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Performance and applicability limits of membrane distillation for real textile industry wastewaters

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ABSTRACT

Membrane distillation (MD) has emerged as a promising approach for the reuse of textile wastewaters, due to its tolerance to high salinity, temperature, and pH. However, its application to real effluents remains uncertain. This study critically assesses MD performance using two real textile wastewaters from cotton fabric dyeing (DYE) and polyester fiber alkaline deweighting (DEW) processes, both characterized by low surface tension (39 and 24 mN m^{-1}, respectively) compared to that of pure water (72.7 mN $m^{-1)}$. Direct contact MD experiments on untreated wastewaters showed early loss of permeate quality occurring at ~30% recovery for DYE and ~ 7% for DEW, indicating rapid membrane wetting. Among several tested pre-treatment options, only adsorption on activated carbon restored surface tension to values comparable to pure water. The adsorption pre-treatment delayed the onset of membrane wetting to 50–60% recovery for DYE and 40–50% for DEW, and improved distillate quality, but did not fully prevent MD performance deterioration. Operation under vacuum conditions increased fluxes by more than twofold, although fouling and wetting remained the limiting factors. Preliminary cost analysis indicated operational costs between ~4.3 € m^{-3} and ~ 63.4 € m^{-3} for a reuse scheme comprising adsorption and MD, strongly dependent on recovery, adsorption demand, and energy management. Overall, the results suggest that the applicability of MD to textile wastewaters is highly dependent on wastewater characteristics and must therefore be evaluated on a case-by-case basis.

1. Introduction

Textile industry plays a central role in the global economy, producing approximately 100 billion new garments annually [1,2], with the global textile consumption projected to triple by 2050 [3]. However, textile manufacturing is also recognized as one of the most water-intensive industrial sectors, contributing to nearly 20% of the world global water use [4–6]. On a global scale, the sector is estimated to consume between 79 and 93 billion m^3 of water per year [4,7], with demand expected to increase by roughly 60% by 2030 [8]. Specific water consumption varies widely depending on the process, ranging from 60 to 400 L of water per kg of fabric produced [9,10]. Textile wastewater composition also varies considerably depending on the specific production steps involved and the raw material being processed. Nevertheless, it is generally characterized by a complex mixture containing high concentrations of colorants, organic matter, salts, surfactants, as well as auxiliary chemicals, such as detergents and softeners [5,6,11,12]. The discharge of untreated or inadequately treated textile effluents determines severe environmental impacts and poses risks to human health [7,13,14].

Conventional wastewater treatment and reuse methods often show limitations when challenged with such complex effluents [7,15,16]. For instance, physical treatments and physicochemical treatments, including ion exchange, filtration and coagulation-flocculation, typically generate secondary waste streams (e.g., toxic sludge), which are associated with further handling and disposal challenges [15,17]. Chemical treatments like oxidation (with, e.g., hydrogen peroxide, ozone), generally require high reagent consumption [7,16,18] and may lead to the formation of undesired and toxic by-products, such as absorbable organic halogens or other intermediates [9,18,19]. In addition, the efficiency of some oxidants, such as ozone, is strongly influenced by operating conditions, requiring careful control [19]. Finally,

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biological treatments, both aerobic and anaerobic, rely on microbial activity to degrade organic matter [7,18], but can be inhibited by typical characteristics of textile streams, such as the presence of recalcitrant compounds (e.g., azoic dyes), heavy metals, surfactants, salt, and by alkaline or acidic pH [13,14,20]. These limitations highlight the need for alternative or integrated treatment approaches capable of handling the complexity of textile wastewaters.

In this context, membrane distillation (MD), a thermally-driven process based on vapor pressure difference across a hydrophobic microporous membrane [21,22], has been increasingly proposed for the treatment, desalination, and reuse of textile and industrial wastewaters [14,17,23]. Key advantages of MD include: (i) 100% theoretical rejection of non-volatile solutes, including dyes, inorganic salts, and heavy metals [24,25]; (ii) ability to treat high salinity streams and streams with high or low pH [26,27]; (iii) favorable operating conditions, such as low pressure and moderate temperatures, typically in the range of 50 to 80 °C [27,28]; and (iv) potential to integrate waste heat. Given that textile effluents are often discharged at elevated temperatures, typically between 60 and 80 °C, MD is frequently considered a suitable candidate for water recovery in this sector [25,29,30], including in (near-)zero liquid discharge frameworks [5,31].

Despite this potential, the applicability of MD to textile wastewater reuse remains uncertain. Most studies reported in the literature rely on simplified synthetic solutions and focus primarily on dye removal [5,23]. Such approaches do not capture the complexity of real effluents and often overlook critical phenomena affecting MD performance, particularly membrane fouling and wetting. While fouling is mainly associated with the deposition of organic matter and dyes, wetting is strongly promoted by the presence of surfactants and auxiliary chemicals, which reduce surface tension (ST) and facilitate liquid penetration into the membrane pores [14,32,33]. As a result, the performance observed with synthetic solutions may substantially overestimate the robustness and stability of MD under realistic conditions.

The present study investigates the treatment of two real textile wastewaters originating from distinct production steps in the framework of textile production, namely, cotton fabric dyeing and polyester fiber alkaline deweighting. By explicitly accounting for the role of surface tension in promoting membrane wetting, this work aims to provide a fair assessment of MD performance under realistic operating conditions. The objective is not to demonstrate the feasibility of MD, but to critically evaluate its limitations, and assess whether pre-treatment strategies can effectively mitigate process constraints. To this end, MD performance is first evaluated on untreated wastewaters, highlighting the extent and onset of membrane wetting. Subsequently, a wide range of pre-treatment strategies, i.e., ultrafiltration, nanofiltration, catalytic oxidation, adsorption, is investigated, with a particular focus on their ability to restore surface tension and improve MD process stability. The effect of adsorption on activated carbon is further analyzed through adsorption isotherms and its impact on MD operation is assessed in both direct contact and vacuum configurations. Finally, the implications of the observed limitations are discussed in terms of achievable recovery and preliminary operational costs, with the aim of linking fundamental mechanisms to practical feasibility. In doing so, the study aims to help define the practical boundaries of MD applicability for textile wastewater reuse and to support a more realistic appraisal of its role in industrial water management.

2. Materials and methods

2.1. Textile wastewaters

The wastewaters investigated in this study were supplied by INOTEX spol. s r.o. (Czech Republic), and originated from two distinct production steps of textile manufacturing, namely, cotton fabric dyeing and polyester fibers alkaline deweighting. These two streams were selected to represent typical textile effluents with different challenges in terms of composition and treatment. In conventional wastewater management at textile facilities, spent process baths are typically combined with wastewater from subsequent washing steps, resulting in partial dilution of the contaminants. In this study, instead, samples were collected directly from the exhausted treatment baths before dilution. This approach represents a more challenging treatment scenario, but allows the intrinsic characteristics of each process stream to be assessed separately and supports the development of stream-specific treatment strategies rather than relying on dilution within mixed wastewater flows.

Note that fabric dyeing is one of the most water-intensive and polluting stages of textile production, accounting for more than 50% of the total wastewater produced in the textile industry [8]. The dyeing process generally involves several operations, such as fabric preparation, dye application, rinsing, washing, and drying [34,35]. Along large volumes of input water, a wide variety of chemical additives are typically used in this context, such as salts, surfactants, and other agents promoting dye uptake [36–38]. As a result, the generated dyeing wastewater (DYE) is characterized by elevated salinity, residual color, alkalinity, and high concentrations of organic matter. The salinity and relatively high pH levels, along with the possible presence of recalcitrant dye, which may impair the use of conventional biological processes, make MD an interesting solution for effluent treatment.

Polyester fibers alkaline deweighting is instead a chemical treatment that allows the modification of the fibers surface, improving their softness, fabric feel, and drapability. This process is generally carried out under strongly alkaline conditions and elevated temperature, up to 130 °C. In the alkaline deweighting process, the outer polymer layer is partially dissolved, and low-molecular-weight organic compounds are released into the process water [39,40]. The wastewater generated in the operation, herein referred to as “DEW”, is therefore characterized by a highly alkaline pH (~12), a substantial organic load, and relatively high salinity. Similarly to dyeing wastewater, such characteristics render the stream from deweighting operations particularly challenging for conventional wastewater treatment technologies, while potentially well suited for MD.

