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Membrane Distillation Trial on Textile Wastewater Containing Surfactants Using Hydrophobic and Hydrophilic-Coated Polytetrafluoroethylene (PTFE) Membranes

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Abstract: Treating wastewater from textile plants using membrane distillation (MD) has great potential due to the high-salinity wastes and availability of waste heat. However, textile wastewaters also contain surfactants, which compromise the essential hydrophobic feature of the membrane, causing membrane wetting. To address this wetting issue, a custom-made membrane consisting of a hydrophilic layer coated on hydrophobic polytetrafluoroethylene (PTFE) was tested on textile wastewater in a pilot MD setup, and compared with a conventional hydrophobic PTFE membrane. The test was carried out with a feed temperature of 60 °C, and a permeate temperature of 45 °C. The overall salt rejection of both membranes was very high, at 99%. However, the hydrophobic membrane showed rising permeate electrical conductivity, which was attributed to wetting of the membrane. Meanwhile, the hydrophilic-coated membrane showed continually declining electrical conductivity demonstrating an intact membrane that resisted wetting from the surfactants. Despite this positive result, the coated membrane did not survive a simple sodium hydroxide clean, which would be typically applied to a membrane process. This brief study showed the viability of membrane distillation membranes on real textile wastewaters containing surfactants using hydrophilic-coated hydrophobic PTFE, but the cleaning process required for membranes needs optimization.

Keywords: membrane distillation; hydrophilic membrane; polytetrafluoroethylene; desalination

1. Introduction

The need for more sustainable industries that can capture waste and recycle clean water from their existing saline effluent drives the need for new desalination technologies. High-efficiency and low-cost thermal processes are an important part of solving some of our most important water problems. One technology that may help achieve this is membrane distillation (MD) [1]. The concept of MD emerged in the 1960s, and was a topic for researchers exploring new membrane materials and systems with high thermal efficiency, but MD literature reported few full-scale installations. MD was previously limited by the availability of membranes, but with the recent availability of high-performance hydrophobic microfiltration membranes, MD may find practical application alongside the highly efficient reverse osmosis, and mature conventional thermal technologies (e.g., multi-stage flash).
Furthermore, opportunities that appear suited to MD can be found due to its compactness as a thermal process and the low cost of materials. MD is a thermally driven separation process which uses a hydrophobic membrane as a physical barrier for polluted water, from which mass transport of vapor is driven by differences in vapor pressure [1]. Therefore, the critical feature of the membrane is its ability to resist pore wetting when in contact with the liquid to be treated [2]. Of the four main MD configurations, direct contact MD (DCMD) is the simplest and most studied for desalination and concentration of a range of industry solutions [3]. In this configuration, the heated solution (feed) is in contact with the surface of the membrane, and is designated the “hot side” where evaporation takes place at the feed–membrane interface. Water vapor is driven by the vapor pressure difference, caused by the temperature gradient across the membrane to the flowing, cold permeate side which condenses into the permeate stream. Because of the hydrophobic characteristic of the membrane, the liquid wastewater cannot penetrate the membrane. This configuration is known for having the highest fluxes, but the main drawback is the heat lost through conduction [3].

In general, the wastewater generated from the textile industry is high in chemical oxygen demand (COD), salt, and surfactants because it comprises spent textile dyes, suspended solids, mineral oils, electrolytes, surfactants, etc. [4]. All this makes textile wastewater difficult to treat.

Treatment of textile wastewaters was explored by several researchers [5–8], highlighting the limitation of conventional technologies. Traditional aerobic biological treatment is generally ineffective because of the poor biodegradability of dyes, and the inhibition of many biological processes [5]. Anaerobic or anoxic pre-treatments are required, as they are better suited for biodegradation of dyes. Coagulation is generally most effective with ferrous sulfate and a cationic polyelectrolyte [6], but it is often unsuitable for streams containing reactive or acid dyes because their removal is less efficient [5,7]. Ozonation can be effective for oxidizing many organic species, but it is ineffective against sulfur, vat, and disperse dyes [5]. Fenton oxidation using Fe$^{2+}$ in the presence of hydrogen peroxide is generally more effective than ozonation, and can be operated at lower cost. Membrane techniques are effective at removing salts [8], but their performance is impacted by fouling from dyes. Moreover, the recovery is limited by the salinity. Adsorption via activated carbon or biomass is typically used, but its limited applicability, low commercial use, and complexity reduce its utility [7]. With wastewater so difficult to treat with one or even multiple processes, exploration of alternatives is needed, and there are few reports on the potential of MD in the treatment of textile wastewater.

