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Performance evaluation of direct nanofiltration process to fouling by treating rinsing-bath effluents for water reuse

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ABSTRACT

In this study, experiments were carried out to evaluate a direct nanofiltration membrane process performance in terms of flux, rejection, and resistance to fouling, for treating two real textile dyeing rinsing waters (indigo blue and sulfur black) collected from rinsing baths of Ksar Hellal factory (SITEX). Based on permeate flux efficiencies and regarding permeate quality in terms of pollutant rejections, indigo blue permeate presented better performances than sulfur black. During volume reduction factor experiments, an average of 99% reduction in turbidity, 97% in COD removal, and a colorless permeate were observed in the case of indigo blue, whereas for sulfur black permeate, these rejections values reached only 67, 86, and 52%, respectively, in terms of turbidity, COD and color removal efficiencies. However, low salt rejection rates were obtained that did not exceed 34% for both rinsing effluents. These results confirm the fouling problem of NF HL membrane; even it presented a significant improvement in permeate quality. The fouling influence after NF stage was evaluated by determining resistances in series. Nevertheless, NF HL membrane seemed to be more sensitive to fouling caused by treating sulfur black effluent. Moreover, the irreversible fouling was more important than the reversible one, for both studied samples.

Keywords: Nanofiltration membrane; Textile rinsing effluents; Fouling; Resistance in series

1. Introduction

Water scarcity and strict legislation make water reuse in dye related industries like textile and leather become more important [1].

In water intensive industries, such as textile industry, water management must approach for economization and rationalization of the use of water resources [2,3].

With the increased demand for textile products, the textile industry and its wastewaters have been increasing proportionally, making it one of the main sources of severe pollution problems worldwide [4]. Textile industry is one of the most chemically intensive industries on the earth and the major polluter of potable water. It generates huge quantities of complex

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chemical substances as a part of unused materials including dyes in the form of wastewater during various stages of textile processing [5].

The wastewaters of the textile industry contain various chemicals with different nature. Large numbers of chemical constituents such as alkali, acids, bleaching chemicals, enzymes, starch, dyes, resins, solvents, waxes, oils, etc. are used in the various steps during textile processing and finally comes out in the effluent after its consumption [5].

In fact, textile dye wastewater is well-known to contain strong color, high pH, presenting large amount of suspended solids, COD, and low bio-degradable chemicals, especially the effluent from the dyeing stages of the dyeing and finishing processes [6]. The primary source of wastewater in textile dyeing operations is spent dye bath and rinsing waters [7].

The contamination of water bodies by synthetic dye stuffs is considered to be a global environmental problem in recent years. It is well-recognized that their existence in aquatic ecosystem is accountable for causing several damages to the environment and can have adverse effects on many forms of life [8,9].

Most synthetic dyes have complex aromatic molecular structures; this makes them inert and hardly biodegradable when discharged into the environment, as they are relatively stable to light and oxidizing agents, and are resistant to aerobic digestion. Hence, the increasing discharge of dyes to the environment has caused great concern [4,10].

As a starting point to implement reuse strategies, rinsing effluents were considered for on-site treatment and reuse in the same or in other production processes, being characterized by a large volume but low concentration of contaminants. Their direct reuse is not suggested for the wide quality variability in contrast to the standard quality required in the processes [11].

Minimizing the impact on the environment implies, besides the optimization of water use schemes within the factory, a step forward in water treatment to obtain an effluent quality suitable for reuse opportunity [11].

Several treatment methods and many techniques have been used or proposed for the removal of synthetic dyes from wastewaters [12,13].

Forgacs et al. [12] have conducted a review of technologies available for the removal of color from textile wastewaters and concluded that traditional techniques are largely ineffective as a result of the inherent stability of these pollutants. The technologies reviewed were adsorption and physiochemical methods, photocatalysis and oxidative methods, and microbiological and enzymatic decomposition [14].

As an alternative method to wastewater treatment technology, membrane technology has proven to be very attractive and effective for the treatment of textile effluents [15].

The application of membrane separation processes does provide the industries with a technology to meet water quality limits and produce reusable water, and has proved to be an effective process in concentrating the bulk of pollutant into small liquid volume for further disposal [2,3,16–18].

The obvious advantages of pressure-driven membrane processes are the purified product, permeate, usually has an outstanding quality, no requirement to the addition of chemicals, low energy requirements, and combination with other separation processes is easy due to the modular construction [15,19].

Recently, nanofiltration (NF) has become a popular method in the dye industry to replace the conventional process [4]. Among all types of membrane process, NF as one of the most exciting membrane technologies has the advantage of retaining relatively small organic molecules from water solution due to the separation mechanisms is shown to be the most effective one for the treatments of synthetic dyes from wastewater [7,13].

The retention of inorganic ions by NF membranes is strongly dependent on the charge of the ions. The rejection is low for salts with monovalent anion and non-ionized organics with a molecular weight below 150 Da, but is high for salts with di- and multi-valent anions and organics with a molecular weight above 300 Da. Thus, NF can be used for the simultaneous removal of sodium chloride (salt) and the concentration of aqueous dye solutions. Typically, the rejection of a divalent ion of the same charge as the membrane is above 95%, whereas the rejection of a monovalent ion of the same charge can be anywhere between 20 and 80% [20].

NF of dyeing bath has started since 1990 and was shown to be essential for treating and reusing textile dye effluents [1,15].

Various works have reported the use of NF membranes for dye separations either for wastewater treatment or process applications [14].

