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Case Report

Wetting challenges in treatment of raw textile wastewater by membrane distillation: A case study

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ABSTRACT

This case study investigated the effectiveness of Direct Contact Membrane Distillation (DCMD) in treating real textile wastewater. Textile wastewater treatment presents a critical challenge in the field of environmental sustainability, requiring innovative approaches for its treatment to mitigate adverse impacts on ecosystems. DCMD emerges as a promising solution for the treatment and reuse of textile wastewater. However, the intricate composition of real textile wastewater represents a major bottleneck for the process, as the effectiveness of DCMD is influenced by numerous factors, complicating its application. In this study, experiments with an untreated sample demonstrate the detrimental impact of suspended solids on membrane performance. The application of simple pretreatment steps prior to DCMD, involving sedimentation and filtration, substantially enhanced the quality of the permeate, resulting in 100 % color removal, 99.99 % turbidity removal, and considerable removal rates for Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC). Nevertheless, wetting remained a significant issue, as evidenced by the persistence of commonly used volatile organic contaminants and surfactants in the textile industry detected within the permeate. The findings in this case study reinforce that DCMD holds promise for textile wastewater treatment but emphasize the necessity of pretreatment and wetting mitigation strategies to fully unlock its potential. This research offers crucial insights for future MD applications in addressing the complexities of textile wastewater treatment.

1. Introduction

The textile industry, while fulfilling one of the most basic demands in our society, represents a significant environmental risk due to its water-intensive processes and the discharge of pollutants into water bodies. According to the European Environment Agency (EEA), dyeing and finishing treatments accounted for 20 % of global clean water pollution, with textile consumption in the EU requiring 9 m^3 of water per person in 2020 [1]. The treatment of textile wastewater is considered challenging due to the complexity of the feed composition, which includes high concentrations of dyes, chemicals, inorganic salts, total dissolved solids (TDS), chemical and biological oxygen demand (COD and BOD), turbidity, and salinity [2]. Furthermore, water reuse has become a crucial concern in industrial applications to protect natural ecosystems and comply with new environmental regulations.

Over the last decades, many techniques have been utilized to treat textile wastewater, such as coagulation/flocculation, adsorption onto activated carbon, oxidation by ozone or chlorination, and membrane separation processes [3]. Recently, membrane distillation (MD) has seen a surge in research thanks to its ability to produce high-quality effluent. MD is a non-isothermal separation technique based on the diffusive and convective transportation of vapor across a hydrophobic microporous membrane [4]. Among the different MD configurations, direct contact membrane distillation (DCMD) is most employed in practice textile wastewater treatment due to its simplicity in design and higher fluxes [5]; in this configuration, both feed and permeate solutions are in direct contact with the membrane surface and the temperature difference leads to a transmembrane vapor pressure gradient that drives mass transfer

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[5]. However, as highlighted in the recent review by Nthunya et al. [6] the economic feasibility of MD remains a key challenge due to factors such as energy consumption, membrane replacement costs, and long-term performance stability. The integration of MD with renewable energy or waste heat sources has been suggested as a potential strategy to improve cost-effectiveness. Given that textile industries release wastewater streams with temperatures up to 80 °C, DCMD can be applied to optimize energy efficiency by dismissing unnecessary, costly heating. In this process, the membrane retains components such as dyes, salts, and non-volatile organic compounds, allowing only vapor molecules to cross the hydrophobic membrane from the hot to the cold side [7,8]. Additionally, other main DCMD advantages encompass the potential recovery and reuse of dyes within the process, the treatment of hypersaline wastewater, and the lower capital expenditure due to the absence of high-pressure and high-temperature components [9,10]. Thus, this technique is considered suitable for Zero Liquid Discharge (ZLD) processes, achieving high water recovery rates and enabling further water reuse [11]. Nevertheless, DCMD performance faces relevant drawbacks that ultimately impact its cost-effectiveness due to the increase in energy consumption, maintenance, membrane damage, and decrease in process performance [12]. The two main bottlenecks are fouling and wetting; fouling entails pore blockages, decreased flux, and reduced hydrophobicity of the membranes, whereas wetting involves the passage of liquid instead of vapor through the membrane pores, thereby compromising the rejection mechanism and negatively impacting permeate quality [13,14]. Currently, Optical Coherence Tomography (OCT) is considered the state-of-the-art tool to monitor *in-situ* the membrane surface under continuous operation without the need for any staining agents [15–19]. OCT has been employed to monitor DCMD operation in real-time. Fortunato et al. [20], Elcik et al. [21], and Guo et al. [22], in studying the efficiency of MD in treating textile wastewater, linked the decrease in membrane flux to the development of fouling membranes under continuous operation [23,24]. Recent studies have claimed to be able to visualize wetting with the aid of the OCT as well [25–28].

Despite the challenges of treating textile wastewater effluent with MD, many authors succeeded in performing lab-scale experiments with excellent rejection rates, high water recovery, and TOC removal [4, 29–32]. For instance, de Sousa Silva et al. [33] obtained higher permeate fluxes and 100 % color rejection rates in the treatment of textile wastewater using a combination of Coagulation/Flocculation (CF) with DCMD. Similarly, Tolentino Filho et al. [34] studied the influence of the dye concentration from textile fibers on MD performance, reporting 98 % membrane rejection with no wetting. Several other studies have shifted their focus to membrane properties and operating conditions to enhance water recovery and dye removal efficiency [6]. However, it is worth noting that most of these studies employed synthetic wastewater and were conducted in short-term operations (under 24 hours). This paper addresses significant gaps in membrane distillation (MD) studies for textile wastewater treatment.