Similar to other membrane technologies, MD faces two effects that are mainly responsible for the degradation of the membrane performance: fouling and wetting. The literature shows that fouling issues in MD cause severe flux decline, while wetting issues cause loss of the membrane hydrophobicity, leading to a passage for contaminants from the feed side into the permeate, and affecting the quality of the water produced [9–11]. The literature also shows that biological processes can remediate these issues by biologically removing retentate carbohydrates and proteins [10]. On the other hand, the membranes can be made to tolerate components that would otherwise compromise their performance. For example, researchers recently modified hydrophobic polyvinylidene fluoride (PVDF) membrane surfaces to create a hydrophilic surface that demonstrated resistance to fouling from oils in solution [12]. However, surfactants can also wet membranes, and membranes are yet unexplored for this application. It is already understood by the textile industry that resistance to surface wetting agents is provided by the addition of hydrophilic coatings. Hydrophilic-coated polyurethane is well known for application to breathable water repellent fabrics, where the polyurethane is coated on hydrophobic polytetrafluoroethylene (PTFE) to prevent contamination from oils and surfactants [13]. Indeed, the hydrophilic polyurethane coating is designed to be selectively permeable to water vapor. The underlying hydrophobic PTFE that prevents liquid water from migrating through the membrane is, therefore, protected by this coating. This commercial material is, therefore, an ideal candidate for the treatment of textile wastewaters rich in surfactants, and potentially fats and oils. The resistance to fats and oils by this membrane was demonstrated in previous work exploring the viability of MD applied in the meat industry [14].
This type of membrane may have multiple applications. Indeed, the literature shows that hydrophilic–hydrophobic membranes used with polyvinyl alcohol (PVA) coatings seemed highly efficient for the treatment of oily feeds via osmotic distillation [15]. In addition, they were successfully used in dispersion-free solvent extraction [16].

This work was concerned with the comparison of two PTFE membranes in the desalination of saline wastewater from a local textile factory operated by Australian Textile Mills (ATM), in an effort to make it suitable for internal re-use. This offsets the need for utilizing scarcer and higher-value potable water, while at the same time reducing the liquid disposal volumes.

This study follows on from two previous MD trials carried out by us. The first aimed to recover water from reverse osmosis (RO) concentrate of groundwater using solar thermal collectors [17]. The second aimed to recover water from ion-exchange regeneration waste produced at a power station, where the MD was powered by low-grade waste heat [18]. This paper presents the outcome of a pilot trial of MD for processing textile wastewaters, which was carried out before a three-month trial that was fed with wastewater from the existing biological treatment process [19]. However, direct treatment of the site’s effluent to avoid biological treatment aligns with the future vision of more intensified water treatment of textile facilities [20]. In moving toward this approach, the challenge is to prevent membrane wetting due to the presence of surfactants in the wastewater. State-of-the-art hydrophobic membranes, found to have high fluxes applied to desalination [21], were tested against a membrane through the novel use of a commercially available hydrophilic-coated PTFE membrane utilized in textile products. This membrane was fabricated for this work at the same textile facility.

2. Materials and Methods

2.1. Membrane and Module

Two different membranes were used to carry out this work. The first membrane selected demonstrated high performance in MD applications, and had an active layer made of polytetrafluoroethylene [21]. The PTFE active layer was supported by a scrim of polypropylene (PP) backing. The membrane was provided by Ningbo Changqi Porous Membrane Technology Co., Ltd. (Ningbo, China). The second membrane used in this work was a hydrophilic-coated hydrophobic PTFE membrane typically applied to waterproof breathable fabrics [13], and recently applied for MD [14]. The membrane was fabricated by ATM by adhering a woven support to the coated PTFE film to make the composite membrane.

The MD module used in this study was an in-house multi-layered design that was previously used in a power station trial [18]. Each membrane was hand cut and then placed between each divider, using gaskets and spacers for both sides. The use of turbulence-promoting spacers was used to improve flow uniformity and mixing in the channels [22], as the thickness of the thermal boundary layer can be reduced by improving the stream turbulence. The membranes used had an effective total area of 0.67 m².

The MD module initially operated using the effluent taken from the company’s combined holding pit, where the wastewater exiting the processes is accumulated before being discharged. Due to the intermittent discharge of a secondary source of wastewater with a potentially high concentration of surfactants, the wastewater was collected from an intermediate tank drawn from the main effluent upstream from the combined holding pit.