A review of NF processes in the textile industries has been compiled by Lau and Ismail [21] has indicated that most commercial membranes either achieve a maximum separation of the dye or high membrane flux. The desirable ideal membrane should exhibit both characteristics [14].

Erswell et al. [22] were one of the first to investigate the prospect of a charged membrane for the reuse of reactive dye liquors. Membrane performance was monitored in terms of dye and salt rejection and permeate flux, under varying conditions. They concluded that NF is a technically feasible process for treatment of the dye bath at high water recoveries [14].

Lopes et al. [23] reported 99% color retention for the two different NF membranes in the treatment of textile wastewaters. In addition to this, Petrinic et al. [24] also reported over 99% color retentions for the treatment of four different reactive dyes with NF membranes [2].

Koyuncu et al. [25] reported similar findings for an actual remazol dye bath wastewater and concluded that inclusion of an NF treatment plant would have a capital expenditure payback period of less than two years [14].

However, membrane fouling is one of the common problems associated with membrane filtration processes that strongly reduces the permeate flux and subsequently changes both membrane selectivity and efficiency [26].

Fouling is caused by dissolved inorganic or organic components, colloids, bacteria, or suspended solids [1,20].

Dye molecules could be found in dissolved or colloidal forms [1,27]. Several types of dyes such as acid, basic, direct, and reactive are water-soluble type while disperse, sulfur, and vat type are in colloidal form.

If the issues raised by the membranes fouling are old, anticipating and adapting the conditions of filtration to minimize fouling is essential for better process control.

Despite many strategies aiming at preventing membrane fouling, including appropriate pretreatments and membrane modification, proper and periodical cleaning is still a vital and effective way to restore membrane performance [28].

The purpose of this study is to investigate and evaluate the feasibility and suitability of a direct NF HL process to treat two selected streams collected from different real textile rinsing dye-bath effluents (indigo blue and sulfur black), in order to establish their permeate quality and evaluate their reusability. Consequently, NF HL membrane sensitivity to fouling was studied.

During NF stage, membrane performance and efficiency was quantified at different operating conditions such as transmembrane pressure and volume reduction factor (VRF).

In this way, membrane filtration of both rinsing effluents samples was tested at laboratory scale to obtain data on permeate quality, in terms of permeate flux and rejection behaviors of salt and organic solutes, as well as on fouling tendency, which was evaluated by determining resistances in series.

2. Materials and methods

2.1. Characterization of real rinsing dyes effluents

The two samples were collected from rinsing baths of SITEX, the tunisian dyeing, gluing, and finishing company, which specializes in the dying of denim fabric (jeans) using indigo and/or sulfur dyes.

These two real effluents correspond to the rinsing waters after fixation of both indigo blue and sulfur black dyes on the textile fibers. Both of these two dyes are commonly used in the cotton industry.

Different dyes (vat and sulfur), chemical substances such as detergents, salts, auxiliaries (e.g. surfactants and emulsifiers), and caustic soda are used in the factory dyeing process. Dyeing effluent is the result of several treatments steps such as, dyeing, rinsing, neutralizing, saponification, and softening. A huge amount of additives and salt is usually used to fix dye. However, more than 40% of the dye is generally found in the effluents [29].

The dyeing process started by supplying the dye bath with dye, salt, and additives at three stages for a period of 15–60 min. This process lasted for 105 min, followed by rinsing the cotton fabric in cold water for 15 min (Fig. 1). Later on the saponification process follows by adding sandopan at 70°C for 10 min. The cotton is then washed twice, for 5 min. Finally, fabric is treated by the softener at 50°C for 10 min before the drying step [29].

The chemical structures and molecular weights of the two used dyes are shown in Figs. 2 and 3. Table 1 represents some physicochemical properties of both two dyes.

Due to the low solubility of indigo blue and the insolubility of sulfur black in water, the manufacturer generally increases their solubility by adding chemicals (such as sodium hydroxide) and by increasing the temperature that usually exceeds 70°C.

The main physicochemical characteristics of the two supplied samples are given in Table 2.

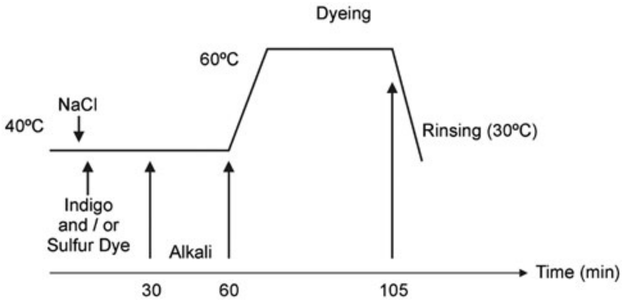

Fig. 1. Dyeing process.

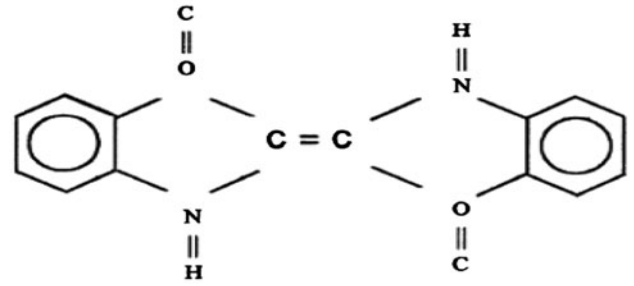

Fig. 2. Chemical structure and molecular weight of indigo blue ($M_{\text{Indigo Blue}} = 262.26\,\text{g}\,\text{mol}^{-1}$).