Our research aims to underscore the importance of considering the authentic characteristics of real wastewater effluents in direct contact membrane distillation studies. In this case study, we evaluated the effectiveness of DCMD treatment on raw wastewater collected from a textile factory. A comprehensive analytical approach was employed, including membrane monitoring and organic characterization of the permeate to address the effluent's complexity and identify the process's challenges. The findings from this research will provide valuable insights to guide future applications of DCMD in addressing the challenges posed by real and complex textile wastewater.

2. Materials and methods

2.1. Materials

For this work, the raw wastewater was collected from a textile leather factory in Italy. The effluent sample was collected from the equalization tank and stored at 4 °C. Table 1 compares the wastewater characteristics with the typical range parameters found in the literature [29,35]. Methyl orange (MO, dye content 85 %) from Sigma-Aldrich (Lot MKCD5974) was added to the raw wastewater at a concentration of 10 mg/L; MO ($C_{14}H_{14}N_3NaO_3S$) is an azo dye commonly used in the textile industry [36].

MO was added to assess the efficiency of the color removal and enable comparison with results from previous studies conducted under similar conditions. For the pretreatment experiment, the textile wastewater was left to sediment for 2 days. Afterwards, the supernatant was transferred to another container and filtered with a Büchner funnel and an 11 μm pore size filter (Whatman No. 1 Filter Paper, 1001–055).

2.2. DCMD experiments

The DCMD experiments were conducted using a lab-scale batch setup (Fig. 1). The system consisted of a DCMD membrane cell (effective membrane area of 33 cm^2) customized to enable OCT *in-situ* monitoring, a 2L feed tank containing textile wastewater, and a permeate tank filled with 0.8 L MilliQ water. The polytetrafluoroethylene (PTFE) membrane was purchased from Aquastill (The Netherlands). The hydrophobic PTFE membrane presented a thickness of 77 μm, 0.17 μm pore size, 83 % porosity, and a contact angle of 120° measured from experiments. The permeate and feed were circulated counter-current by two gear pumps (EW-07002-25, Cole-Parmer, USA). The temperatures were constantly maintained by heat exchangers (CORIO CD-600F Refrigerated/heating circulator, Julabo, Germany) and controlled by the temperature sensors integrated with conductivity meters (TetraCon 325, Xylem Analytics, Germany). The conductivity meters, were installed at the inlet and outlet of feed and permeate flow cells, to allow the simultaneous assessment of the feed concentration factor and the wetting rate in the permeate. Cross-flow velocity and outlet temperature were measured by digital cross-flow meters (mini CORI-FLOW™ M15, Bronkhorst, Netherlands) placed near the flow cell.

The experiments were conducted at a feed temperature of 50 °C, a feed flow rate of 25 L/h, and cross-flow velocity of 0.21 m/s. The permeate temperature was 20 °C, the flow rate was set at 16 L/h, and the cross-flow velocity was 0.13 m/s. The experimental conditions, including water flow rate and temperature, were carefully selected based on insights gained from previous studies [20,23,24]. Three feed spacers, in addition to a permeate spacer, were kept on the permeate chamber in the membrane cell to allow permeate flux and maintain a flat membrane. The mass change of the produced permeate was recorded every minute using a Sartorius electronic balance (PRACTUM 6101-1S). The instruments were connected to a computer and controlled by Lab View software.

The permeate flux J (L/m^2•h, LMH) was calculated using Equation (1):

Table 1
Comparison of sample from this study and average textile wastewater characteristics.

Parameter	Unit	Sample	Typical range[a]
COD	mg/L	3254 ± 505	50–5000
TOC	mg/L	1517 ± 261	49–390
pH	–	3.33	2–12.3
TSS	mg/L	470	15–8000
TDS	mg/L	3858	1500–10160
Turbidity	NTU	563	9.4–450.0
Temperature	°C	–	28.9–80
Conductivity	μS/cm	5197 ± 1717	57–92200

[a] Modified from Mokhtar et al. [29], and de Araújo et al. [35], Bidu et al. [37] Wang et al. [38].