2.2. Site Test Setup

The pilot plant was operated at the ATM site at Wangaratta, Victoria, Australia. The aims for the pilot plant were to treat the wastewater produced during the fabrics manufacture process, to produce water to a high-quality standard suitable for plant re-use, and to demonstrate the capability for using waste heat as the source of energy.
The plant was designed with an estimated capacity on the order of 480 L·day⁻¹ based on the upper flux values of 30 L·m⁻²·h⁻¹. However, flux (and plant capacity) is dependent on temperature, available waste-heat, and membrane fouling. Stated flux and capacity assumed a 60 °C waste-heat source with approximately 14 kW of available waste heat, with cooling water at approximately 20 °C. The temperature of the MD pilot-scale system is shown in Figure 1.

**Figure 1.** Membrane distillation (MD) pilot-scale system.

The system consisted of two tanks with a capacity of 85 L each, which served as feed (hot loop) and permeate (cold loop) reservoirs. The hot loop had two filters (25 µm and 5 µm) used to reduce the amount of solids in the feed as the water became concentrated, thus reducing membrane fouling [23,24]. A plate heat exchanger (HX) was used for the heat transfer between the feed and the heat source. The heat source was provided from the site's steam-condensate return line to the boilers, the temperature of this condensate was highly variable, fluctuating between 80 °C and 100 °C. The permeate was cooled in a plate heat exchanger using the same site's cooling water circuit (15–20 °C) and permeate was cooled in a plate heat exchanger using the same site's cooling water circuit. Both the hot feed and the cold permeate loops were pumped by two centrifugal pumps in a counter-flow arrangement through the membrane module. The plant was equipped with control systems and data logging to enable continuous unattended operation.

The temperature and pressure of the feed and permeate were monitored at their respective inlets and outlets using data logging. Electric conductivity (EC) sensors were used in the feed and permeate systems and data logging to enable continuous unattended operation.

The temperature and pressure of the feed and permeate were monitored at their respective inlets and outlets using data logging. Electric conductivity (EC) sensors were used to indicate the concentration of dissolved solids, which was translated to salt rejection. Cycle rejection. The typical flow was around 16 L·min⁻¹ in the feed to the membrane module. The typical flow was around 16 L·min⁻¹ in the feed loop, and 14 L·min⁻¹ in the permeate loop. Sodium sulfate solution (30 g·L⁻¹) was used as feed at the beginning of each test to confirm the membrane performance flux and salt rejection. Upon starting operation of the MD plant, evidence of intact membranes and their effective operation was indicated by the permeate tank increasing in level while EC declined. Meanwhile, the feed tank decreased in level and increased in EC.

### 2.3. Water Quality Analyses

Analyses of the effluent and the permeate produced were carried out to indicate the separation performance of the system and membrane intactness. Various parameters were measured to confirm the membrane performance flux and salt rejection. Upon starting operation of the MD plant, evidence of intact membranes and their effective operation was indicated by the permeate tank increasing in level while EC declined. Meanwhile, the feed tank decreased in level and increased in EC.
2.3. Water Quality Analyses

Analyses of the effluent and the permeate produced were carried out to indicate the separation performance of the system and membrane intactness. Various parameters were measured to determine their quality. The total dissolved solids (TDS) was estimated using the EC value. The conversion factor, dependent on the chemical composition of the TDS, can vary between 0.55 and 0.8. A value of 0.63 is commonly used as an approximation if the actual factor is not known [25] (TDS ≈ 0.63 × EC). The EC and the pH were measured using a WTW Multiline P3 pH/LF equipped with an EC meter and a pH probe. The values of total nitrogen (TN), nitrate (NO$_3^-$), nitrite (NO$_2^-$), ammonium (NH$_4^+$), chemical oxygen demand (COD), and total phosphorus (TP) were obtained using Merck Millipore pre-prepared test kits for the Spectroquant instrumentation: 1.14763.0001 (TN), 1.14547.0001 (NO$_2^-$), 1.14542 (NO$_3^-$), 1.14543.0001 (TP), 1.14558.0001 (NH$_4^+$), 1.14541.0001 (COD), and Merck Millipore Spectroquant Pharo 300.

The rejection of the compounds was defined by the membrane rejection coefficient, defined as

$$R = 1 - \frac{C_f}{C_r},$$

(1)

where $R$ is the rejection of the membrane for a given component; $C_f$ and $C_r$ are the concentrations of the rejected component in the filtrate (permeate) and the retentate, respectively [26].

Finally, the flux through the membrane ($J$) was determined as

$$J = \frac{Q_p}{A}.$$  

(2)

Interpreted as the process productivity, it was defined by the permeation rate, $Q_p$, divided by the membrane surface, $A$. It also represented the velocity of the fluid perpendicular to the surface of the membrane [27].