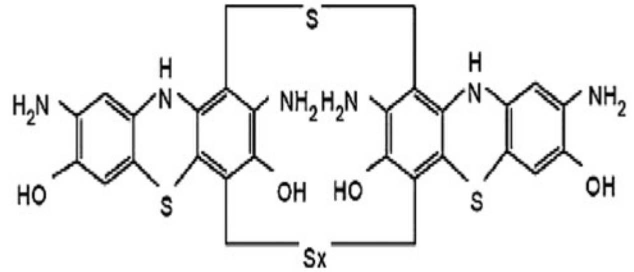

Fig. 3. Chemical structure and molecular weight of sulfur black ($M_{\text{Sulfur black}} = 657\,\text{g}\,\text{mol}^{-1}$, with $x = 3.35$).

Table 1
Indigo blue and sulfur black properties

Dye	Indigo blue	Sulfur black
Empirical formula	$C_{16}H_{10}N_2O_2$	$C_{24}H_{18}O_4N_6S_{(3+x)}$
Molecular weight ($\text{g}\,\text{mol}^{-1}$)	262	657
Melting (°C)	390–392	50–60
Water solubility	0.1 g/100 ml	insoluble
$\lambda_{\max}$ (nm)	610	630

2.2. Experimental procedure

2.2.1. NF membrane characteristics

One type of commercial NF membrane, HL flat sheet membrane was used in this study. This tested membrane was provided by GE Osmonics, Florida, USA, with an effective surface area of 140 cm^2. The HL membrane is presented by the manufacturer as one that can be used for water softening and color removing. The HL membrane was made of polyamide. The polyamide surface layer within its low volume of contact angel assures high hydrophilicity of the membrane [30,31]. The support of HL membrane was made of polysulfone. This "thin film" type membrane was less or more negatively charged in the experiments conditions.

Table 2
Characteristics of the rinsing textile wastewater samples of the SITEX

Parameters	Rinsing wastewaters	
Type of dye	Indigo blue	Sulfur black
pH	8.27	8.44
Conductivity ($\mu\text{S}\,\text{cm}^{-1}$)	1,790	1910
Turbidity (NTU)	196.09	12.78
COD ($\text{mg}\,\text{L}^{-1}$)	120	182
Color	2.43	4.44

Prior to the experiments, the NF HL membrane was soaked overnight in high purity water obtained from Millipore unit. Then, the tested membrane was prefiltered with a non-recirculated pure water feed volume of 2 L to clean any humectants materials which may be coated onto/in the membrane surface/pores.

During experiments, before using a fresh membrane, it was compacted at high pressure using pure water. The compaction pressure was checked at 15 bar.

Then, pure water permeability coefficient (L_o) was determined by measuring the pure water flux (J_o) vs. transmembrane pressure (ΔP) for NF HL membrane. The Darcy law is used to fit the pure water permeability data defined by Eq. (1):

$$J_o = L_o \times \Delta P = \frac{\Delta P}{\eta_{\text{water}} \times R_m} \tag{1}$$

with $L_{o\ \text{average}}$ (HL) = 14.233 $\text{L}\,\text{h}^{-1}\,\text{m}^{-2}\,\text{bar}^{-1}$. Where J_o is the clean water permeate flux.

Table 3 lists the NF HL membrane characteristics.

2.2.2. Membrane filtration unit

Experiments were carried out using a cross-flow filtration system depicted in Fig. 4. This system has been described in details in a previous paper [34].

A membrane sheet of 140 cm^2 was placed in the Osmonics Sepa CF II (Minnetonka, MN, USA) commercial test cell. Additionally, the SEPA CF is a cross-flow filtration module, which is the most common mode of operation in actual membrane filtration processes [35].

Feed solution was contained in a 2 L feed vessel maintained at a constant temperature of 25°C by a circulating thermostatic bath. A high-pressure pump was used to pull feed solution to the membrane cell [34].

Flow valves controlled permeate and concentrate flow and the pressure acting on the membrane in the

Table 3
Characteristics of NF HL membrane [31]

Parameters	HL
Surface material	Polyamide
Support material	Polysulfone
Type of membrane	Thin film
Cut-off ($g\,mol^{-1}$)	150–300
Surface charge	negative
Pore diameter size (nm)	0.58
pH range	3–9
Max. temperature (°C)	50
Max. pressure (bar)	40
Contact angle (°)	51.9 ± 1.0 [32]
Average roughness (nm)	10.1 ± 12.8 [32]
Isoelectric point (pH)	3.3 [33]
Zeta potential (mV) (pH = 4, t = 25°C)	−4.0 [33]

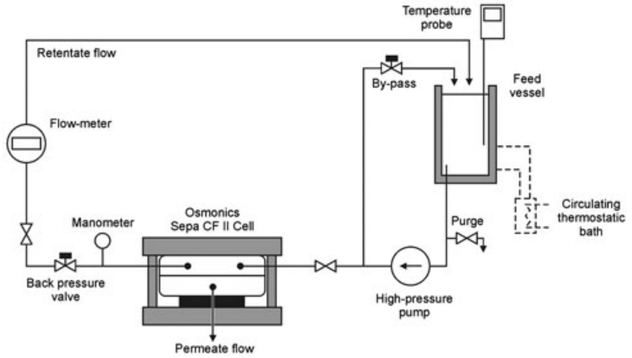

Fig. 4. Schematic diagram of the nanofiltration system setup.

test unit. Due to the high pressures required by the membranes, it was necessary to use a cooling bath to control the temperature of the feed [35].