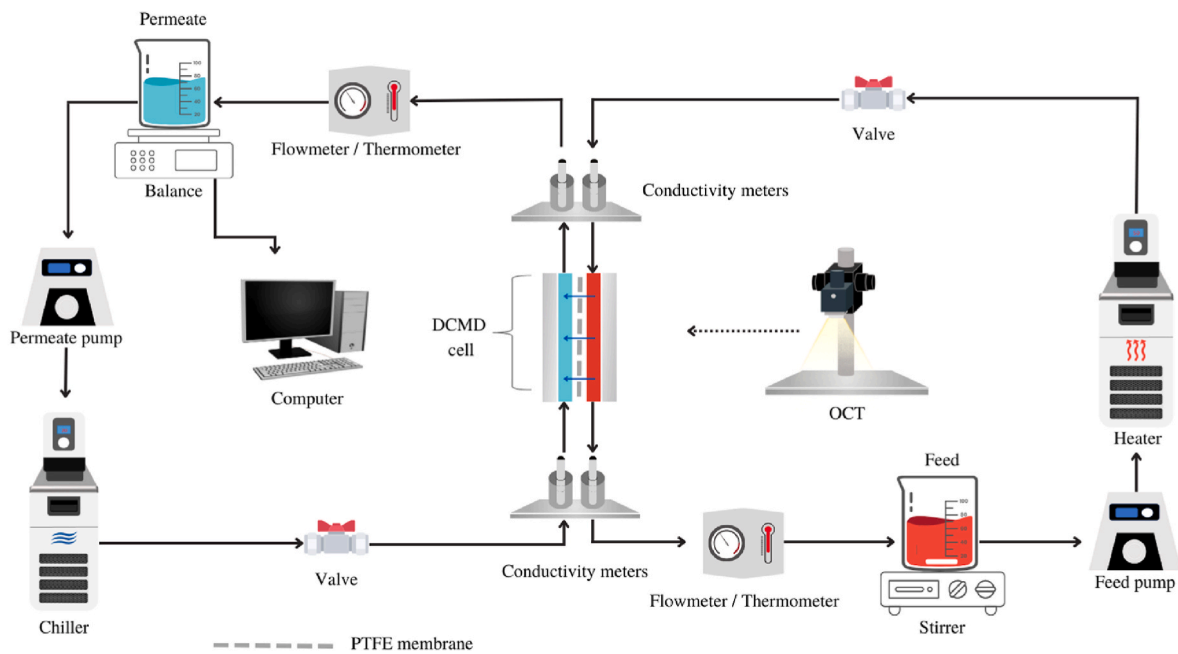

Fig. 1. DCMD experimental setup.

$$J = \frac{\triangle W}{\triangle t \cdot A} \quad (1)$$

Where $\triangle W$ is the change in permeate volume (L), $\triangle t$ is the permeate collection time (h), and A is the effective area of the membrane (m^2).

An optical coherence tomography (OCT) imaging was carried out using the GANYMEDE–II–SP2 (Thorlabs GmbH, Germany) to investigate fouling and wetting in real time. The OCT was equipped with the objective lens LSM03-BB (Thorlabs GmbH, Germany). An A-scan averaging of 3 was used for the acquisition of 2D OCT datasets, parallel to the flow direction. The scans were acquired every 15 min at a fixed position (middle of the cell), to monitor the fouling development during the entire operation. Two-dimensional (2D) OCT scans had a resolution of 3319 × 1024 pixels, corresponding to 6.64 mm × 2.20 mm (width × depth). The 2D OCT scans were imported in ImageJ (FiJi software). The original scans were cropped, and the brightness and contrast were adjusted.

2.3. Feed and permeate characterization

Total suspended solids (TSS) were measured by filtering 100 mL of the raw wastewater through a 47 mm pre-weighed glass filter (ProWeigh filter, Lot 94404220182R2). Total dissolved solids (TDS) were measured by filtering 20 mL of feed sample through a glass fiber filter disc and drying the filtered solvent at 180 °C in a pre-weighed evaporating dish. The sample was then cooled and the mass of residues left was weighed. TDS and TSS analyses were performed in triplicate to guarantee the accuracy of the results. Chemical Oxygen Demand (COD) was determined using Hach kits (TNT 822, USA). For Total Organic Carbon (TOC), feed and permeate samples were diluted and filtered through a 0.45 μm pore-sized syringe filter before being analyzed by the Total Organic Carbon Analyzer (TOC-LCSH, Shimadzu). Turbidity was measured using a turbidity meter (Micro 100 Turbidimeter, HF Scientific, USA). The absorbance spectra of the wastewater (feed and permeate) samples were evaluated by UV–vis spectrophotometer (UV-1900i, SHIMADZU), with a 1 cm path length quartz cell. The spectra were recorded from 190 to 1100 nm, and the wavelength with the maximum absorbance was noted. The color removal efficiency was calculated using the following formula:

$$\text{Color removal (\%)} = \frac{(A1 - A2)}{A1} \times 100 \quad (2)$$

Where A1 is the absorbance of the untreated wastewater sample with added MO, and A2 is the absorbance of the permeate.

Feed recovery efficiency was calculated by dividing the volume of the collected permeate (Vp in L) by the volume of the treated feed solution (Vf in L), as in the following expression:

$$\text{Feed recovery (\%)} = \frac{Vp}{Vf} \times 100 \quad (3)$$

The permeate was analyzed using an Agilent GC7890A gas chromatography (GC) coupled with an MS5975c mass spectrometry (MS) system. Liquid-liquid extraction was employed for sample preparation, with 1 mL of Methyl *Tert*-Butyl Ether (MTBE) and 1 g of sodium chloride (NaCl) added to 3 mL of the sample to enhance phase separation. Compounds isolation was achieved using a DB-WAX column.

During GC analysis, Helium was used as the carrier gas, with an inlet temperature of 250 °C and an injection volume of 1 μl. The oven temperature followed a programmed sequence, starting at 50 °C for 1 minute, increasing at a rate of 10 °C/min to 240 °C, and maintaining at 240 °C for 14 minutes. Mass spectrometer parameters included a Quad temperature of 150 °C, an MS source temperature of 230 °C, and a scan range from 35 to 500. Compound identification relied on the NIST 20 (2020) mass spectral library.