2.2. Characteristics of the wastewater samples

Both wastewater samples were characterized by means of measurements of total organic content (TOC, TOC-LDSH FA, E200, Shimadzu, Milan, Italian branch), pH (pH 70 Vio, XS, Italy), electrical conductivity (COND 70 VIO, XS, Italy), and surface tension (Sigma 700, Biolin Scientific, Sweden). Surface tension was used as a proxy of surfactants concentration and, in general, as an indication of MD feasibility. Surface tension measurements were carried out with a platinum Du Nouy ring. Before each measurement session, the instrument calibration was checked according to the manufacturer's instructions. During the measurement, the ring was immersed into the wastewater sample, placed in a 50 mL glass vessel and maintained at a temperature of 20 ± 1 °C. The ring was then slowly lifted upward through the liquid-air interface. The force required to pull the ring free from the surface was directly converted by the instrument into the corresponding surface tension value. Ten measurements of the same sample were carried out consecutively, and the mean value is reported. Between different measurements, the platinum ring was thoroughly rinsed with deionized water and briefly passed through a Bunsen burner flame to remove any residual contaminants and avoid cross-contamination. No pre-treatment was performed before measuring the surface tension of the raw wastewater. For GAC-, PAC-, and photocatalysis-treated samples, filtration through a 0.45 μm cellulose acetate filter was performed prior to surface tension measurement to remove residual suspended particles (activated carbon or photocatalyst) that could interfere with the measurement. No additional treatment was required for UF and NF permeates, as the membrane pore size was already smaller than 0.45 μm. The main characteristics of the effluents are summarized in Table 1.

Table 1
Main characteristics of the tested textile wastewaters.

Parameter	Wastewater	
	Dyeing (DYE)	Deweighting (DEW)
pH	11.1 ± 0.1	12.8 ± 0.1
Electrical conductivity (EC, mS cm^{-1})	60.0 ± 0.2	32.0 ± 0.2
Total organic carbon (TOC, mg L^{-1})	300 ± 15	4500 ± 50
Surface tension (mN m^{-1})	39.0 ± 1.5	24.0 ± 1.2

2.3. Pre-treatment strategies

2.3.1. Adsorption on activated carbon

Granular activated carbon (GAC) and powdered activated carbon (PAC) adsorption were evaluated as pre-treatment options for the removal of surface tension-reducing compounds from the investigated textile wastewaters. Batch adsorption tests were conducted on both DYE and DEW wastewaters. Changes in surface tension were used as an operational proxy for the removal of surface-active compounds. For each wastewater, GAC and PAC were added separately at dosages within the range 0–25 g L^{-1} into a 50 mL of sample in sealed glass vessels, and continuously mixed with a magnetic stirrer for 24 h. Then, the samples (from both GAC and PAC tests) were filtered through 0.45 μm cellulose acetate filters (GVS, Italy), and the surface tension was measured. Organosorb 10 GAC was used for adsorption tests. The material has a particle size distribution of 0.60–2.36 mm, with at least 90% of particles under 2.36 mm, and 93% over 0.60 mm, according to ASTM D2862. PAC was obtained by milling Organosorb 10 GAC to a particle size range of 10–100 μm.

A similar batch procedure was adopted to prepare the feed solution for the MD experiments, using 500 mL samples. Based on the adsorption results, a dosage of 10 g L^{-1} (both GAC and PAC) was selected. After adsorption, both GAC- and PAC-treated samples were filtered through 0.45 μm cellulose acetate filters (GVS, Italy) before being fed to the MD system, ensuring that suspended carbon particles did not enter the membrane module. Surface tension was measured after filtration to ensure consistency with the adsorption tests results.

Adsorption isotherms for GAC adsorption were fitted using the Freundlich model: $q_{eq} = K_F C_{eq}^{\frac{1}{n}}$, where q_{eq} is the adsorbed quantity of surface-active compounds per unit mass of carbon at equilibrium, K_f is the Freundlich constant, $\frac{1}{n}$ is the heterogeneity factor, and C_{eq} is the surface-active compound concentration in the solution at equilibrium. Since the absolute concentration of surface-active compounds was not directly measured, C was approximated as the difference between the surface tension of pure water and the measured surface tension of the wastewater, according to: $C = ST_{\text{pure-water}} - ST$. This approach assumes a proportional relationship between the decrease in surface tension and the concentration of surface-active compounds in the solution [41]. While this approximation does not provide absolute concentration values, it allows a consistent and comparative assessment of the adsorption behavior and carbon dosage requirements within the scope of this study. It should be noted that, under these assumptions, the Freundlich parameters represent a description of the adsorption behavior based on surface tension response rather than absolute compound concentrations, and are therefore intended only for interpretative purposes within the context of this study.

2.3.2. Membrane-based processes (ultrafiltration, nanofiltration)

Membrane-based processes, namely, ultrafiltration (UF) and nanofiltration (NF) were evaluated as alternative pretreatment options for the removal of surface tension-reducing compounds from both the investigated wastewater samples. UF tests were performed with a cross-flow bench-scale system, built according to a standard configuration, including an inverter-controlled volumetric pump, a thermally insulated volumetric feed tank, and a tubular membrane housing module [42]. Three different TiO_2-based ceramic membranes (TAMI industries, France) with an active area of 47.1 cm^2, a length of 250 mm, and pore sizes of respectively 150, 15, and 1 kDa, were tested. The operating pressure was set at 1.5 bar and monitored with a manometer (SPAN, USA), while the selected flow rate was 150 L h^{-1}, corresponding to a cross-flow velocity of 2.1 m s^{-1}. The permeate flux was measured continuously by monitoring the change in weight of the filtered solution, which was collected in a beaker placed on a computer-interfaced scale. Weight measurements were taken every 3 min.

NF tests were performed using a bench-scale cross-flow system consisting of a 5 L feed tank, a high-pressure pump (Hydra-cell pump, Wanner Engineering, Inc., USA), and a membrane module (model CF016D, Sterlitech, USA) with a total active area of 20.6 cm^2. Trisep TS80 membranes (Mann+Hummel, Germany) were employed. A back-pressure valve (Swagelok, USA) was used to set the desired pressure. Pressure and flow rate were monitored with a manometer (SPAN, USA) and a flowmeter (ASA, Italy), respectively. The feed solution temperature (22 ± 2 °C) was regulated through a recirculating chiller (Lauda, Germany) equipped with a stainless-steel coil submerged in the feed tank [43]. The system was operated in an open-loop mode with a cross-flow velocity of 0.23 ± 0.02 m s^{-1}, a feed pressure of 20 ± 2 bar for DYE and 30 ± 2 bar for DEW. Permeate was collected in a beaker placed on a computer-interfaced scale, with weight measurements every 3 min, allowing for a continuous measurement of the permeate flux. Permeate samples were collected at regular time intervals for surface tension measurement.

2.3.3. Photocatalysis and enhanced photocatalysis

Photocatalysis experiments were conducted using TiO_2 (Carlo Erba, Italy) as the catalyst, at concentrations of 0.2 and 1 g L^{-1} [44]. Tests were carried out on 25 mL wastewater samples, placed in a jacketed glass beaker for temperature control. The reactor was placed for 24 h under a UV-A lamp (Philips, The Netherlands) providing an irradiance of 17 ± 2 W m^{-2}. The lamp was pre-heated for at least 30 min before the beginning of each test. At the end of the irradiation period, the samples were filtered through 0.45 μm cellulose acetate filters (GVS, Italy) before surface tension measurements.

Enhanced photocatalysis experiments were carried out by adding H_2O_2 (30% *w*/w, Carlo Erba, Italy). Two dosing protocols were implemented for each TiO_2 concentration (0.2 and 1 g L^{-1}). In the first protocol, four equal aliquots of H_2O_2 were added at 15 min intervals, to reach a final nominal concentration of 200 mM. In the second protocol, three equal aliquots were added at 15 min intervals, to reach a final nominal concentration of 100 mM. After completion of the treatment, the solution was filtered through 0.45 μm cellulose acetate filters (GVS, Italy) before surface tension measurements.