The transmembrane pressure was controlled by a back-pressure valve (stainless steel control valve), mounted on the retentate outlet. The pressure was monitored through a digital manometer located on the outlet of the cell [34].

2.2.3. Conduction of NF experiments

After attained steady state, the experiments were performed in batch concentration mode (collecting permeate separately and recycling the retentate to the feed/retentate tank) and were performed at a constant cross-flow rate of $1\,L\,min^{-1}$, with increasing transmembrane pressures from 2 to 12 bar. A volume of 25 mL of permeate was collected for each pressure and time to estimate the permeation flux. The flux values reported later are those obtained at steady state. The permeate flux was checked frequently over longer time period [31].

During each experiment, the following parameters were determined: transmembrane pressure (ΔP) and VRF that are defined by Eqs. (2) and (3):

$$\Delta P = \frac{(P_i + P_e)}{2} - P_p \qquad (2)$$

where P_i is the inlet pressure, P_e is the exit pressure, and P_p is the permeate pressure (usually $P_p = P_{atm}$) [29,36].

The permeate was not returned to the feed tank resulting in increasing feed concentration. As the feed solution was reduced continuously in the batch concentration mode experiments, the feed quality continuously degraded.

$$\mathrm{VRF} = \frac{V_i}{V_r} \qquad (3)$$

where V_i and V_r are, respectively, the initial and the retentate volumes.

The VRF is defined as the ratio of the initial volume of the solution process and the final volume of retentate. It is an important parameter in concentration operating mode.

After each run, the membrane was cleaned according to the recommendations of the manufacturer. The membrane permeability was checked by using pure water at room temperature [29,36].

The efficiency of the different parameters removal as COD, conductivity, turbidity, and color, after each treatment, was determined using the rejection parameter determined by Eq. (4):

$$R\,(\%) = 100 \times \left(1 - \frac{X_{permeate}}{X_{feed}}\right) \qquad (4)$$

where $X_{permeate}$ and X_{feed} represent the measured parameters (COD, conductivity, turbidity, color, etc.), respectively, in the feed and the permeate streams [37].

2.3. Analytical methods

In the present work, the pH was measured with a CONSORT C832 (multi-parameter analyzer) type pH-meter that was calibrated routinely with buffer solutions in the range of the pH values used in the experiments [38].

The conductivity was measured by a Cyberscon 200 RS 232 conductivity-meter. The turbidity of the samples was measured by a Turb 555 IR type turbidity-meter.

The COD values were obtained using a Fisher Bioblock Scientific reactor COD 10119 type COD-meter. The COD is the measure of oxygen consumed during the oxidation of the organic matter by a strong oxidizing agent. COD was estimated by open reflux method. The protocol presents a method derived from the standard AFNOR T90-101 [29].

The color intensity of feed and permeate samples was analyzed by a Jenway 6705 type UV–visible spectrophotometer, for measuring the absorbance of the two rinsing wastewaters at maximum wavelength $\lambda_{\max}$ (610 nm for indigo blue and 630 nm for sulfur black).

3. Determination of hydraulic filtration resistance during NF process

The study of fouling models is significant for better understanding of the fouling mechanism and better predicting of fouling formation, and would provide a useful tool for practical design and operation.

The basic model used for determining filtration resistance occurring during permeate transport through porous membranes is similar in form to the Kedem–Katchalsky Eq. (5) derived from the irreversible thermodynamics [39,40]:

$$J_p = \frac{\Delta P - \sigma.\Delta\pi}{\eta_{\text{sample}} \times R_{\text{tot}}} \tag{5}$$

where J_p is the sample permeate flux ($\text{m}^3\,\text{m}^{-2}\,\text{s}^{-1}$), ΔP the transmembrane pressure (Pa), $\Delta\Pi$ the osmotic pressure (Pa), σ the reflection coefficient, η_{sample} the viscosity of textile sample (Pa s), and R_{tot} the total filtration resistance (m^{-1}).

Generally, the driving force and filtration resistance can be changed due to fouling and concentration polarizations over time, resulting in a decrease of permeate flux.

Ko and Pellegrino [41] explained that the filtration resistance caused by concentration polarization accounted for the reduction of the effective transmembrane pressure by increased osmotic pressure. However, in order to explain permeate flux decline with various filtration resistances including concentration polarization, the resistance-in-series model is usually used by Eq. (6) [39,42–44]:

$$R_{\text{tot}} = \Sigma\, R_i = R_m + R_{cp} + R_f \tag{6}$$

where the total filtration resistance R_{tot} is composed of each filtration resistance caused by the membrane itself, R_m (the inherent hydraulic resistance of clean membrane), concentration polarization, R_{cp}, and fouling, R_f. The effect of R_{cp} on overall resistance R_{tot} can be removed by replacing the feed solution with clean water [29,39].

The most important factor for flux decline is fouling resistance, R_f, which can be reduced by proper methods such as cross-flow filtration. The fouling can be divided into reversible and irreversible fouling according to the attachment strength of foulants to the membrane surface.

For example, reversible fouling resistance R_{rf} caused by loosely attached foulants is easily removed by a strong shear force or backwashing. R_{rf} is the external fouling resistance due to concentration polarization and deposition of solids (cake layer) on the membrane surface. This part of the external fouling can be removed by washing or cleaning the membrane with pure water, after each filtration experiment [36].

On the other hand, fouling that corresponds to the "definitive" loss of a part of the permeability is generally called "irreversible fouling."

Irreversible fouling resistance R_{if} caused by strong attachment of foulants such as pore blocking, is difficult to remove by such physical control methods [39].