2.4. Scanning Electron Microscopy

Scanning electron microscopy (SEM) images were obtained using a Nikon/JEOL Neo-Scope JCM-5000 SEM (Melville, NY, USA) with 10 kV accelerating voltage and capturing secondary electron detection. All specimens were dried in a desiccator overnight, and gold-coated for two minutes before SEM analysis.

3. Results and Discussion

3.1. Membrane Analysis

Figures 2 and 3 show the SEM images of the two membranes utilized in this study. The left (a) images show the membrane from the support side, and the center images show the membrane cross-section. Figure 2c shows the PTFE surface of the standard hydrophobic membrane, while Figure 3c shows a closer view of the cross-section of the coated PTFE. The coating appears dense from SEM analysis, as previously reported for the same membrane type [14]. Comparing Figure 2 with Figure 3 shows greater membrane exposure for the scrim-supported membrane, leading to the conclusion that the scrim support with wide openings used on the standard PTFE membrane was expected to lead to higher flux than the tighter-woven support used on the hydrophilic-coated hydrophobic PTFE membrane. Also, pores on the standard hydrophobic PTFE membrane can be seen in Figure 2c, while, as reported previously, the coated membrane appeared similar when imaging the PTFE through the support while the polyurethane coating was dense [14]. The membranes had the key elements for application to an MD pilot module (supported thin porous hydrophobic layers).
Figure 2. Standard polytetrafluoroethylene (PTFE) membrane: (a) scrim support (backing); (b) membrane side view; and (c) membrane front view.

Figure 3. Hydrophilic-coated hydrophobic PTFE membrane: (a) woven support (backing); (b) side view; and (c) side view (zoomed in).
3.2. Initial Plant Performance

Figure 4 shows the typical results obtained with the Na$_2$SO$_4$ test on the standard PTFE membrane. The Na$_2$SO$_4$ solution was used as a means to check pilot plant performance before adding the textile wastewater. The aim of this was also to confirm the intactness of the membrane module sealing. The wastewater feed was then added after flushing the membrane and rig with clean tap water.

The EC slowly rose on the feed side while it decreased slowly on the permeate side. A salt rejection of 99.5% was calculated from the EC values. The membrane integrity was confirmed by this test, and the pilot plant was deemed ready to treat the textile wastewater. The test was then repeated on the hydrophilic-coated hydrophobic PTFE membrane, obtaining similar results.

3.3. Analysis of Wastewater Used in Trial

The feed effluent (wastewater) quality was highly variable due to several production operations occurring intermittently. However, Table 1 shows typical operational values, and those representing the tests presented here.

| Parameter                | Value |
|--------------------------|-------|
| pH                       | 7.76  |
| Electrical Conductivity (EC; $\mu$S·cm$^{-1}$) | 976   |
| Total Dissolved Solids (TDS; mg·L$^{-1}$) | 605   |
| Total Nitrogen (TN; mg·L$^{-1}$) | 11    |
| Nitrate (NO$_3^-$; mg·L$^{-1}$) | 8     |
| Nitrite (NO$_2^-$; mg·L$^{-1}$) | 0.97  |
| Ammonium (NH$_4^+$) (mg·L$^{-1}$) | 1.12  |
| Chemical Oxygen Demand (COD; mg·L$^{-1}$) | 2830  |
| Total Phosphorus (TP; mg·L$^{-1}$) | 3.10  |
| Color                    | Colored |
The wastewater was relatively high in COD, as expected for textile wastewaters [4,28]. The COD values were significantly high in the COD, which is expected to peak in wastewater from the textile industry. The COD values were also relatively high in the wastewater, especially in the presence of dyes. However, the COD values were moderate, but depended on the processes used at the site. In this case, the COD values were over 100 mg L⁻¹. In this study, the COD values were over 100 mg L⁻¹, suggesting a potential contribution of sodium hydroxide cleaning to the wetting. Saponification reactions of organics with sodium hydroxide are possible contributors to COD values, especially for textile effluents, where sodium hydroxide is commonly used for pad-dyeing and other finishing processes.[30]

In textile effluents, ammonia can be present in high concentrations, especially in the presence of dyes. Ammonia values were especially low for textile wastewaters, with typical values below 0.1 mgNH₃-N L⁻¹. In this case, the EC values were over 100 mS cm⁻¹, suggesting liquid transfer from the feed into the permeate through wetted membrane pores. This was confirmed by the observation of foam and color in the permeate tank after 120 h of the run. One important aspect that resulted from this experience is the possible contribution of sodium hydroxide cleaning to the wetting. Saponification reactions of organics with sodium hydroxide can lead to the formation of organic acids, which can cause membrane fouling. In this study, the EC and TDS values were slightly lower than expected, suggesting that only a small amount of organics were present in the permeate.