2.4. MD configurations

MD experiments were performed in direct contact (DCMD) and vacuum (VMD) configurations. The bench-scale DCMD system [45] included: a thermally insulated feed tank, a distillate tank, two inverter-controlled pumps (one for each stream, Fluid-o-Tech, Italy), and a two-plate cell module for membrane housing, with an active area of 140 cm^2 (model SEPA, Sterlitech, USA). The flow rate of both feed and distillate was set at 25 L h^{-1} and controlled by flowmeters (ASA, Italy). Feed and distillate solutions were fed at 55 ± 2 °C and 20 ± 2 °C, respectively. Temperature was controlled with a heater (Thermo Fisher, USA) and a cooler (Ametek Brookfield, USA). Distillate electrical conductivity was continuously monitored with a XS COND 70 VIO conductivity meter (XS instruments, Italy). During DCMD tests, the electrical conductivity of the distillate solution was evaluated as previously presented by Scelfo et al. [43]. The initial volume of the feed solution was approximately 1.3 L for all tests, while the distillate tank was filled with approximately 1 L of deionized water. Tests were carried out with the aim of reaching the highest possible recovery before membrane wetting.

The feed circuit of the bench-scale VMD system (Fig. S1) was identical to that of the DCMD system, except for the two-plate membrane cell (model CF016-FO, Sterlitech, USA). In this case, however, the feed tank was placed on a computer-interfaced scale, and the distillate flux was measured monitoring the decrease in weight of the feed solution. The distillate circuit included: a sealed tailed flask connected to a vacuum pump to collect the condensed distillate, a bubble condenser connected to a cooler (Ametek Brookfield, USA), a valve to allow sampling without losing vacuum in the membrane cell, and a manometer (SPAN, USA). The pressure of the vacuum line was set at 200 mbar. Periodically, the valve was shut and the flask replaced to collect distillate samples for EC and TOC measurements. Once the new flask had been positioned, the valve was reopened and distillate collection started again. The process took around 10 s and the pressure in the cell was constant. Tests were carried out with the aim of reaching the highest possible recovery before membrane wetting. For both DCMD and VMD tests, a PVDF membrane (pore size 0.2 μm, thickness 150 μm, porosity 83%. GVS, Italy) was employed.

Distillate EC was used as an indicator to assess MD performance in both configurations, particularly for the identification of membrane wetting. Specifically, in this study the onset of wetting was defined as the first recovery value at which distillate EC showed a sustained increase above the initial baseline, persisting in subsequent measurements and exceeding the variability observed during the stable operating period. Since the vapor transport through an intact hydrophobic membrane prevents the transport of non-volatile compounds, an increase in distillate conductivity was considered as evidence of wetting and loss of membrane integrity. In VMD experiments, TOC measurements were also performed to further support EC-based assessment.

2.5. Energy consumption and cost evaluation

A preliminary estimation of the energy demand and of the operational costs was carried out for treatment trains including adsorption (GAC or PAC) followed by DCMD or VMD, for both wastewaters. The following assumptions were adopted: (i) the water production rate of a hypothetical full-scale system was fixed at 100 $m^3\ d^{-1}$, consistent with the capacity of some of the largest currently operating systems [46,47]; (ii) the recovery values were set according to the results obtained in the lab-scale tests; (iii) the cost of GAC and PAC was assumed to be 2 € kg^{-1} and 1.50 € kg^{-1}, respectively, based on the authors' experience; (iv) the energy cost was assumed to be 0.15 € kWh^{-1}, consistent with the price of energy in Italy; (v) considering the typical temperature of textile wastewaters, generally between 60 °C and 80 °C, the thermal energy required to sustain the process was assumed to be available as waste heat at no cost, so that no heating demand was included in the assessment. It is important to note that, although the thermal input is assumed to be free, the heat transferred across the membrane must nonetheless be removed on the distillate side. The associated cooling demand was therefore the only thermal term included in the estimate. All energy terms are expressed per unit volume of distillate produced.

Two plant configurations were considered. In the first, the system operates without internal heat recovery, so that the entire thermal load transferred across the membrane is removed by the cooling system. In the second, a heat exchanger recovers part of the heat from the distillate loop and returns it to the feed, thereby reducing the residual cooling duty. Heat recovery remains relevant even though waste heat is assumed to be free, because it acts on the cooling requirement rather than on the heating requirement. For the configuration with heat recovery, the specific thermal energy consumption (SEC_{th}) of the DCMD system was estimated with the model proposed by Christie et al. (Eq. (1)):

$$SEC_{th} = \frac{h_v}{\eta_{th}} \frac{\Delta T_{MD} + \Delta T_{HX}}{\Delta T - \Delta T_{MD}} \quad (1)$$

where ΔT_{MD}, the trans-membrane temperature difference, was assumed to be 10 °C, consistent with values commonly reported in the literature [48,49]; ΔT, the temperature difference between the hot and the cold stream, was set at 35 °C (55 °C feed and 20 °C distillate); ΔT_{HX}, the temperature difference between the streams in the heat exchanger, was assumed to be 5 °C; the thermal efficiency (η_{th}) was set at 0.85; and the latent heat of vaporization of water (h_v) at 55 °C was taken as 2370 kJ kg^{-1}. Under these assumptions, Eq. (1) returns a specific thermal demand of 465 kWh_{th} per cubic meter of distillate. At steady state, and with a thermal input available at no cost, this quantity also corresponds to the heat that must be removed by the cooling system.

In the configuration without internal heat recovery, the cooling duty is not an independent design variable but is fixed by an energy balance on the distillate loop. At steady state, the sensible heat gained by the recirculating distillate stream (Eq. (2)) must equal the latent heat released by the condensing vapor (Eq. (4)). The distillate recirculation ratio R, defined as the ratio between the recirculated distillate flow rate and the distillate production rate, and the temperature rise of the distillate stream ΔT_d are therefore not independent, but related by $R = h_v / (c_p \bullet \Delta T_d)$. Assuming a temperature rise of the distillate stream of 10 °C, from 20 °C to 30 °C, a recirculation ratio of approximately 57 is required. Consequently, the cooling duty of the configuration without heat recovery is fixed at 658 kWh_{th} per cubic meter of distillate, irrespective of the recirculation ratio adopted, and coincides with the latent heat of the distillate produced.

$$Q_{cooling}(DCMD) = \dot{m} \bullet c_p \bullet \Delta T \quad (2)$$

where $\dot{m}$ represents the mass flow rate of the recirculating distillate stream, c_p is the specific heat capacity of water (4.184 kJ $kg^{-1}\ K^{-1}$), and ΔT_d is the temperature rise of the distillate stream across the membrane module.

The thermal cooling duty was then converted into electrical energy consumption considering two alternative cooling technologies. In the first, cooling is provided by a mechanical vapor-compression chiller with a coefficient of performance (COP) of 4, corresponding to 0.25 kWh of electricity per kWh of heat rejected; this option reproduces the conditions adopted in the laboratory tests, in which the distillate was maintained at 20 °C. In the second, heat is rejected to the ambient by means of an evaporative cooling tower, with a specific electricity consumption of 0.03 kWh per kWh of heat rejected, accounting for fans and circulation pumps. It should be noted that evaporative cooling cannot maintain the distillate at 20 °C, since the achievable temperature is limited by the ambient wet-bulb temperature; such a system would operate with a distillate temperature of approximately 30 °C and hence with a lower driving force and a lower distillate flux than measured here. The two options are therefore reported as bounding cases rather than as strictly equivalent alternatives.

The pumping power (P_{pump}) was estimated using Eq. (3):

$$P_{pump} = Q \bullet \Delta P \bullet \frac{1}{\eta} \quad (3)$$

where Q is the volumetric flow rate, ΔP is the pressure loss in the system (set as 1 bar), and η is the pump efficiency (assumed to be 0.7). The flow rates were derived from the recirculation ratio imposed by the energy balance ($R \approx 57$) rather than assumed independently. Three pumps were considered for the DCMD configuration, serving the feed loop, the distillate loop, and the cooling circuit that rejects the residual heat; the same three loops are present both with and without internal heat recovery, the heat exchanger being placed in series on the existing feed and distillate streams rather than requiring dedicated circulation pumps. For the VMD configuration only the feed loop was considered, since no distillate recirculation is required.