3. Results and discussion

3.1. Textile wastewater characterization

In the last years, MD has been proposed as an emerging treatment strategy for textile wastewater, gaining increased attention [39]. However, nearly 90 % of the MD studies regarding the treatment of textile wastewater published in the literature, focus on the use of synthetic solutions, often representing only one step of the textile process (dyeing). It should be noted that it is very challenging to recreate the complexity of these wastewaters in lab studies by using synthetic recipes that usually consist only of a simple mixture of dyes and salts to water [3,9,20,29,30,40]. Moreover, those recipes do not include organic solvents or surfactants, which are considered a major issue in terms of membrane rejection and wetting. Our research thoroughly highlights this critical aspect, underscoring the importance of considering the real wastewater effluent's characteristics. For instance, referring to Table 1, the characterization of the wastewater used for this case study is compared with the range of industrial values reported in the literature [29,35]. The untreated raw textile wastewater was characterized by high concentration of organic content, TOC of 3254 mg/L and COD of 1517 mg/L, turbidity of 563 NTU, pH of 3.33, TSS of 470 mg/L and 3857 mg/L. Another major gap identified in the literature is represented by the length of the experiments. Specifically, only few studies conducted long term experiments (ranging from 2.5 to 48 h) in untreated wastewater (Dow et al. [13], Mokhtar et al. [29], and Li F et al. [31]). Therefore, this case-study aims to assess the performance of MD in treating real wastewater to comprehensively evaluate the efficiency of this technology.

3.2. Treating raw wastewater in DCMD

To begin the investigation and understand the behavior of real textile wastewater, an experiment was carried out with an untreated textile wastewater sample in a DCMD unit, under the operating conditions reported in Section 2.2.1. Permeate flux and conductivity were monitored over time while simultaneously checking the membrane surface with the OCT. The OCT has been widely employed in MD studies to acquire 2D scans of the membrane surface under continuous monitoring [15,20,25]. Remarkably, in this study, starting from the beginning of the operation, it was possible to notice the presence of a cloud of particles above the membrane surface, due to the presence of solids in the micrometers size range in the feed (Fig. 2a–I). This phenomenon resulted from the high concentration of suspended solids in the untreated wastewater. To the best of our knowledge, this was never reported in previous studies that employed synthetic solutions consisting mainly of dye [20–22].

During the first hour of operation, a stable permeate flux of approximatively 11 LMH was registered. Despite the stable permeate flux, the conductivity steadily increased over time at a rate of approximately 1 μS/cm*min within the first 2 h of operation. Afterwards, membrane fouling was noticeable, with the formation of a 120 μm thick fouling layer on the membrane surface (Fig. 2a–II). Suddenly, around 3:30 h of the process, the membrane started moving, and visibility was lost in the OCT (Fig. 2a–IV). This event occurred simultaneously with a considerable spike in flux (up to 121 LMH) and conductivity (up to 972 μS/cm) of the permeate, as depicted in Fig. 2 b. The sharp surge in flux observed in Fig. 2 can be attributed to a temporary reduction in flow resistance due to membrane wetting or degradation. The results suggested that as wetting begins, the loss of membrane hydrophobicity facilitates the passage of liquid water into the pores, temporarily increasing permeability and causing a sudden spike in flux. However, as the system adjusts to the compromised membrane, pressure decreases, leading to a subsequent drop in flux. This transition is accompanied by a steady increase in permeate conductivity, indicating the progressive transport of feed contaminants through the wetted membrane structure. This phenomenon is compatible with full wetting, when liquid transport