### 3.4. Performance of Standard Hydrophobic PTFE Membrane

Figure 5 shows the feed and permeate profile. The average flux over the course of this test was 12.1 L m⁻² day⁻¹. The trial was operated over 10 days, corresponding to a runtime of 240 h. Over this time, the trial suffered from membrane fouling, resulting in a 10-fold increase in permeate resistivity and a slight reduction in the permeate EC, suggesting about a six-fold increase in membrane resistance. However, the EC started rising slowly between 120 h and 160 h, indicating high-quality membrane performance. The trial was operated over 10 days, corresponding to a runtime of 240 h. Over this time, the trial suffered from membrane fouling, resulting in a 10-fold increase in permeate resistivity and a slight reduction in the permeate EC, suggesting about a six-fold increase in membrane resistance. However, the EC started rising slowly between 120 h and 160 h, indicating high-quality membrane performance. The trial was operated over 10 days, corresponding to a runtime of 240 h. Over this time, the trial suffered from membrane fouling, resulting in a 10-fold increase in permeate resistivity and a slight reduction in the permeate EC, suggesting about a six-fold increase in membrane resistance. However, the EC started rising slowly between 120 h and 160 h, indicating high-quality membrane performance.

![Figure 5. EC of the feed and permeate cycle containers while treating the textile wastewater on the hydrophobic membrane.](image-url)

Noting the rate of increase in EC, it is indicative of membrane wetting. The rapid increase in the permeate EC suggests liquid transfer from the feed into the permeate through wetted membrane pores. This was confirmed by the observation of foam and color in the permeate tank after 120 h of the run. One important aspect that resulted from this experience is the possible contribution of sodium hydroxide cleaning to the wetting. Saponification reactions of organics with sodium hydroxide can lead to the formation of organic acids, which can cause membrane fouling. In this study, the EC and TDS values were slightly lower than expected, suggesting that only a small amount of organics were present in the permeate.

The pH of the feed had a significant effect on the rate of the removal efficiency of easily ionized volatile compounds, such as ammonia [32].
One important aspect resulted from this experience is the possible contribution of sodium hydroxide cleaning to the wetting. Saponification reactions of organics with sodium hydroxide in the landfill leachate solution can lead to these phenomena. In fact, oil and greases are typically found in textiles and can react with NaOH solution. This oil could then, despite the gradual wetting observed during the run, be the main motivation for testing a membrane that contained a hydrophilic coating, in an attempt to avoid the wetting effect from surfactant by-products from membrane cleaning.

Figure 6 shows the temperature profile obtained using the standard hydrophobic membrane. The feed side “hot in” temperatures ranged between 35 °C and 60 °C, representing the temperatures available from the waste heat at this site.

Table 2 shows the water quality indicators of the retentate (concentrated waste) and permeate just before the cleaning operation. The permeate product was of good quality, where EC, nitrate and nitrite, COD, and TP all exhibited more than 98% rejections across the membrane.

A salt rejection of 98.9% based on EC was demonstrated during the majority of the run, which was expected for this membrane and system [31,32]. For rejection to be reduced by 1% (64.1%) when sent through the NaOH high temperature treatment, the feed side was held constant at 39 °C, while the feed temperature was lowered to 35 °C to reduce the high temperature in the pilot production test and to avoid increased paper pumping [33]. Tests showed that the introduction of a filter just after the hot loop HX reduced the deposition of bulk organic or colloidal matter on the membrane much like it improved water recovery, achieved via removing the calcium hydroxide in the solution are a possible reason, as these lead to surfactants, which lead to membrane wetting. In fact, oil and greases are typically found in textiles and can react with NaOH solution. This oil could then, despite the gradual wetting observed during the run, be the main motivation for testing a membrane that contained a hydrophilic coating, in an attempt to avoid the wetting effect from surfactant by-products from membrane cleaning.

Figure 6 shows the temperature profile obtained using the standard hydrophobic membrane.
of negatively soluble salts, such as calcium salts, via scaling [34]. Tests showed that the introduction of a filter just after the hot loop HX reduced the deposition of bulk organic or colloidal matter on the membrane much like it improved water recovery, achieved via removing the calcium sulfate which accumulated on the membrane in previous operation [24]. Visual observation of the membrane or the membrane fouling will be shown later in this section.