The cooling duty of the VMD configuration, and that of the DCMD configuration without internal heat recovery, were both estimated with Eq. (4):

$$Q_{cooling}(VMD) = \dot{m} \bullet h_v \quad (4)$$

where h_v is the latent heat of vaporization of water at the operating temperature. In VMD the condenser must remove the latent heat released during vapor condensation, whereas in DCMD without heat recovery the same quantity of heat is transferred to the distillate stream and must subsequently be rejected by the cooling system. Pumping requirements for VMD were estimated as described above, with the addition of a vacuum pump, whose consumption was assumed at 6 kWh m^{-3} according to literature data [50].

The consumption of GAC was estimated from the isotherms reported in Fig. 3. Specifically, the maximum adsorption capacity, S_f, was calculated using the Freundlich relationship: $S_f = K_f \bullet C_0^{\ 1/n}$. The resulting GAC requirement was derived by a mass balance, assuming complete utilization of the adsorption capacity up to S_f, in order to meet the target removal of surfactants from the treated streams. As specified in section 2.3.1, the concentration of surfactants was not directly measured; C_0 was therefore approximated as the difference between the surface tension of pure water and the measured surface tension of the wastewater before treatment.

3. Results and discussion

3.1. MD performance on raw textile wastewaters

Fig. 1 illustrates the performance of DCMD tests using untreated, raw wastewaters. Two parameters were monitored: distillate flux (productivity) and distillate EC, the latter used as a proxy to assess ionic rejection. In the case of DYE wastewater (Fig. 1a), distillate flux ranged from 4 to 8 kg m^{-2} h^{-1} and exhibited a continuous decline throughout the experiments. Distillate EC remained stable up to a recovery factor of 30%, after which it began to increase. This initial rise in EC at 30% recovery was identified as the onset of membrane wetting, marking the beginning of performance deterioration. Beyond this threshold, the EC followed a monotonically increasing trend, preceding a sharp increase after 50% recovery, suggesting more extensive liquid penetration into the membrane pores [51,52]. Similar considerations can be made regarding DEW wastewater (Fig. 1b). However, distillate flux was lower, namely, between 4 and 6 kg m^{-2} h^{-1}, and the onset of membrane wetting was observed substantially earlier, at approximately 7% recovery. This behavior is consistent with the surface tension measurements of the raw wastewaters (Fig. 1c). Indeed, both DYE and DEW exhibited a considerably low surface tension compared to pure water (72.7 mN m^{-1} at 20 °C), suggesting a high tendency to membrane wetting [32,33]. Specifically, DEW showed a much lower surface tension compared to DYE stream, suggesting a higher propensity for liquid entry in the pores. Overall, while the flux decline in both wastewaters indicated the presence of fouling, likely due to the progressive deposition of organic matter on the membrane [53,54], the process limitations did not appear to be fouling-dominated, but mostly wetting-driven. This is evidenced by the fact that the loss of distillate quality occurred before a major distillate flux decline could be observed.

3.2. Effect of pre-treatment

To evaluate the removal of surface-active compounds, several pre-treatment techniques were investigated, namely, adsorption on activated carbon, both granular (GAC) and powdered (PAC), UF, NF, photocatalysis, and enhanced photocatalysis. Their efficacy was quantified by measuring the surface tension of the treated effluent. Results for both DYE and DEW are summarized in Table 2.

Adsorption with GAC and PAC was the only treatment that restored the surface tension to levels comparable to pure water (72.7 mN m^{-1} at 20 °C). Conversely, UF and photocatalysis increased surface tension only partially, and in no case approached the value of pure water; NF achieved the largest improvement among the non-adsorption options but

Table 2
Results of the different pre-treatments tested for the textile wastewaters. For photo-catalysis and enhanced photo-catalysis only the test that produced the higher surface tension was reported. Complete results of the different concentration of catalyst and enhancer can be found in the Supporting Information section (Table S1). All the results presented are obtained as an average of at least two replicate, independent tests.

Pretreatment process	Resulting Surface Tension (mN m^{-1})	
	DYE	DEW
Untreated wastewater	39.0 ± 1.5	24.0 ± 1.2
Ultrafiltration (150 kDa)	36.9 ± 1.3	29.4 ± 0.1
Ultrafiltration (15 kDa)	41.5 ± 2.3	33.5 ± 0.9
Ultrafiltration (1 kDa)	44.6 ± 1.8	44.6 ± 1.0
Nanofiltration	64.9 ± 1.0	53.5 ± 2.2
Photocatalysis	44.7 ± 1.8	29.5 ± 1.5
Enhanced photocatalysis	53.3 ± 1.7	36.9 ± 2.6
Granular activated carbon adsorption*	71.6 ± 1.2	72.2 ± 1.5
Powdered activated carbon adsorption*	72.6 ± 0.4	72.2 ± 0.2

* Values measured at equilibrium (24-h contact) in batch mode.

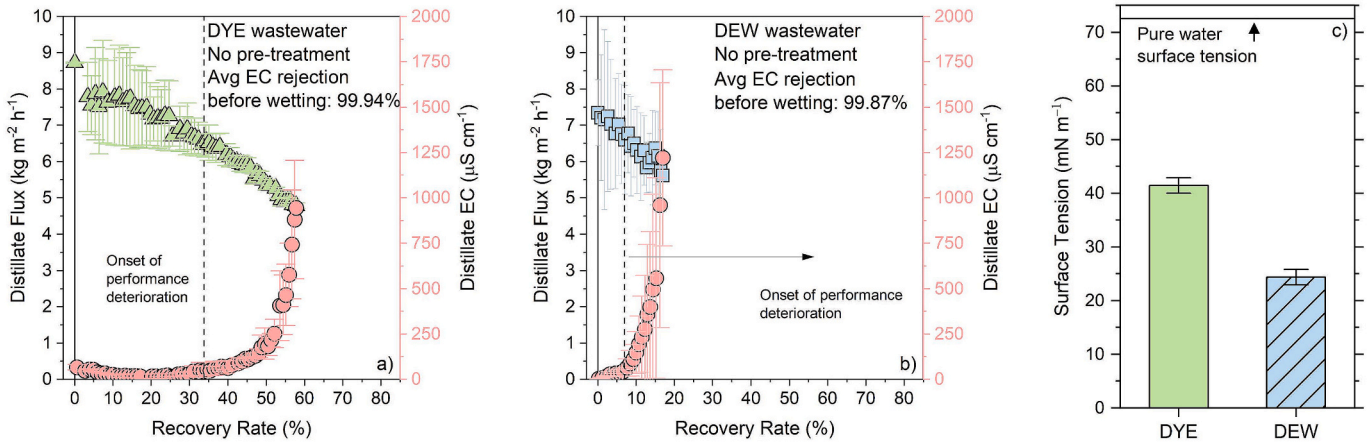


Fig. 1. Results of direct contact membrane distillation tests performed on raw textile industry wastewaters. The evolution of distillate flux (left y-axis) and distillate electrical conductivity (EC, right y-axis) as a function of recovery rate is shown for wastewaters from (a) the dyeing process (DYE) and (b) the synthetic fiber deweighting (DEW) process. Experiments were carried out without pre-treatment. The vertical dashed line indicates the onset of membrane wetting, defined as the first recovery at which distillate EC showed a sustained increase above the stable baseline (Section 2.4). Error bars represent one standard deviation based on two independent, replicate tests. Panel (c) reports the initial surface tension of the two wastewaters.

still fell short of the benchmark. Overall, the investigated pre-treatment methods demonstrated higher efficiency on DYE, with NF being the only process, aside from activated carbon adsorption, to show some, albeit incomplete, positive impact on DEW.

The performance of GAC and PAC in batch adsorption tests is reported in Fig. 2a and Fig. 2b, respectively. Similar trends were observed with both wastewaters, with surface tension values increasing with higher adsorbent dosages. Both adsorbents restored the surface tension to the benchmark of pure water, although the required dosage differed. As expected, based on its higher specific surface, PAC was more effective than GAC, achieving a complete surface tension recovery with a dosage of approximately 5 g L^{-1} for both wastewaters. In contrast, GAC required significantly higher dosages, up to 25 g L^{-1}, to reach similar results. However, an acceptable recovery level was achieved with a dosage of approximately 10 g L^{-1}. Despite the significant difference in the initial surface tensions of the two untreated streams, similar activated carbon dosages were required to reach the benchmark.