R_{if} is the fouling resistance, resulting from the contributions of the external and internal fouling resistances. R_{if} is due to pore blocking and adsorption of materials onto the membrane surface and pores, and therefore, it cannot be removed by water cleaning [36].

During filtration, particles are transported to the membrane surface by permeation drag. Concentration of particles on the membrane surface reaches its maximum value after a short initial filtration and a gel and cake layer starts to form [39].

Moreover, an initial reversible fouling layer might be transformed into an irreversible fouling layer due to the formation of a strong matrix of fouling layer with dissolved materials and to compaction of the fouling layer during continuous filtration [45]. Formation of these fouling layers can be explained as a special case of concentration polarization. Consequently, the following Eq. (7) is used to describe the total filtration resistance [39]:

$$R_{\text{tot}} = R_m + R_{cp} + R_{rf} + R_{if} \tag{7}$$

The experiment procedure consisted of several cycles of membrane filtration: The first step consisted on determining the pure water permeability of each new membrane. The membrane resistance, R_m, was determined according to the following Eq. (8):

$$R_m = \frac{\Delta P - \sigma\Delta\pi}{\eta_{water} \times J_o} \tag{8}$$

In the second step, the textile wastewater was filtrated and permeate was collected. During this step, a study of the effect of transmembrane pressure ΔP on permeate flux was carried out in order to determine the total resistance according to Eq. (9):

$$R_{tot} = R_m + R_{cp} + R_f = \frac{\Delta P - \sigma\Delta\pi}{\eta_{sample} \times J_p} \tag{9}$$

In order to eliminate membrane blocking effects after textile rinsing wastewaters treatment, a step of washing was performed at low pressure. Pure water washing allowed determining the fouling and concentration polarization resistances R_f and R_{cp} according to Eqs. (10) and (11) [39]:

$$R_f + R_{cp} = R_{tot} - R_m = \frac{\Delta P - \sigma.\Delta\pi}{\eta_{sample} \times J_p} - \frac{\Delta P - \sigma\Delta\pi}{\eta_{water} \times J_p} \tag{10}$$

$$R_f = \frac{\Delta P - \sigma\Delta\pi}{\eta_{water} \times J_{washing}} - R_m \tag{11}$$

where $J_{washing}$ represents the permeate flux after the pure water washing step. The previous washing step allows us to determine the total fouling resistance $R_f = R_{rf} + R_{if}$, after textile rinsing wastewater treatment [39].

In order to determine separately, the reversible fouling resistance R_{rf} and the irreversible one R_{if}, it was necessary to add a second intensive washing step which allows us to eliminate the reversible fouling effects and to determine R_{if} value according to Eq. (12) [29,39]:

$$R_{if} = \frac{\Delta P - \sigma\Delta\pi}{\eta_{water} \times J_{intensive\ washing}} - R_m \tag{12}$$

The R_{rf} can be deduced using Eq. (13) [39]:

$$R_{rf} = R_f - R_{if} \tag{13}$$

4. Results and discussions

4.1. Application of NF in two textile rinsing waters treatment

Using NF HL membrane previously characterized, the two textile rinsing waters (indigo blue and sulfur black) were treated by NF process in two different operating conditions: the first condition consisted on studying the influence of the operating pressure on permeate flux ($\Delta p = 2$; 4; 6; 8; 10; and 12 bar) and the second one consisted on keeping a constant optimal operating pressure ($\Delta p = 10$ bar) and studying the effect of VRF.

Permeate flux is an important parameter in the design and economical feasibility analysis of membrane separation processes.

Fig. 5 illustrates the permeate flux values with transmembrane pressure for pure water and dyeing rinsing waters (indigo blue (Fig. 5(a)) and sulfur black (Fig. 5(b))).

From this figure, it is clear that there is an increase of permeate flux with increasing driving force (ΔP), which indicates that the operation is in the pressure–controlled region.

This increase has been explicated by Chakraborty et al. [46], who showed that with an increase in operating pressure (at a fixed feed concentration), the driving force across the membrane increases leading to an enhancement of permeate flux [36].

As mentioned in the Spiegler–Kedem model [47], the water flux of NF membrane is in a linear relationship and in direct proportion to the transmembrane pressure, which is the difference between operating pressure and osmotic pressure [48].

The measured fluxes corresponding to the two rinsing waters are lower than the pure water fluxes obtained after membrane compaction. This is typically due to the osmotic pressure difference induced by the separation but also to the higher viscosities of the permeating solutions compared to water [1,49].

Fig. 5 shows that the lowest flux values corresponding to the two rinsing waters were obtained at the alkaline conditions. Effect of pH could be explained by the effects of dye aggregation and related influence on the dye hydrophobicity under different pH conditions.

In fact, likewise, Koyuncu et al. suggested that, under alkaline conditions, the formation of a strong and stable dye–salt complex will result in an increase in dye hydrophobicity on membrane surface [50]. Due to the increase in dye hydrophobicity, adsorption of dye molecules on membrane surface increased and low flux values were obtained [51].

From Fig. 5(b), we also note that the permeate flux decreases more and the deviation is much lower and smaller in the case of sulfur black dye rinsing water. This is related to the difference between molecular weights and spatial configuration of the two studied dyes.