The salt rejection of almost 99% estimated from EC meant that the permeate produced was even lower in salts than normal tap water determinate at 100 µS·cm$^{-1}$. A COD rejection of 98% indicated high level of rejection of organic matter in the feed. TN, NO$_3^-$, NO$_2^-$, and TP had a high level of removal (over 97%). The lower (64%) rejection for TN when compared with that of COD or EC was potentially due to ammonia. Due to its volatile nature, ammonia can pass through the membrane as vapor and condensed on the permeate [36]. This was not extending the lifetime of the permeate EC increased. However, in this case, EC rejection remained very high, close to the nonvolatile species represented by TP, suggesting that the majority of the ammonia was in nonvolatile ammonium form (or organically bound), and remained on the feed side of the membrane. This was due to carbonate being required for it to pass through the membrane [36] which was not available in the feed wastewater.

The profile of the EC using the coated membrane for treating the textile wastewater is shown in Figure 7. After the weekend shutdown, it increased to 6 L·m$^{-2}$·h$^{-1}$, decreasing to 4.8 L·m$^{-2}$·h$^{-1}$ before cleaning, and then increased to 5.2 L·m$^{-2}$·h$^{-1}$ after cleaning. At the end of the run, flux reached 4 L·m$^{-2}$·h$^{-1}$. After the weekend, new feed effluent was added into the feed tank, which explains the sudden EC drop. A different trend of rising EC was observed on the feed side. Initially, in the first 25 h of operation, the EC increased significantly at a

Figure 7. Image of hydrophobic PTFE membrane after treatment of textile wastewater.

3.5. Performance of Hydrophilic-Coated Hydrophobic PTFE Membrane

The profile of the EC using the coated membrane for treating the textile wastewater is shown in Figure 8. This trial was operated over seven days, corresponding to a total runtime of 106 h. Over the first 28 operating hours, the feed was concentrated from 4 mS·cm$^{-1}$ to around 7.5 mS·cm$^{-1}$, suggesting about a two-fold concentration ratio. Flux at 20 h was 5.2 L·m$^{-2}$·h$^{-1}$. After the weekend shutdown, it increased to 6 L·m$^{-2}$·h$^{-1}$, decreasing to 4.8 L·m$^{-2}$·h$^{-1}$ before cleaning, and then increased to 5.2 L·m$^{-2}$·h$^{-1}$ after cleaning. At the end of the run, flux reached 4 L·m$^{-2}$·h$^{-1}$. After the weekend, new feed effluent was added into the feed tank, which explains the sudden EC drop. A different trend of rising EC was observed on the feed side. Initially, in the first 25 h of operation, the EC increased significantly at a
The hydrophobic PTFE membrane showed higher average fluxes (~12 L·m⁻²·h⁻¹) than the coated PTFE membrane (~5 L·m⁻²·h⁻¹) when processing the textile wastewater. The differences in fluxes could be due to either the coating reducing the mass transfer, thereby lowering the flux, or different features of the scrim layer inhibiting mixing on the permeate side, or the different PTFE membrane properties (pore size, porosity, or thickness). The hydrophilic-coated hydrophobic membrane varied according to these three conditions in comparison to the hydrophobic PTFE membrane, as shown in Figures 2 and 3. Optimizing the performance of this membrane for MD application is subject to further work in this study. However, this study aimed to first verify if the new membrane chemistry would resist the wetting nature of the real textile industry wastewater when treated by MD. A key difference observed here was the ongoing decline in the permeate EC, where the hydrophobic membrane only showed a declining EC in the first 30 h of operation (Figure 5), before rising EC occurred from then on, starting when the feed EC was only around 3 mS·cm⁻¹. Meanwhile, the coated PTFE membrane (~5 L·m⁻²·h⁻¹) showed a continual decline for more than 70 h of exposure to the wastewater, where feed EC peaked decreasing until it reached 20 µS·cm⁻¹, where it stabilized.

Cleaning of the coated PTFE membrane was also investigated. A sodium hydroxide 1 wt % solution was added to the feed, simulating the cleaning of the coated PTFE membrane. The coated membrane was, therefore, able to resist the wetting experienced by the hydrophobic PTFE membrane. The coated membrane was, therefore, able to resist the wetting experienced by the hydrophobic PTFE membrane.

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Figure 8. EC of the feed and permeate cycle containers while treating the textile wastewater on the hydrophilic-coated hydrophobic PTFE membrane.