To further characterize the GAC adsorption process, equilibrium data were fitted using the Freundlich model. This analysis is essential to estimate the activated carbon requirements for GAC full-scale applications, which are typically implemented in fixed-bed columns or filtration units, where exhausted GAC is periodically replaced. In contrast, PAC is generally directly dosed within the treatment line and subsequently removed, making isotherm modeling secondary for the process design [55]. Therefore, the choice between GAC and PAC affects not only the removal efficiency of surface-active compounds, but also influences the process scalability, operational costs, and the overall layout of the system. Fig. 3a and Fig. 3b show the GAC isotherm and the Freundlich model fitting, for DYE and DEW, respectively. Based on the experimental results, a dosage of 10 g L^{-1} was selected for both GAC and PAC to pretreat wastewaters for subsequent DCMD tests. This value represents the minimum dosage allowing for an acceptable surface tension recovery for both streams.

3.3. MD performance after adsorption pre-treatment

Fig. 4a and b illustrate the performance of DCMD tests conducted on DYE and DEW streams, respectively, pre-treated with 10 g L^{-1} GAC. DYE distillate flux was unaffected by the adsorption pre-treatment, maintaining values consistent with those shown in Fig. 1 for the untreated stream. However, substantial improvements were observed in the distillate quality. Specifically, the onset of membrane wetting was delayed to approximately 50% recovery, and the measured distillate electrical conductivity remained consistently lower than in the untreated case. However, a gradual deterioration of membrane performance was still evident, which limited the maximum achievable recovery.

Similar trends were observed for DEW. In this case, however, the pre-treatment also positively affected the distillate flux, which remained approximately 15% higher than what was observed for the untreated stream throughout the tests. This improvement may be associated with an increase in the surface tension of the pre-treated wastewater, which could prevent partial wetting in the early stages [56,57]. In addition, the adsorption process likely reduced the organic load of the stream, possibly removing a significant part of the foulants that would hinder water transport [53,54]. A visible improvement was achieved for wetting onset, which was considerably delayed compared to the untreated stream. Nonetheless, the maximum achieved recovery was limited to 40%.

Additional DCMD tests were conducted using wastewaters pre-treated with PAC to compare the two adsorbents' effects on wetting and distillate quality (Fig. 4c and d). DYE distillate flux was lower compared to that measured after GAC pre-treatment, particularly in the second part of the test, where fouling effect likely became prominent. However, the new pre-treatment allowed for a greater recovery. Signs of membrane performance deterioration were observed around 60% recovery. Although distillate EC increased more rapidly after the onset of wetting than in the GAC experiments, PAC delayed the onset of wetting, allowing stable operation up to higher recovery values. Similar consideration can be made about the DEW stream. Specifically, while initial flux values were slightly lower than those observed after GAC, the flux decline was comparable. Again, PAC adsorption allowed to push the process further, achieving around 50% recovery before membrane wetting occurred and distillate quality dropped. Also in this case, once wetting was initiated, a steeper increase in distillate EC was observed compared with GAC. However, the relatively large experimental

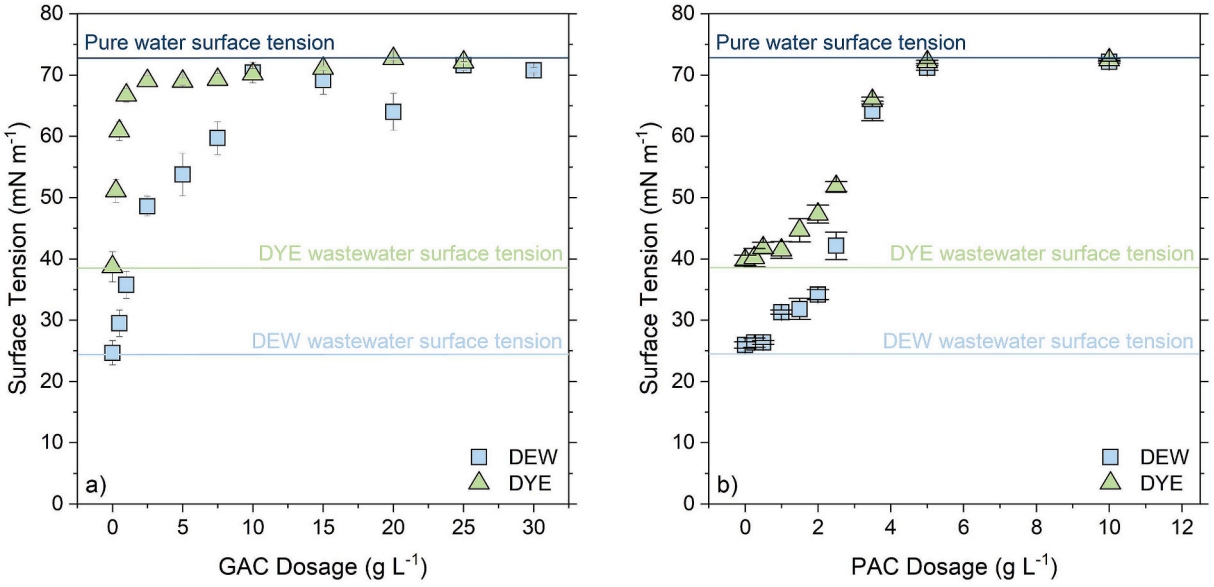


Fig. 2. Effect of activated carbon adsorption on the surface tension of textile industry wastewaters. Batch adsorption tests were performed using (a) granular activated carbon (GAC) and (b) powdered activated carbon (PAC) at increasing dosages. Surface tension was measured after 24 h of contact. The surface tension of pure water (72.7 mN m^{-1} at 20 °C) is shown as a reference and represented by a horizontal blue line, while the surface tension of the untreated wastewaters is also reported for comparison. Error bars represent one standard deviation based on two independent, replicate tests. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

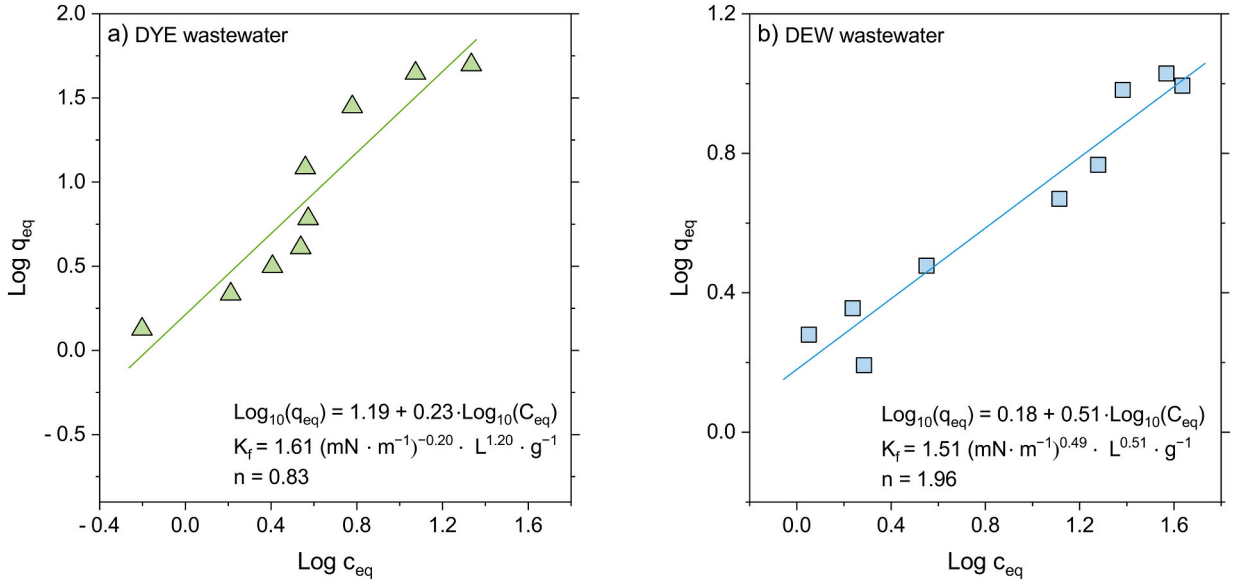


Fig. 3. Granular activated carbon adsorption isotherms obtained for (a) dyeing (DYE) wastewater and (b) deweighting (DEW) wastewater. Symbols denote experimental equilibrium data, reported as adsorbed amount at equilibrium (q_{eq}) versus equilibrium concentration in solution (C_{eq}). Solid lines represent the Freundlich model fitted to the data, expressed in its nonlinear form as $q_{eq} = K_F C_{eq}^{\frac{1}{n}}$, and in the linearized logarithmic form as $Log_{10} q_{eq} = Log_{10} K_F + \frac{1}{n} Log_{10} C_{eq}$. The corresponding linear regressions, along with the estimated Freundlich parameters K_f and n, are reported within each panel. Both isotherms are presented on logarithmic coordinates.

variability after wetting, as reflected by the error bars, suggests that this behavior should be interpreted with caution, and further investigations would be required to clarify the underlying mechanism.