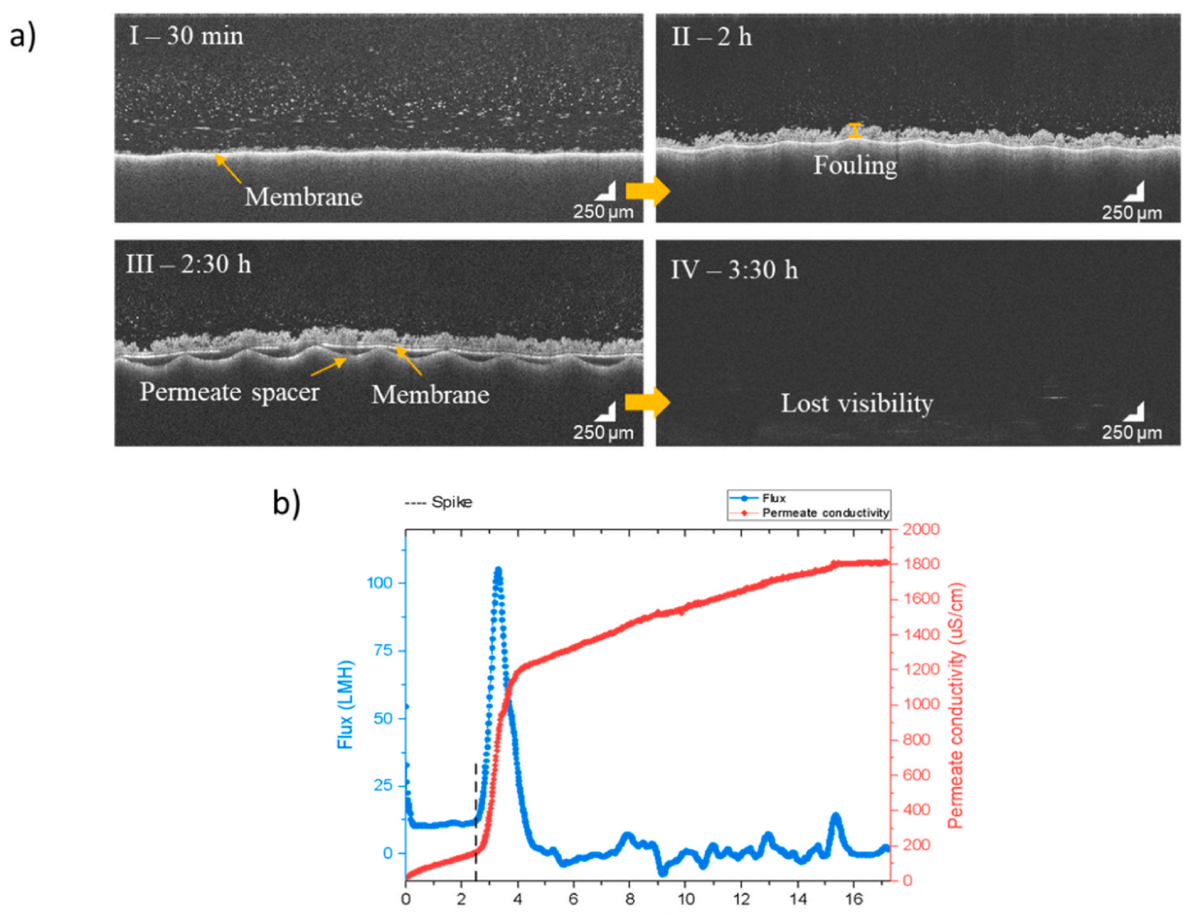

Fig. 2. (a-I) OCT images capturing a large quantity of suspended solids, which are the observable white dots floating on top of the membrane; (a-II) Fouling on the membrane due to suspended solids; (a-III) Separation between membrane and membrane spacer, likely due to sudden passage of the feed; (a-IV) Visibility is lost around 3:30 h, resulting from an erratic flux. (b) DCMD applied to pure textile wastewater showing a spike in permeate flux and conductivity due to full membrane wetting; the dotted line indicates the exact moment of the spike.

replaces vapor transport, and the hydrophobic membrane ceases to act as a barrier due to the loss of hydrophobicity [40].

In Fig. 2a–III, the hypothesis is further supported by an OCT scan acquired just before the loss of visibility. This scan shows a separation between the membrane and permeate spacer, most likely due to the sudden passage of the feed to the permeate side.

Clear evidence of the occurrence of wetting was also supported by the change in the color of the permeate along with the heavily stained membrane, indicating the passage of dye (Fig. 3). After the process, the membrane presented several stained dots scattered heterogeneously. The stains increased toward the outlet side, where they covered the membrane surface entirely, and they can also be seen on the permeate side (Fig. 3 d). The contact angle analysis performed in this experiment demonstrated that the membrane turned hydrophilic in those stained spots. Moreover, the OCT imaging analysis showed a clear difference in correspondence to the stained spots. Similar patterns on membranes were found by Bauer et al. [25] in studying the membrane wetting with the OCT. These findings suggest that the process failure can be ascribed to the high concentration of suspended solids in the wastewater, which impacted the membrane integrity, leading to a sudden increase in permeate flux and conductivity.

3.3. Suspended solids removal

For the following experiment, it was essential to remove the suspended solids from the wastewater sample to test the hypothesis that they were causing damage to the membrane. Sedimentation of the feed sample was performed, and the wastewater was filtered with an 11 μm filter. The filtered effluent was then used as feed in the DCMD setup, using the same conditions as the first experiment. As illustrated in Fig. 4, the permeate flux of 11 LMH remained stable throughout the 24 hours of operation. The conductivity rate in this experiment was 75 % lower than the first attempt, despite still presenting clear evidence of wetting. After the removal of suspended solids, no particles were observed above the surface in the OCT scans (Fig. 4 c). These OCT scans showed very little fouling compared to the first experiment, presenting a fouling layer with an average thickness of around 20 μm after 24 hours of operation. This result suggests that the thickness of the fouling layer was linked to the high concentration of suspended solids in the feed.

After the experiment, no increase in the turbidity of the permeate effluent was registered, indicating significant color rejection by the membrane, around 100 % (Table 2). Additionally, the contact angle of the DCMD membrane indicated that it retained its hydrophobic proprieties, except for a few locations at the inlet. To this extent, the contact angle analysis showed a gradient towards the membrane length, turning slightly hydrophilic (85° angle) in proximity of the inlet. The results achieved in this second experiment by pretreating the wastewater with sedimentation and filtration, corroborate the idea that the high concentration of suspended solids in the raw wastewater led to membrane mechanical disruption in the first experiment. However, despite the successful removal of the majority of the suspended solids and the avoidance of mechanical damage to the membrane, the final permeate conductivity in the second experiment was 444 μS/cm, indicating the occurrence of wetting. Indeed, the continuous increase in permeate conductivity is initially driven by membrane wetting, which compromises hydrophobicity and allows volatile compounds to pass into the permeate. Moreover, as highlighted by Hardikar et al. [41], temperature and concentration polarization can also contribute by reducing the vapor pressure driving force, further promoting volatile compound transport. In summary, removing suspended solids is crucial to prevent membrane damage and reduce fouling in DCMD processes, but it is not enough to prevent wetting.