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Cleaning of the coated PTFE membrane was also investigated. A typical hydrophobic hydrophilic PTFE membrane was employed, where cleaning was carried out prior to treatment of textile wastewater. The feed EC rose and fell, as shown in Figure 8 between 73 h and 76 h, and may have been due to the stabilization of the membrane. With the coated membrane, EC was slightly lower when compared with the hydrophobic membrane, proving that although both membranes had a high salt rejection, EC was superior for operation in an effluent with a pH lower than 7. However, from the hydrophobic membrane, a slightly better binding of active particles in the cleaning process. Although the coated PTFE membrane was more robust to the hydrophobic PTFE membrane, in regular operation, and instead of the wetting effect, a strongly cleaning compromised its integrity as a salt-rejecting membrane [37]. Figure 9 shows the membrane appearance after treatment of the textile wastewater (including the cleaning operation). Some spots appeared on the surface, which were likely due to fouling from larger particles. However, the coated membrane showed no obvious wetting (transparent areas) when compared with the hydrophobic membrane (Figure 7). Regardless, sodium hydroxide cleaning affected both membranes. While this is useful in cleaning the membrane, the sodium hydroxide reaction increases the solubility of solutes by hydrolysis and solubilization [38], indicating its ability to remove some fouling with the hydrophilic membrane (Figure 7). In regard to sodium hydroxide cleaning affecting both membranes, while this is useful in cleaning the membrane, the sodium hydroxide reaction increases the solubility of solutes by hydrolysis and solubilization, which, therefore, this makes for MD applications in terms of further work on the membrane, the need for water treatment and membrane selection becomes more necessary. Cleaning of the coated PTFE membrane was also investigated. A typical hydrophobic hydrophilic PTFE membrane was employed, where cleaning was carried out prior to treatment of textile wastewater. The feed EC rose and fell, as shown in Figure 8 between 73 h and 76 h, and may have been due to the stabilization of the membrane. With the coated membrane, EC was slightly lower when compared with the hydrophobic membrane, proving that although both membranes had a high salt rejection, EC was superior for operation in an effluent with a pH lower than 7. However, from the hydrophobic membrane, a slightly better binding of active particles in the cleaning process. Although the coated PTFE membrane was more robust to the hydrophobic PTFE membrane, in regular operation, and instead of the wetting effect, a strongly cleaning compromised its integrity as a salt-rejecting membrane [37]. Figure 9 shows the membrane appearance after treatment of the textile wastewater (including the cleaning operation). Some spots appeared on the surface, which were likely due to fouling from larger particles. However, the coated membrane showed no obvious wetting (transparent areas) when compared with the hydrophobic membrane (Figure 7). Regardless, sodium hydroxide cleaning affected both membranes. While this is useful in cleaning the membrane, the sodium hydroxide reaction increases the solubility of solutes by hydrolysis and solubilization [38], indicating its ability to remove some fouling with the hydrophilic membrane (Figure 7). In regard to sodium hydroxide cleaning affecting both membranes, while this is useful in cleaning the membrane, the sodium hydroxide reaction increases the solubility of solutes by hydrolysis and solubilization, which, therefore, this makes for MD applications in terms of further work on the membrane, the need for water treatment and membrane selection becomes more necessary. Cleaning of the coated PTFE membrane was also investigated. A typical hydrophobic hydrophilic PTFE membrane was employed, where cleaning was carried out prior to treatment of textile wastewater. The feed EC rose and fell, as shown in Figure 8 between 73 h and 76 h, and may have been due to the stabilization of the membrane. With the coated membrane, EC was slightly lower when compared with the hydrophobic membrane, proving that although both membranes had a high salt rejection, EC was superior for operation in an effluent with a pH lower than 7. However, from the hydrophobic membrane, a slightly better binding of active particles in the cleaning process. Although the coated PTFE membrane was more robust to the hydrophobic PTFE membrane, in regular operation, and instead of the wetting effect, a strongly cleaning compromised its integrity as a salt-rejecting membrane [37]. Figure 9 shows the membrane appearance after treatment of the textile wastewater (including the cleaning operation). Some spots appeared on the surface, which were likely due to fouling from larger particles. However, the coated membrane showed no obvious wetting (transparent areas) when compared with the hydrophobic membrane (Figure 7). Regardless, sodium hydroxide cleaning affected both membranes. While this is useful in cleaning the membrane, the sodium hydroxide reaction increases the solubility of solutes by hydrolysis and solubilization [38], indicating its ability to remove some fouling with the hydrophilic membrane (Figure 7). In regard to sodium hydroxide cleaning affecting both membranes, while this is useful in cleaning the membrane, the sodium hydroxide reaction increases the solubility of solutes by hydrolysis and solubilization, which, therefore, this makes for MD applications in terms of further work on the membrane, the need for water treatment and membrane selection becomes more necessary.