Based on the results obtained in the DCMD configuration, additional tests were then carried out in a VMD configuration, following PAC adsorption (10 g L^{-1}). While the VMD systems can be more susceptible to wetting because of the vacuum applied on the distillate side, they typically achieve higher productivity and efficiency and are therefore generally preferred for large-scale applications [58–60]. This configuration was therefore selected to evaluate a possible process scale-up. Fig. 5 illustrates the results of the VMD tests for DYE (Fig. 5a) and DEW (Fig. 5b), respectively. For set recovery rates, the values of distillate flux, conductivity, and TOC are reported in the graphs. As expected, the observed productivity was higher than in DCMD, with flux values more than doubling for both streams. Interestingly, the initial distillate quality was relatively low, with EC values higher than 1 mS cm^{-1}. The initial poor permeate quality may have resulted from transient pore wetting during startup. Rapid establishment of vacuum and associated transmembrane pressure fluctuations can temporarily promote liquid intrusion into membrane pores before thermal and hydraulic stabilization is achieved [51,61]. After an initial transitory period, the EC decreased, and the distillate quality became acceptable, stabilizing at values ranging from 100 μS cm^{-1} to 200 μS cm^{-1}, corresponding to dissolved solids concentrations below 100 mg L^{-1}. TOC followed the same trend as electrical conductivity.

Overall, the DYE stream showed robust performance, and this time the limiting factor did not appear to be associated with wetting, but possibly fouling. A 65% recovery was achieved without a deterioration of membrane rejection. However, the flux sharply declined after 50% recovery and became lower than 10 kg m^{-2} h^{-1}. This behavior may be related to fouling phenomena, possibly intensified by the vacuum conditions that promoted the deposition of foulants on the membrane surface. Conversely, the DEW stream exhibited a different limitation and wetting occurred earlier. Signs of performance deterioration were observed at approximately 40% recovery, and the distillate quality (electrical conductivity and TOC) sharply decreased with the advancement of the test. Overall, the two streams showed different limitations for VMD treatment, with fouling being a major issue for DYE and wetting preventing a high recovery for DEW. Despite the observed improvements, MD performance remained constrained, and stable operation at high recovery could not be achieved even after adsorption pre-treatment.

To further investigate the interaction between the membranes and the wastewaters, and the modification of the membrane surface during operation, contact angle measurements were performed (Table S2). The pristine PVDF membrane exhibited a water contact angle of 138.1 ± 1.9°, confirming its strongly hydrophobic character. When measured with the raw wastewaters, the contact angle was 120.0 ± 7.9° for DYE and 92.0 ± 8.5° for DEW. The latter is not significantly different from 90°, the threshold below which liquid intrusion into the membrane pores becomes highly favorable, which is consistent with the very early onset of wetting observed for this stream at approximately 7% recovery, whereas DYE retained a margin against spontaneous intrusion and wetted only at 30% recovery.

Contact angles measured on the membranes recovered after the tests confirmed that the membrane surface was itself modified during operation. Using pure water as a probe liquid, the contact angle decreased from 138.1 ± 1.9° for the pristine membrane to 70.0 ± 11.1° for the membrane operated with raw DYE, that is below 90°, indicating an irreversible loss of hydrophobicity. Membranes operated with pre-treated wastewaters showed intermediate values, between 90.6 ± 3.0° and 113.0 ± 13.5°, indicating that adsorption pre-treatment limited, but did not prevent, the modification of the membrane surface. When the measurement was instead performed with the corresponding wastewater rather than pure water, the loss of hydrophobicity was more evident: the contact angle of DEW on the DEW-wetted membrane was 75 ± 5°, and a drop of DYE on the DYE-wetted membrane spread and was absorbed within a few seconds, so that no stable contact angle could be measured, consistent with complete wetting. The visual appearance of the membranes recovered after the raw-wastewater tests is shown in Fig. S2.

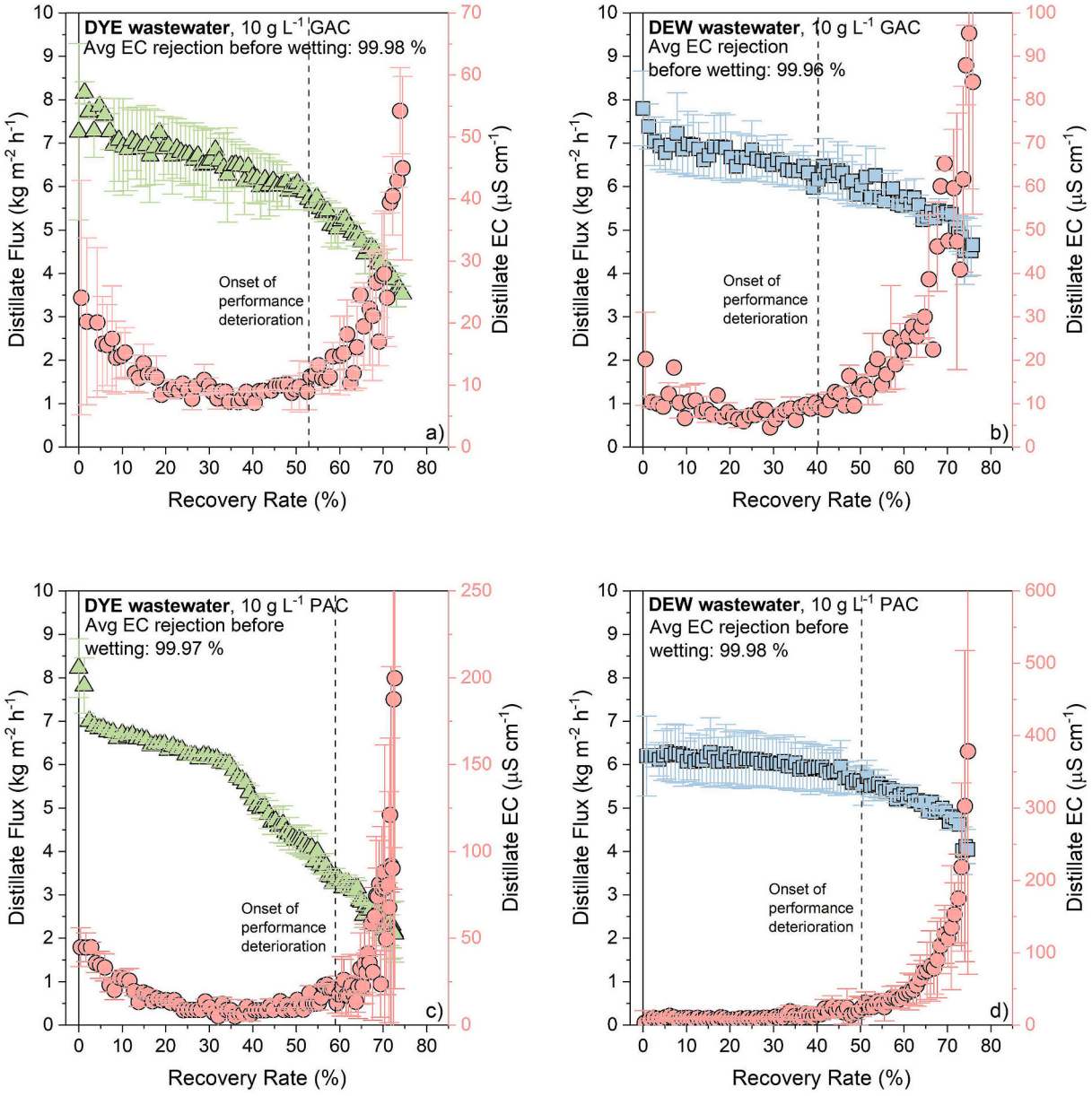


Fig. 4. Performance of direct contact membrane distillation (DCMD) treating textile wastewaters pre-treated by adsorption with activated carbon at a dosage of 10 g L1. Panels (a) and (b) report results for dyeing (DYE) and deweighting (DEW) wastewaters, respectively, pre-treated with granular activated carbon (GAC), while panels (c) and (d) show the corresponding results for wastewaters pre-treated with powdered activated carbon (PAC). Distillate flux (left y-axis) and distillate electrical conductivity (EC, right y-axis) are presented as a function of recovery rate. The vertical dashed line indicates the onset of membrane wetting, defined as the first recovery at which distillate EC showed a sustained increase above the stable baseline (Section 2.4). Error bars represent one standard deviation based on two independent, replicate tests.