Indeed, the high molecular weight cut-off (MWCO) of sulfur black dye ($M_{Sulfur\ black} = 657\ g\ mol^{-1}$) causes

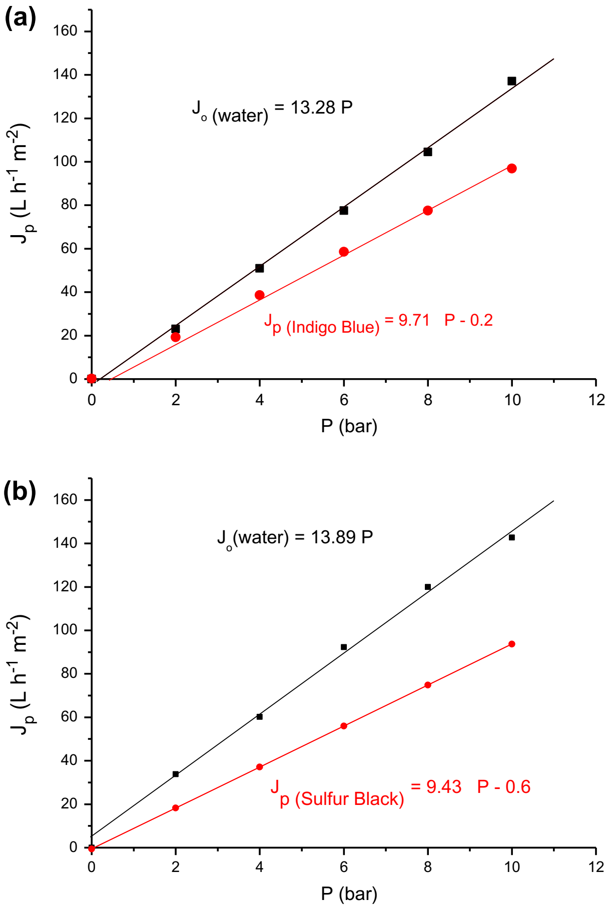

Fig. 5. Effect of transmembrane pressure on pure water and rinsing water fluxes a) Indigo blue b) Sulfur black.

higher pore blocking by feed components and leads to higher flux decline. As a result, higher pore blocking by components of NF HL membrane may be possible reason for higher flux decline of this NF membrane. However, the pore plugging of a NF membrane does not depend only on the molecular weight of the dye [26].

Moreover, this can be also explained by the difference between the feed solution compositions. In fact, sulfur black wastewater is more loaded with salts (higher conductivity) and organic matter (higher COD) than water indigo blue dye water. This charge could be responsible for the membrane pore blocking, and consequently membrane fouling, which was suspected to be more pronounced when treating the sulfur black rinsing water.

Bruggen et al. [52,53] reported that the water flux decreases more when an organic compound is present that adsorbs on the membrane surface; the more adsorption, the more flux decline [54].

Kilduff et al. [55] showed that the presence of organic matters caused greater flux decline resulting from a combination of cake resistance and increased rejection of NaCl by negatively charged organic and inorganic functional groups [54].

Additionally, the increased dye adsorption on membrane surface results in an increase in the resistance to water permeation and consequently, a decline in permeate flux and thus a decrease of water permeability. Therefore, the water permeability declines continuously with the increasing transmembrane pressure [56].

Schafer et al. [57] reported that the pressure had a strong effect on aggregates deposition and flux. The flux decline cannot be recovered, indicating that the pressure has significant role in the reduction of flux and foulants deposition rate on the NF membrane processes [54].

Al-Amoudi et al. [58] reported that when the operating pressure was increased gradually in order to maintain the NF recovery, organic fouling took place on the NF membrane surface [54].

It is to point out that, at low transmembrane pressure of 2 bar, the water permeability to the dye solution is quite close to the distilled water, especially in the case of indigo blue, as shown in Fig. 5(a). This means that fouling is negligible under such conditions, which was confirmed by the fact that nearly no adsorption of dye was observed on the surface of the filtrated membrane.

The efficiency of membrane filtration processes for the removal of the two studied rinsing dyes waters (indigo blue and sulfur black) was estimated based on rejection measurements.

A sensitivity analysis showed that the economics of the process are very dependent on the energy consumption of the NF process, and the energy consumption can be directly related to the applied transmembrane pressure. Consequently, optimization of the transmembrane pressure was performed. Previous experimental results using NF HL membrane suggested 10 bar as an optimal transmembrane pressure for the NF experiments [59]. For this reason, influence of VRF on permeate rejection was studied on keeping an optimal constant operating pressure ($\Delta p = 10$ bar).

Several permeate samples were collected (25 mL) at each experiment and then analyzed by various analytical techniques.

The rejection changes of pollution indices during VRF experiments, after the two studied rinsing waters treatments, are presented in Fig. 6. It can be seen that the rejections were increased during VRF experiments. The highest rejection was at a maximum value of VRF equal to 1.45.

NF HL membrane showed high removal efficiency for all studied parameters, excepting in salt rejection.

On the other hand, the tested membrane presented various removal efficiencies for the different studied parameters.

Similarly, a slight variation in turbidity rejection rate of both treated rinsing waters with NF was observed as a function of VRF.

As can be clearly seen from Fig. 6(a), it is found that NF HL membrane demonstrated excellent turbidity removal regardless of the membrane pore structure and samples characteristics. The highest turbidity removal efficiency was 99% in the case of indigo blue, while a mean value not exceeding 67% was observed in the case of sulfur black (Fig. 6(b)).

With respect to COD and color reduction, gradual rejection rates increase were observed for both treated rinsing waters. In the case of indigo blue (Fig. 6(a)), COD was rejected highly by NF HL membrane as COD reduction ranged from 16% to 100%, while the color rejection rate varied from 70% to 97%. The dye rejection was high enough to remove all color from the feed solution. However, in the case of sulfur black (Fig. 6(b)), the COD reduction and color rejection rate achieved only rejections, respectively, up to 86 and 52%.