3.4. Permeate quality and organic content

Table 2 presents quality parameters for the experiments with and without pretreatment, offering valuable insights into the effectiveness of DCMD for real textile wastewater. When pretreating the textile wastewater with sedimentation and filtration, it was possible to achieve 100 % color removal, and 99.99 % turbidity removal, enabling high feed recovery (94 %) without decline in permeate water flux. These findings highlight the most significant advantage of MD, which is the capability to attain rejection factors of almost 100 % for non-volatile solutes [32]. They also reinforce the potential of DCMD within textile wastewater

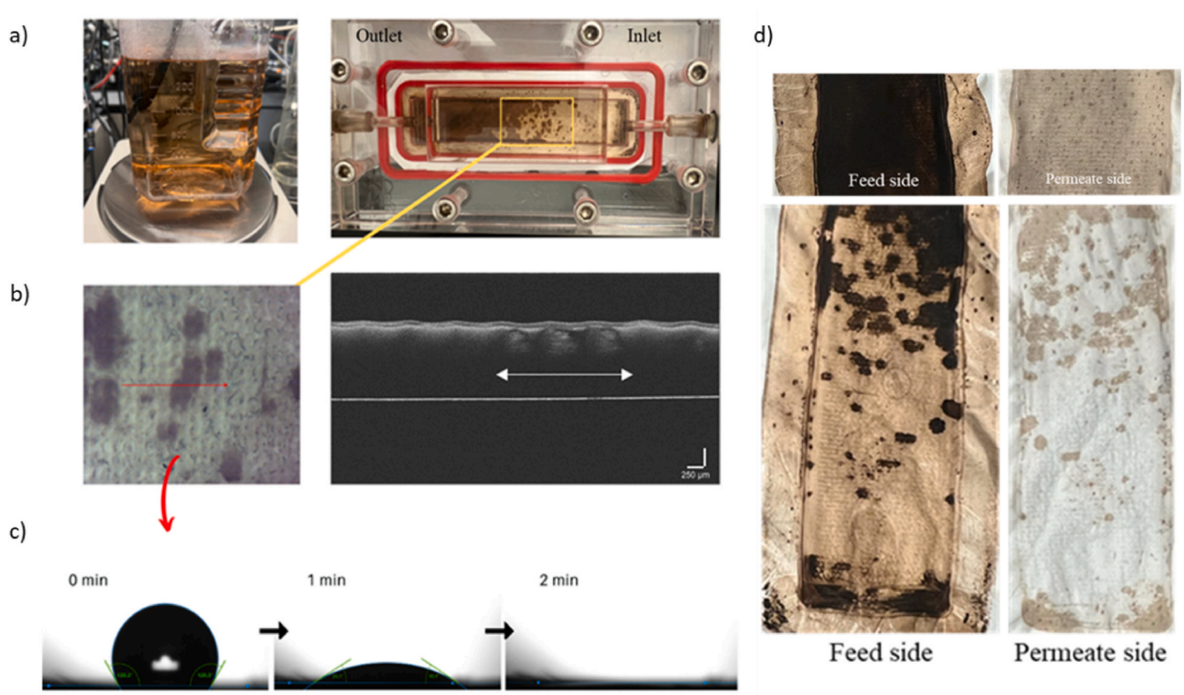

Fig. 3. Mechanism failure. a) Heavily wetted permeate and stained PTFE membrane; b) Mechanical damage to the membrane in detail; (c) Contact angle analysis: the membrane turned hydrophilic in the stained areas; d) Stains visible from the feed and permeate side of the membrane.