3.4. Practical implications, costs, and limitations

From a practical perspective, the results discussed above, taken all together, suggest that surface tension can be used as a preliminary screening parameter to assess the suitability of MD treatment for textile WW. Streams exhibiting surface tension values significantly below that of pure water are prone to early wetting, which limits the achievable recovery before wetting onset and increases treatment costs due to the need for extensive pre-treatments such as adsorption. Under these conditions, MD may not represent a competitive option compared with treatment processes that do not require extensive surface-tension restoration before operation. Conversely, wastewaters with a sufficiently high surface tension, either intrinsically or after pre-treatment, can sustain stable operation at moderate recovery values and represent more suitable candidates. In that sense, surface tension is not only a mechanistic parameter but also a key determinant of economic feasibility.

Specifically, the results of this study indicate that adsorption-based pre-treatments may support MD operations with real textile wastewaters. Further optimization, such as increasing the activated carbon dosage or introducing additional pre-treatment steps (e.g., adding a photo-catalysis step after adsorption), could enhance the achievable recovery and potentially improve performance. Nevertheless, several aspects must be considered when evaluating these options. First, the introduction of additional pre-treatment steps requires extra operational units which would increase the overall complexity of the treatment train and result in a larger footprint. In addition, both energy and material consumption must be considered when evaluating the overall feasibility

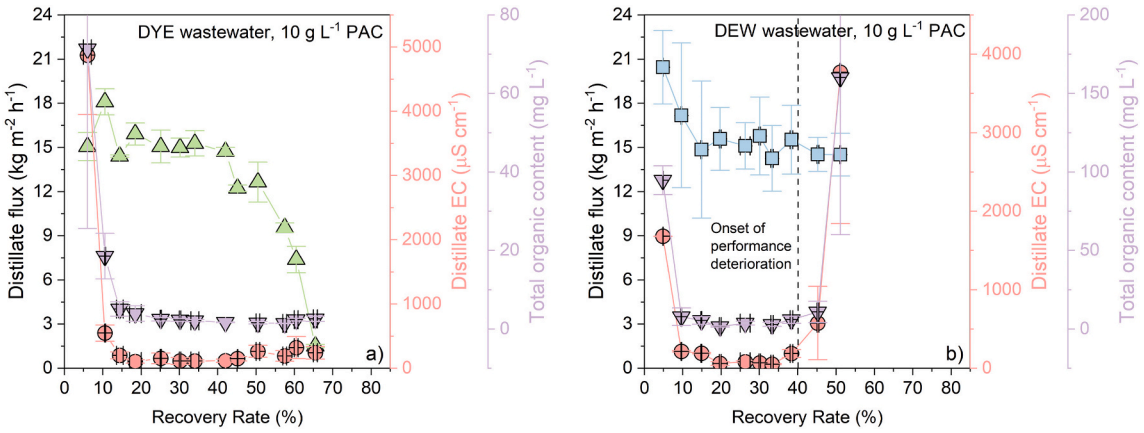


Fig. 5. Performance of vacuum membrane distillation (VMD) treating textile wastewaters pre-treated by adsorption with powdered activated carbon (PAC, 10 g L^{-1}). Panels (a) and (b) report results for dyeing and deweighting wastewaters, respectively, showing distillate flux (left y-axis), and distillate electrical conductivity and total organic content (EC, red right y-axis and TOC, purple right y-axis respectively) as a function of recovery rate. Lines connecting data points are solely meant as a guide for the eye. The vertical dashed line indicates the onset of membrane wetting, defined as the first recovery at which distillate EC showed a sustained increase above the stable baseline (Section 2.4). Error bars represent one standard deviation based on two independent, replicate tests. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the process.

Therefore, a preliminary estimation of the energy demand was carried out as described in Section 2.5. Table 3 reports the specific energy consumption of treatment trains combining adsorption with either DCMD or VMD. Since the energy demand per unit volume of distillate is not affected by the type of adsorbent or by the wastewater treated, the results are reported as a function of the MD configuration only. In the absence of internal heat recovery, the cooling duty is fixed by the energy balance at 658 kWh_{th} per cubic meter of distillate for both configurations: in DCMD the distillate stream must absorb the latent heat released by the condensing vapor, while in VMD the same quantity of heat must be removed by the condenser. Internal heat recovery reduces the residual cooling duty of DCMD to 465 kWh_{th} per cubic meter. The corresponding electrical demand, however, depends far more strongly on the cooling technology adopted than on the MD configuration: with a mechanical chiller, cooling alone accounts for 116 to 165 kWh m^{-3}, whereas the same duty rejected through an evaporative cooling tower requires only 14 to 20 kWh m^{-3}. Pumping contributes marginally in both configurations (2.3 to 6.7 kWh m^{-3}), and the vacuum pump adds a further 6 kWh m^{-3} in VMD. These results indicate that the cooling system is by far the dominant energy consumer, and that the way in which heat is rejected, rather than the MD configuration itself, governs the overall energy demand. Internal heat recovery lowers the residual cooling duty, and hence the electrical demand, only when cooling is provided mechanically; when heat is rejected evaporatively the corresponding saving becomes marginal, since the cooling term is already small.

The operational costs, expressed as € m^{-3} of distillate product for the same systems, are reported in Table 4, while Fig. S3 shows the contribution of the individual cost items to OPEX. Costs are reported separately for the two cooling options, since these were found to dominate the energy demand; for DCMD, the ranges correspond to the configurations with and without internal heat recovery. For GAC, material consumption was estimated from the adsorption capacity derived from the isotherms, assuming operation in a replaceable fixed-bed unit. For PAC, instead, the selected dosage was assumed to be continuously applied to the full treated flow. Therefore, the comparison reflects two different implementation modes rather than intrinsic adsorption capacity alone.

For DYE wastewater, the relatively high adsorption capacity of GAC resulted in a reduced daily consumption of the material, thereby allowing longer intervals between GAC replacement or regeneration, and making this system the least expensive option, with costs ranging from 4.3 to 5.1 € m^{-3} with evaporative cooling and from 19.6 to 26.9 € m^{-3} when mechanical cooling is required. In contrast, the use of PAC for the same wastewater resulted in substantially higher costs, driven by continuous dosing and hence by a much larger material consumption (1600 kg d^{-1} compared to 56 kg d^{-1} estimated for GAC). It should be noted, however, that both adsorption strategies present practical limitations. PAC requires continuous dosing followed by an additional solid-liquid separation step before the treated wastewater can be fed to the MD unit. Depending on the treatment configuration, this separation may rely on sedimentation, filtration, or membrane-based processes, leading to increased process complexity and to the generation of spent carbon sludge requiring further handling or disposal. Moreover, incomplete

Table 3
Specific energy consumption of a system employing adsorption followed by DCMD or VMD, expressed per cubic meter of distillate produced. Thermal cooling duties are reported as kWh_{th} m^{-3}, while all remaining entries are electrical consumptions in kWh m^{-3}. For DCMD, ranges correspond to the configurations with and without internal heat recovery.

Item	DCMD	VMD
Cooling duty, thermal – without heat recovery	658	658
Cooling duty, thermal – with heat recovery	465	–
Cooling, electrical – mechanical chiller (COP 4)	116–165	165
Cooling, electrical – evaporative cooling tower	14–20	20
Pumping	6.7	2.3
Vacuum pump	–	6.0
Total – with mechanical chiller	123–171	173
Total – with evaporative cooling	21–27	28

Table 4
Operational costs, expressed as € m^{-3}, of a system employing adsorption followed by DCMD or VMD. The costs include the energy required for cooling and pumping and the adsorbent required for the pre-treatment of the wastewater. Results are reported for the two cooling technologies considered; for DCMD, the ranges correspond to the configurations with and without internal heat recovery.

