the reactive blue dye is an anionic dye, the negatively charged molecule of reactive blue dye could be repelled by the surface charge of the PTFE membrane due to electrical repulsion force. Hence, only water vapor could pass through the hydrophobic membrane. Previous work reported that humic acid can also adsorb on the surface of the NF membrane by polar bond formation.[36] It has been recognized that humic substances in raw water favorably adsorb onto the surface of hydrophobic membranes. Moreover, the Ca^{2+} ions present in the wastewater might serve as a main bridging ion between humic acid and the hydrophobic PTFE membrane. Therefore, high retention of reactive blue dye and humic acid by the MD membrane could be achieved, as shown in Figure 10a. Humic acid fouling of the MD membrane might be due to the deposition of humic acid layer on the membrane surface as well as the adsorption of humic acid foulants in the membrane pores.

Figure 10b illustrates that the permeate color was slightly increased from 20 to 25 ADMI with an increase in the humic acid concentration from 2 to 20 mg/L. Humic acid deposition on the membrane surface can form a loose layer and tends to increase the hydrophilicity of the membrane due to the hydroxyl and carboxylic funtional groups.[37] The increased hydrophilicity of the MD membrane from humic acid deposition might increase the transport of some molecules of

a)

b)
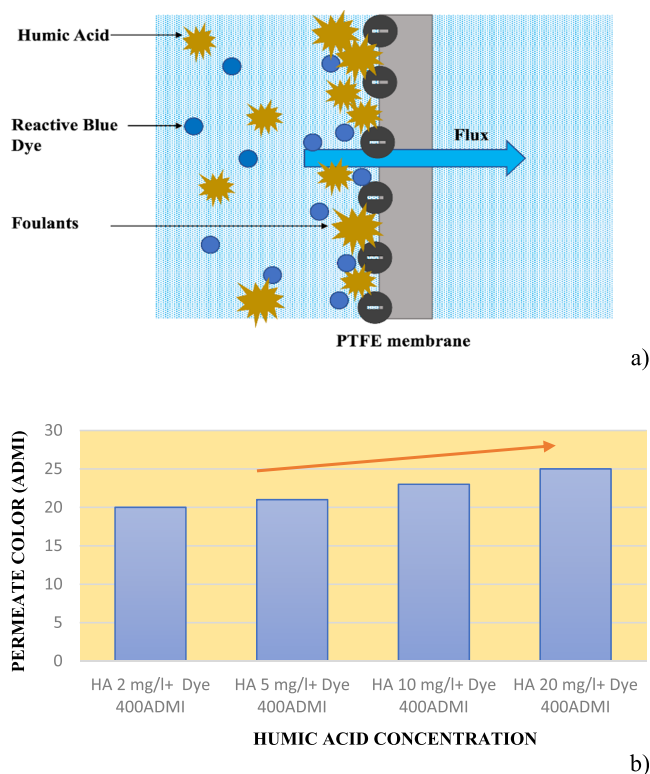
Figure 10. Possible mechanism of color and HA removal by the negatively charged PTFE in the DCMD system. (a) Removal of color and HA by the negatively charged PTFE membrane. (b) Effect of humic acid concentration on the permeate color.

reactive blue dye through the MD membrane. Humic acid deposits are typically loosely packed and porous, and traditionally, in UF and MF systems, they are effectively eliminated through backwashing. As the concentration of humic acid was increased, the cake formation was more prominent due to the deposition of HA on the membrane surface.[35] The cake filtration model was also used to describe the transport mechanism of membrane distillation by considering the aggregation of humic fouling, which could affect the transport resistance of the system.[33]

Criscuoli et al.[38] reported that the molecular weight of the dye could also affect the permeate flux. RBBR (remazol brilliant blue R) and RB5 (reactive black 5), which have higher molecular weights, gave a higher flux compared with indigo vat blue with a lower molecular weight. The negative charge property of the PTFE membrane surface that was used in this research can repel and reject the negatively charged anions in the mixed wastewater due to electrical repulsion force.[39] The negatively charged membrane surface could reject the negatively charged dye more than the positively charged dye. There was a stronger attraction of the membrane surface and then a lower permeate flux for the positively charged dye compared with the negatively charged dye. Therefore, a higher removal efficiency can be obtained by the negatively charged group of reactive dyes.

Although the humic acid concentrations were increased from 2 to 20 mg/L, high color removal efficiencies were nearly the same in this research investigation. The negatively charged surface of the MD membrane might also repel the negatively charged reactive dye molecules. Moreover, the possible adsorption of humic acid on the membrane surface did not

significantly change the humic acid removal efficiencies by the DCMD system in this study. Therefore, a low humic acid concentration in the permeate water could be obtained.

In this research work, the color removal under different humic acid concentrations was performed to understand the role of humic acid in the DCMD treatment process. Humic acid concentrations were varied to 2, 5, 10, and 20 mg/L. There was only 20 ADMI residual color in the permeate water when 2 mg/L HA was added to the mixed wastewater, while 25 ADMI residual color was detected for 20 mg/L HA addition. Although humic acid concentration was increased 10 times, the residual color in the permeate was increased only about 5 ADMI. According to Meng et al.,[18] the amphiphilic nature of humic acid could cause its adsorption−desorption to the PVDF membrane. Therefore, some research could detect humic acid in the permeate flux. In this experiment, the adsorption of humic acid did not significantly interfere with the color removal efficiency by the negatively charged PTFE membrane in DCMD operation. It can be suggested that the concentration of the feed side could influence the membrane permeate flux rather than the permeate quality. The color removal efficiencies were rather constant at about 94−96%, whereas the concentration of the feed humic acid was changed from 2 to 20 mg/L. The auxiliary components did not affect the reactive dye removal by the negatively charged PTFE in the DCMD operation. However, higher humic acid concentrations should be further tested in the future to better understand the correlation of humic acid and color concentration for the DCMD removal efficiency.

4. CONCLUSIONS

The fouling analysis of the DCMD system from humic acid foulant was described in treating the mixed wastewater in this study. The permeate DCMD flux could be described by the Antione equation. Higher temperatures resulted in higher permeate fluxes by the temperature difference. The flux of DCMD with this wastewater treatment had around 10 to 26% reduction, compared with the flux of DI water. The flux decline was due to humic acid deposition on the DCMD membrane surface. An increase in humic acid concentration in the mixed wastewater could build up more fouling layers on the membrane surface. As a result, a higher resistance was generated. Fouling could cause temperature polarization that increases the filtration rate and mass transfer of the vapor to the membrane pores. The estimated flux was obtained from the calculated β value. The color removal efficiencies were over 90% for all cases of feed temperatures and humic acid concentrations in this study. Therefore, the DCMD system is promising for color and humic acid removal from the mixed wastewater that can be further applied for real textile wastewater with natural organic contaminants.

■ AUTHOR INFORMATION

Corresponding Author

Chavalit Ratanatamskul − *Department of Environmental Engineering, Chulalongkorn University, Bangkok 10330, Thailand; Research Unit on Innovative Waste Treatment and Water Reuse, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand;* ● orcid.org/0000-0001-9537-7289; Email: Chavalit.R@chula.ac.th

Author

Pyae Phyo Kywe − *Department of Environmental Engineering, Chulalongkorn University, Bangkok 10330, Thailand; Research Unit on Innovative Waste Treatment and Water Reuse, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c04932

Notes

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