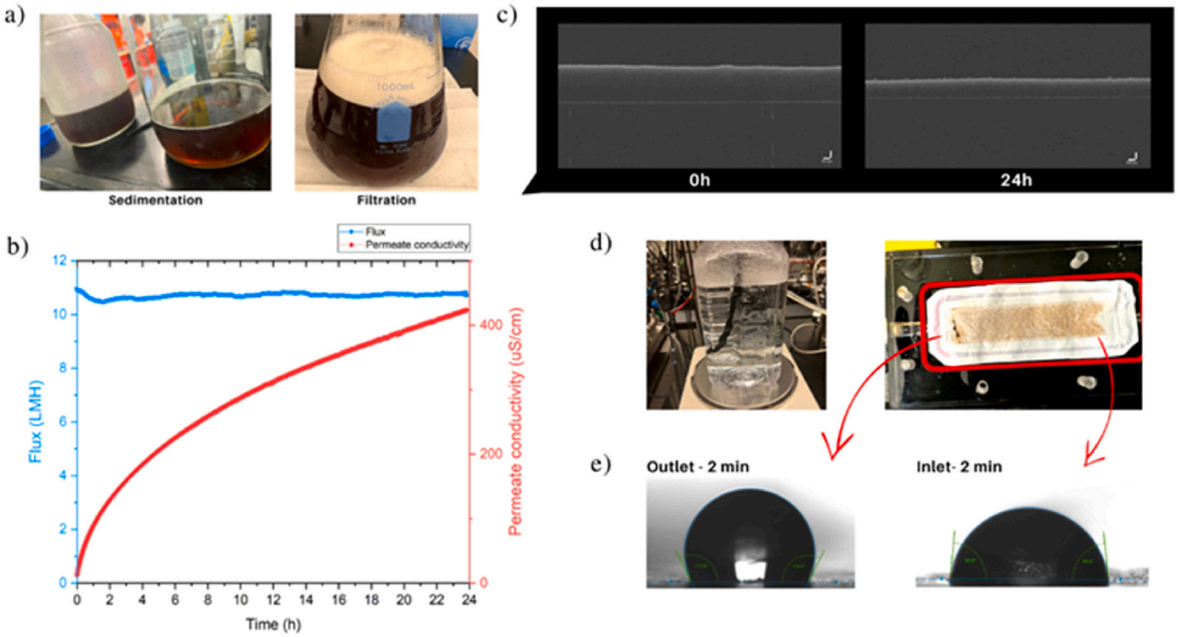

Fig. 4. a) Pretreatment to remove suspended solids; b) Stable flux and partial wetting demonstrated with increasing conductivity; c) OCT showing minimal membrane fouling after 24 h of the process; d) Clear permeate and stained PTFE membrane after the experiment; e) Membrane remained hydrophobic in the outlet but turned hydrophilic in a few spots, like the inlet.

Table 2
Quality parameters, expressed in %, for trial without pretreatment (Exp 1) and with pretreatment (Exp 2).

Quality parameters	Color removal	Turbidity removal	Feed recovery	COD removal	TOC removal
Exp 1	94	99.97	53.83	80.47	77.48
Exp 2	100	99.99	94.20	92.50	87.82

treatment and demonstrate that pretreatment plays a crucial role in improving the process.

Previously, using DCMD and PTFE membranes in real textile wastewater, Li et al. [31] achieved a 90 %–96 % COD removal and 94 %–100 % color removal in untreated and pretreated textile wastewater, respectively; Zhang et al. [42] reported 98 % feed recovery for fractionated effluent and 38 % for ozonized pretreated effluent; Shirazi et al. [32], reduced COD, color, and TDS up to 98.6 %, 99.8 %, and 99.4 %, respectively. Comparing our results with these values, it becomes

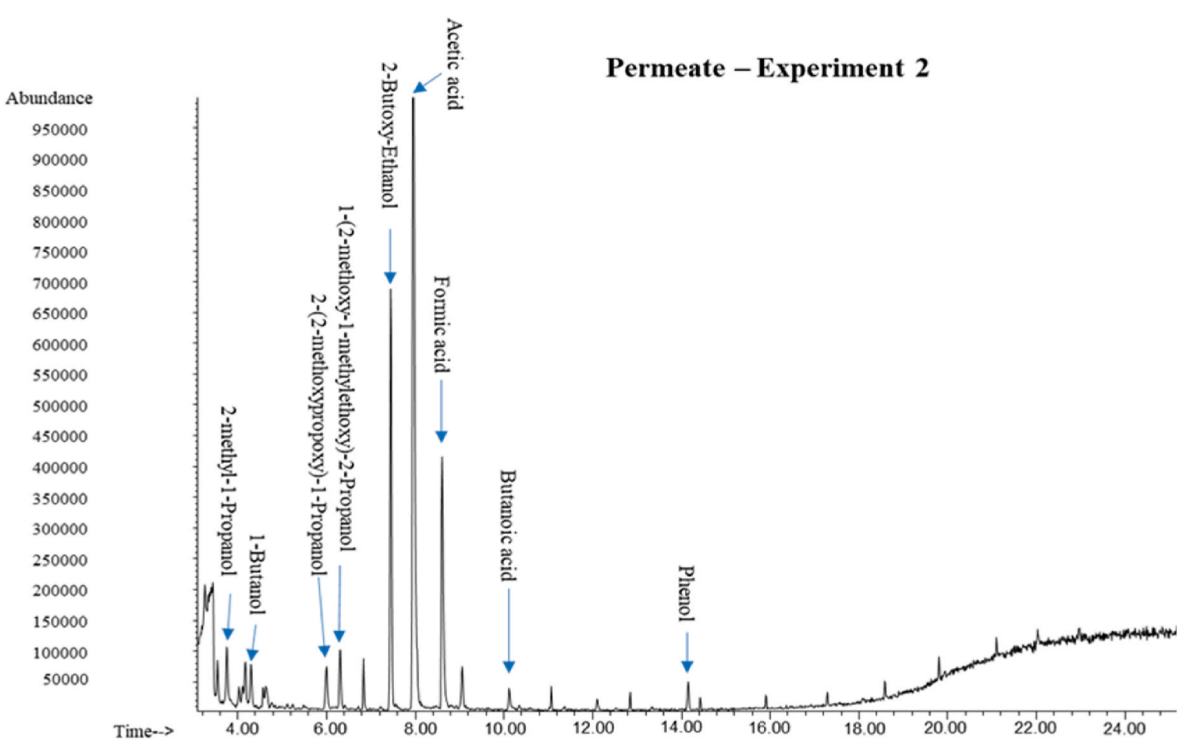

Fig. 5. Chromatogram of permeate from experiment 2 with pretreatment.

evident that our simplified pretreatment approach yields comparable results.