The obtained permeates characterization after rinsing water treatment using the same HL NF membrane shows that the rejections efficiency was significantly better, when treating the indigo blue rinsing water compared with sulfur black dye solution treatment. This performance difference may be due to several phenomena that may occur during NF membrane treatment [60].

Although sulfur black dye presents the higher molecular weight (657 g mol^{-1}) comparing to indigo blue (262 g mol^{-1}), and despite NF membrane is known for higher rejection of molecular weight compounds, its corresponding rejection rates in all terms were the lowest one. Indeed, the difference between rejection rates obtained for each dye rinsing water can be partially attributed to the relative difference between particle sizes of pollutants compared to the NF HL membrane pore size.

In fact, the cut-off is connected mainly to the size of pores of the membrane, but also, it is influenced by the shape of the molecule to be filtered, by its load, by its degree of hydration, the pH, and the ionic strength of the solution to filter, the operating pressure, and the permeation flow, the elasticity and the load of the membrane.

Principally, it can be concluded that separation efficiency in terms of COD, color, and turbidity in rinsing effluents, is not only governed by sieving mechanism, due to steric hindrance, but also the rejection characteristic of NF membranes is a combination of size exclusion, electrostatic repulsion mechanisms, and adsorption.

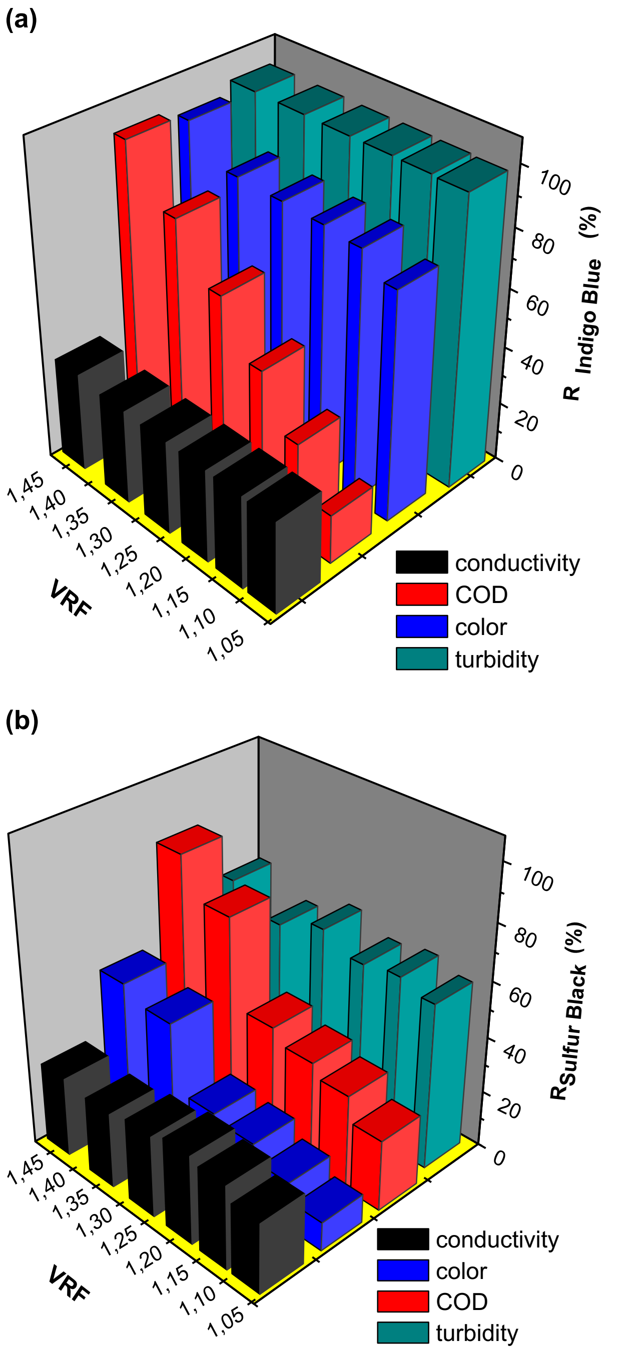

Fig. 6. Effect of volume reduction factor on conductivity, turbidity, COD and color rejections after rinsing water treatment using NF HL at $\Delta p = 10$ bar and $\theta = 25$ ℃. (a) Indigo blue (b) Sulfur black.

In previous works, it was not also found any relationship between the color retention and molecular weight of the dyes. Dye molecules can be adsorbed on membrane surface, which affects the retention because of physicochemical interactions, i.e. hydrophobic interactions (dispersion forces), polar interactions (dipole forces), and charge transfer (hydrogen bonding). The nature of the membrane material, the solute type and the solute concentration are important characteristics that allow determine the extent of dye adsorption [61,62].

At low solute concentrations, electrostatic repulsions are predominant so that high retentions are obtained [63].

Therefore, the obtained maximum rejections may be attributed to the ionization of the sulpho, amino, and carboxyl groups present in dye molecules. In fact, dye molecules have those groups as substituent bound to the aromatic rings. Depending on the pH of the solution in contact with the membrane, those functional groups could interact with the NF membrane that can be charged, containing functional groups as carboxyl, amide, and amino, increasing the electrostatic repulsion between dye molecules and membrane surface and, consequently, the color rejection [61,62,64,65].