Table 3. Retentate and permeate quality of the hydrophilic-coated hydrophobic PTFE membrane.

| Parameter | Retentate (before Cleaning) | Permeate (before Cleaning) | Rejection (%) |
|-----------|-----------------------------|-----------------------------|---------------|
| pH        | 6.21                        | 6.21                        | 97.8          |
| EC (µS cm⁻¹) | 2300                       | 11.97                       | 99.5          |
| TDS (mg L⁻¹) | 3650                       | 19                           | 99.5          |
| TN (mg L⁻¹) | >18                        | 13.5                         | 25            |
| NO₃⁻ (mg L⁻¹) | 0.749                      | 0.025                        | 96.7          |
| NO₂⁻ (mg L⁻¹) | 1                          | 0.4                          | 60            |
| NH₄⁺ (mg L⁻¹) | 1                           | 0.4                          | 60            |
| COD (mg L⁻¹) | 4335                       | 284                          | 93.4          |
| TP (mg L⁻¹) | 15.2                        | 0.5                          | 96.7          |

Figure 9. Image of the hydrophilic-coated hydrophobic PTFE membrane after testing with textile wastewater.
The coated membrane’s anti-wetting performance under conventional operation was demonstrated, but further developments in cleaning methods are needed for its sustainable operation. Ammonia transport into the permeate, which can influence EC measurement even on intact membranes, was ruled out, as the permeate started visibly foaming. Furthermore, observation of the membrane removed from the rig showed transparent spots on the surface, identifying wetted areas. The coated PTFE membrane, on the other hand, exhibited superior wetting resistance. However, both membranes showed a rising EC after cleaning with 1 wt % NaOH solution at room temperature, which was attributed to wetting of the membranes. The coated membrane’s anti-wetting performance under conventional operation was demonstrated, but further developments in cleaning methods are needed for its sustainable operation.

### Table 3. Retentate and permeate quality of the hydrophilic-coated hydrophobic PTFE membrane.

| Parameter | Retentate (before Cleaning) | Permeate (before Cleaning) | Rejection (%) |
|-----------|-----------------------------|-----------------------------|---------------|
| pH        | 6.21                        | 7.86                        | -             |
| EC (µS·cm⁻¹) | 3650                      | 19                          | 99.5          |
| TDS (mg·L⁻¹)  | 2300                       | 11.97                       | 99.5          |
| TN (mg·L⁻¹)    | 42                         | 0.9                         | 97.8          |
| NO₃⁻ (mg·L⁻¹)  | >18                        | 13.5                        | 25            |
| NO₂⁻ (mg·L⁻¹)  | 0.749                      | 0.025                       | 96.7          |
| NH₄⁺ (mg·L⁻¹)   | 1                          | 0.4                         | 60            |
| COD (mg·L⁻¹)   | 4335                       | 284                         | 93.4          |
| TP (mg·L⁻¹)     | 15.2                       | 0.5                         | 96.7          |

Figure 10 summarizes the wetting phenomenon on both membranes.

4. Conclusions

This study aimed to compare standard hydrophobic PTFE membranes used for MD with a novel hydrophilic-coated PTFE membrane material for the treatment of textile industry wastewater. Hydrophilic-coated PTFE membrane material for the treatment of textile industry wastewater. Uniquely in this work, the approach of the trial was the treatment of effluent directly from the plant, for a future vision of intensified membrane processing of wastewater when compared with the current use of biological treatments. Therefore, wetting from surfactants was an expected problem, which was a focus of the application of the coated PTFE membrane used. The MD process needed to demonstrate its demand for the ability to produce high-quality water suitable for plant re-use, utilizing real plant viability to produce high-quality water suitable for plant re-use, utilizing real plant temperature from available waste heat.

The standard hydrophobic PTFE membrane demonstration showed a good salt-rejection rate of around 99%. However, gradual wetting was observed, indicated by a rise in EC after 30 h of operation. Ammonia transport into the permeate, which can influence EC measurement even on intact membranes, was ruled out, as the permeate started visibly foaming. Furthermore, observation of the membrane removed from the rig showed transparent spots on the surface, identifying wetted areas. The coated PTFE membrane, on the other hand, exhibited superior wetting resistance. However, both membranes showed a rising EC after cleaning with 1 wt % NaOH solution at room temperature, which was attributed to wetting of the membranes. The coated membrane’s anti-wetting performance under conventional operation was demonstrated, but further developments in cleaning methods are needed for its sustainable operation.

### Author Contributions

J.V.G. performed the experiments and the data analysis. N.D. conducted the SEM analysis, and collaborated with the experiments and the data analysis. N.M. and J.Z. provided expert input into the revision of the article. L.N. provided resources and expertise at the textile plant trial location. S.G. and D.P. supervised the study, and provided scientific discussion. All the authors contributed to the writing and revision of the article.

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