However, in contrast with the higher turbidity reduction, our TOC and COD removals are lower, around 87.8 % and 92.5 %, respectively. These results, combined with the steady increase in permeate conductivity, even after pretreatment, underscore the persistence of wetting during the operations. Wetting holds significant implications for this type of process, especially regarding possible water reuse and recovery. Therefore, it is necessary to gain a comprehensive understanding of the permeate's composition and its true applicability. To shed light on the intricate dynamics at play within the system and assess the specific organic compounds permeating through the membrane, a Gas Chromatography-Mass Spectrometry (GC-MS) analysis was conducted for the permeate of the second experiment (Fig. 5).

The GC-MS results indicated the presence of volatile organic compounds (VOCs), including acetic acid, formic acid, butanoic acid, 2-methyl-1-propanol, 1-butanol, phenol, as well as the surfactant 2-butoxyethanol in the sample. These compounds account for the observed lower TOC removal values and elevated conductivity, impacting the efficiency of the DMCD-based treatment system. In the realm of textile industries, these chemicals play crucial roles in enhancing color vibrancy, durability, and overall quality of the textile products (Table 3). Therefore, the wetting observed in this study is strongly influenced by the presence of specific organic compounds in the textile wastewater. The VOCs such as acetic acid, formic acid, and butanol, are small, polar molecules that due to their volatility can diffuse through the membrane in vapor form [43]. However, their accumulation in the permeate suggests that wetting has occurred, enabling the direct transport of feedwater contaminants. Additionally, nonionic surfactants, such as 2-butoxyethanol, play a crucial role in impacting the membrane's hydrophobicity by reducing surface tension and facilitating liquid entry into the membrane pores. These surface-active agents lower the liquid entry pressure (LEP) and enhance the risk of pore intrusion, leading to partial or full wetting over time [44].

Remarkably, within the scope of this case study with real textile wastewater, fouling did not appear to be a significant factor in reducing efficiency in the same way wetting did. While fouling and wetting are distinct phenomena, they can be interconnected, as certain types of fouling (e.g., organic or inorganic) may alter membrane surface properties and contribute to wetting depending on their severity [40]. However, in this study, the formation of a fouling layer on the membrane was significantly reduced by the pretreatment, and no noticeable impact on permeate flux was observed. Moreover, in MD, fouling can often be mitigated through routine cleaning and maintenance protocols, making it a more manageable and reversible issue in contrast to wetting [45]. This distinction highlights the importance of addressing both factors while emphasizing wetting as the key challenge in this case. The development of superhydrophobic, omniphobic, Janus membranes, and membranes specifically designed for VOCs removal has recently gained momentum as a promising approach to mitigate membrane wetting in MD [43,44]. While membrane modifications improve performance, they have limitations, particularly when dealing with complex feed conditions. Implementing effective pretreatment strategies to reduce VOC and surfactant concentrations before filtration could be key to enhancing membrane longevity and overall efficiency in MD systems. In light of this, and based on the present case study, wetting emerges as the major bottleneck in this type of process, posing a significant threat to the efficiency of textile water treatment with Direct Contact Membrane Distillation (DCMD). Future research should prioritize a thorough exploration of the wetting problem, aiming to understand the mechanisms and specific constituents responsible for inducing it. In particular, further studies should investigate the interplay between operating conditions (such as temperature, flow rate, and transmembrane pressure) and wastewater composition, including the concentration of volatile organic compounds and surfactants. Ultimately, it is necessary to evaluate alternative pretreatment techniques to enhance MD operation, and ensure high-quality permeate production in textile wastewater treatment.

Table 3
Organic compounds found in the DCMD permeate and their use in the textile process.

Chemical	Use
Acetic acid and Formic Acid	Enhancing color Promoting dye solubility, penetration, and fixation Increasing the color fastness Removing natural fats and greases through saponification before tanning.
Butyric acid	Deliming hides during the leather tanning process.
2-methyl-1-propanol	Serving as an emulsifying agent for textile specialties.
2-butoxy ethanol	Acting as a leather protector.
Phenol and derivatives	Used in the (re)tanning of leathers as aromatic syntans.
1-butanol	Utilized in dye-containing formulations.

4. Conclusions

This case study aimed to investigate the behavior of real textile wastewater in DCMD treatment. The raw wastewater used in this study had high organic content, turbidity, acidity, and suspended solids, which led to mechanism failure in the trial performed without pretreatment. In this case, full wetting was attributed to mechanical damage to the membrane caused by the high concentration of suspended solids. Subsequently, the combination of sedimentation followed by filtration as pretreatment achieved 100 % color removal, 99.99 % turbidity removal, 94.20 % feed recovery, 92.50 % COD removal, and 87.82 % TOC removal. However, despite pretreatment's crucial role in reducing its extent, the wetting issue persisted during the operation. A GC-MS analysis of the permeate revealed the presence of volatile organic contaminants and a surfactant. This shifts the focus from fouling, as suggested in previous studies, to wetting as the primary operational obstacle for treating this type of effluent. To address this concern, future research should prioritize a comprehensive examination of wetting in DCMD treatment of textile wastewater to identify the ideal procedure for obtaining reusable permeate.

CRediT authorship contribution statement

Mariana E. Rodrigues: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Raffaele Cucciniello:** Investigation. **Andreia Farinha:** Methodology, Investigation. **Johannes Vrouwenvelder:** Writing – review & editing, Supervision, Resources, Investigation. **Luca Fortunato:** Writing – review & editing, Supervision, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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