Configuration	DYE (€ m^{-3})	DEW (€ m^{-3})
GAC + DCMD – mechanical cooling	19.6–26.9	40.4–47.7
GAC + DCMD – evaporative cooling	4.3–5.1	25.1–25.9
PAC + DCMD – mechanical cooling	43.4–50.7	48.4–55.7
PAC + DCMD – evaporative cooling	28.1–28.9	33.1–33.9
PAC + VMD – mechanical cooling	49.0	63.4
PAC + VMD – evaporative cooling	27.3	41.7

removal of PAC particles prior to MD operation could contribute to particulate fouling on the membrane, highlighting the importance of an effective separation step. On the other hand, GAC can be implemented in fixed-bed adsorbers, avoiding downstream solid-liquid separation, but requires dedicated adsorption columns together with periodic media replacement or regeneration, increasing capital expenditures and operational complexity. These additional infrastructure, operational and solid-handling requirements were beyond the scope of the present operational cost assessment, but they should be considered when selecting the most appropriate pre-treatment strategy for full-scale implementation.

As expected, treatment of DEW resulted in higher overall costs. The specific cost associated with a system comprising GAC adsorption as pre-treatment was estimated in the range of 25.1 to 25.9 € m^{-3} with evaporative cooling and of 40.4 to 47.7 € m^{-3} with mechanical cooling. The marked difference between DYE and DEW can be primarily attributed to the much lower adsorption capacity of GAC for DEW, which was approximately 10 times lower than that observed for DYE, and to the lower achievable recovery, which requires treating larger volumes of feed water to reach the same production capacity. In the case of PAC adsorption, the costs did not vary appreciably compared to DYE, since the selected dosage remained the same, with differences arising from the higher treated volume.

A similar analysis was conducted for VMD. In the absence of internal heat recovery, the cooling duty of VMD coincides with that of DCMD, and the higher operational cost of VMD arises almost entirely from the additional electricity required by the vacuum pump. The difference becomes more pronounced when DCMD is operated with internal heat recovery, since the cooling demand of VMD cannot be reduced in the same manner without condensing at a higher temperature. It is important to highlight that the higher costs associated with DEW treatment were amplified by the low recovery (~40%) observed at the laboratory scale prior to membrane performance deterioration, which would limit the feasibility of a large-scale implementation. Despite the higher operational costs, VMD offers higher productivity, which could reduce membrane area requirements and system installation space, partially compensating for the increased energy demand.

These estimates indicate that the economic feasibility of MD is strongly dependent on the achievable recovery and on the adsorption demand, which are in turn governed by the surface tension of the feed, as well as on the availability of a low-cost heat sink for the rejection of the condensation heat. The costs associated with the management of the concentrated retentate were not explicitly included in this analysis. Nevertheless, low recovery leads to the generation of large volumes of concentrate requiring further treatment or disposal, and would therefore further increase the overall cost and reduce the feasibility of the process. When comparing the estimated costs obtained in this study with those reported in the literature for other treatment chains, MD generally appears to be more expensive than conventional alternatives. Although direct comparison is limited by differences in wastewater composition and treatment objectives, literature values provide a useful cost reference. Bilińska et al. [62] reported costs ranging from 1.2 to 2.2 € m^{-3} for ozone-based advanced oxidation processes (though mainly for dye removal), while Solmaz et al. [63] reported a cost of approximately 5 € m^{-3} for ozonation for both color and COD removal from biologically pretreated textile wastewater. Lower costs (0.47 € m^{-3}) were reported for electrocoagulation units aimed at COD, color, and turbidity removal [64]. Wu et al. [6] reported a cost of 5.73 € m^{-3} for a process combining forward osmosis and membrane distillation. For more established full-scale treatment systems, Yang et al. [65] reported an operating cost of 1.41 € m^{-3} for a conventional activated sludge (CAS) process treating textile wastewater, while Yin et al. [66] reported an operating cost of approximately 0.44 USD m^{-3}, corresponding to approximately 0.40 € m^{-3}, for an industrial textile wastewater reuse treatment train based on UF, RO, and ozonation. Among the configurations analyzed in this study, DCMD preceded by GAC adsorption applied to the dyeing wastewater was the only option approaching the cost of established alternatives, and only where heat can be rejected evaporatively (4.3 to 5.1 € m^{-3}). The economic viability of MD in this application is therefore governed as much by the availability of a low-cost heat sink as by the characteristics of the wastewater itself. Nevertheless, for a large fraction of textile wastewaters, particularly those characterized by a low surface tension, the need for extensive pre-treatments may offset the potential advantages of the MD technology.

4. Conclusion

This study evaluated the applicability of membrane distillation for the treatment of real textile wastewaters originating from cotton fabric dyeing and polyester fibers alkaline deweighting processes. The results suggest that MD performance is strongly governed by the surface tension of the feed solution, which directly affects membrane wetting and, consequently, process stability and achievable recovery. Experiments conducted on raw wastewaters demonstrated rapid deterioration of separation performance, with early onset of wetting, particularly for the deweighting stream characterized by very low surface tension. These findings indicate that studies based on synthetic solutions may overestimate MD applicability, as they do not account for the presence of surface-active compounds and for the complexity typical of real effluents. Among the pre-treatment strategies investigated, adsorption on activated carbon was the only approach capable of restoring surface tension to values comparable to pure water and significantly improving MD performance. However, the adsorption pre-treatment mitigated but not fully eliminated wetting phenomena.

Preliminary cost estimations showed that the combination of high adsorbent consumption and limited recovery determined relatively high operational costs, particularly for wastewaters with low surface tension. In addition, low recovery values imply the generation of large volumes of concentrate requiring further handling, which would further increase the overall cost and limit the MD process feasibility. Overall, the results indicate that MD cannot be considered a broadly suitable technology for this type of effluents. Its use is restricted to a subset of streams characterized by sufficiently high surface tension, either intrinsically or after limited pre-treatment. In practical terms, textile wastewaters characterized by persistently low surface tension should be excluded from consideration for MD, unless substantial pre-treatment is already required for other process objectives.

From a broader perspective, these cost estimates delineate both the opportunity and the boundary of membrane distillation for textile wastewater reuse. Because MD is driven by low-grade thermal energy, its attractiveness rests on the availability of waste heat, which is frequently abundant in textile finishing plants; where such heat is available and can be removed through a low-cost sink, the treatment of a favorable stream such as the dyeing wastewater after activated-carbon adsorption approaches the cost of established treatment and reuse schemes. This condition, however, also defines the limitation: the cost of the process is dominated by the removal of the condensation heat and by the adsorbent demand, both of which escalate sharply as the surface tension of the feed decreases and the achievable recovery falls. The economic viability of MD for textile effluents is therefore not a property of the technology alone but of the specific combination of stream, site, and available heat management, and it is most likely to be realized as a targeted polishing or concentration step on selected streams, rather than as a general-purpose treatment for textile wastewaters as a whole.

Taken together, these results suggest that feed surface tension can be used as a first-level screening parameter for MD applicability. In the present study, streams with surface tension below approximately 40 mN m^{-1} underwent wetting at low recovery (30% for DYE at 39 mN m^{-1} and 7% for DEW at 24 mN m^{-1}), and restoration to values close to that of pure water was required to sustain operation up to 40–60% recovery. On this basis, we tentatively propose that textile streams with surface tension below ~40 mN m^{-1} should be regarded as unsuitable for direct MD

treatment, and that pre-treatment targets should aim at restoring surface tension to values approaching that of pure water. The intermediate range was not investigated experimentally here, and identifying the minimum surface tension compatible with stable operation, which is expected to depend also on membrane properties and on the nature of the surface-active compounds, remains an open question and a relevant objective for future work.

CRediT authorship contribution statement

Lorenzo Craveri: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Giorgia Luccini:** Writing – review & editing, Investigation, Data curation. **Olga Chybová:** Writing – review & editing, Resources, Funding acquisition. **Lenka Martinková:** Writing – review & editing, Resources. **Barbara Ruffino:** Writing – review & editing, Methodology, Investigation. **Alberto Tiraferri:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Funding acquisition, 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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2026.110727.

Data availability

Data will be made available on request.

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