Kosutic and Kunst [66] show that the rejection of organic compounds depends on sieving parameters (pore size and solutes). In addition to this factor, Van der Bruggen et al. [67] conclude that the polarity and charge of organic matter may influence their retention, especially when the size of the membrane pores is large enough.

Molecular diffusion is also another factor that affects rejection, as mentioned by Chellam and Taylor [68]. The ionic compounds rejection in NF occurs as a result of charge interactions between the membrane surface and ions (Donnan exclusion) [69]. NF membrane module is on solution–diffusion mechanism [70].

During VRF experiments and for both studied rinsing waters (Fig. 6), we note that the reduction in conductivity was significantly low and salt rejection does not undergo a significant change as a function of VRF. The maxima were obtained for a VRF equal to 1.42. These rejection values reached 33.69 and 28.32%, respectively, for indigo blue and sulfur black dye feed solutions.

It is generally known that UF is not effective in reducing conductivity compared to it is reported that polyamide NF which possesses nano-scale pore size coupled with negative surface charge [71]. However, salt rejection by NF membrane could be influenced by the combination of the size exclusion and diffusion control theories [70,72]. It indicated that serious membrane fouling could even occur with the ongoing of the experiment but not be detected by ordinary examination. Therefore, the judgment of membrane efficiency loss and membrane fouling simply by indication of flux decline may be inadequate. The result in Fig. 6, implies that the rejection variation of the solution conductivity might be a convenient and proper method to indicate the membrane fouling during long-run [70].

The most important membrane properties which affect the rejection are permeability, MWCO, surface charge, and hydrophobicity/hydrophilicity. In general, the size exclusion is dominant mechanism for rejection of large components such as organic compounds. The rejection will generally increase with the molecular size. Therefore, the lower salt rejection can be attributed to this fact that inorganic salt compounds that cause conductivity are considerably smaller than organic compounds of the studied dyes rinse waters. Hence, these compounds pass easier through to the membrane pores [26].

Other possible interpretation can also be taken into consideration: anionic salt particles will have anionic repulsion between them and the carboxyl groups of negatively charged NF membrane. This can affect the solution conductivity.

Salt charged molecules rejection in NF is typically explained by a combination of size effects and electrostatic repulsion between the anionic particles of salt solute and the negatively charged membrane [49].

This sequence can be explained in terms of both the effects of steric hindrance and electrostatic action, which affect the rejection characteristic of the charged NF membranes to charged solutes [56,67].

It is well-known that charge repulsion effects become less important at increasing bulk ionic concentrations and/or decreasing membrane charge density. This phenomenon is generally explained by assuming a Donann equilibrium between the bulk solution and the membrane [49].

Due to the complexity of the solutions investigated, other mechanisms could be, directly or indirectly, involved in the rejection of salts and dyes [49].

It is known from the literature that most dye effluents are saline solutions, and the type and concentration of the salts that present in the dye effluents will affect the rejection of dye molecules as well as the permeate flux [56].

Recently, Badani et al. [73] investigated the effect of sodium chloride concentration on the removal of Acid Orange G. They found that the presence of salt increases the dye rejection but a great loss in the flux is observed as the concentration of NaCl increases [1].

It is evident also that inorganic colloids bounded by sticky organic fouling layer accumulated on the membrane surfaces might enhance the fouling layer formation of the NF HL membrane [74].

However, in the literature, there are no studies covering transport models, which is specifically polyvalent for colored textile wastewaters. The salt transport mechanism in NF is complicated in the organic dye and other compounds presence, and this makes the transport analysis much more difficult [21].

4.2. Evaluation of membrane fouling by the model of resistances in series

According to the results found previously (paragraph 4.1), in terms of permeate flux and rejection; it seems to NF HL membrane sensitivity to fouling was more pronounced after sulfur black dye water treatment. To confirm this hypothesis and in order to specify which resistance contributed to flux decline, the various filtration resistances were determined for NF HL membrane using the resistance in series model. The different filtration resistances values are illustrated in Table 4.

Table 4 shows that in the case of the NF HL membrane, the intrinsic membrane resistance R_m is the dominant resistance which affects the permeate flux, and this for the two rinse waters studied. The intrinsic resistance, R_m, was observed to make the highest contribution to flux decline in NF membrane. Indeed, values of R_m/R_{tot} reached 80.4 and 87.64%, respectively, for indigo blue and sulfur black, for a low value of transmembrane pressure equal to 2 bar.

Membrane fouling resulting from the interaction of dye molecules with the functional groups of the membrane surface will form a foulant layer which increased hydraulic resistance to water permeation and thereby leading to a decline in permeate flux [29].

Also we note, as transmembrane pressure increases gradually, that R_{cp} and R_{tot} increase, generating lower values of R_m/R_{tot} reaching 74.46% for the indigo blue rinsing water, and 71.76% for the sulfur black wastewater, with a transmembrane pressure equal to 10 bar.

The same table shows that resistances dues to concentration polarization (R_{cp}) and to fouling (R_f) limit NF HL membrane performance. They were observed to make important contributions to flux decline. Indeed, the ratios R_{cp}/R_{tot} and R_f/R_{tot} ranged from 12 to 20%.

This observation points to the occurrence of membrane fouling. The membrane fouling resulting from the adsorption of solute and colloidal deposition on the membrane surface and inside of the membrane pores decreased the effective pores size of NF membranes [31].

Nevertheless, the study of the treatment of textile rinsing wastewaters showed that HL membrane seemed to be more sensitive to fouling caused by treating sulfur black rinsing water, since the ratios R_f/R_{tot} are higher compared with those obtained by treating indigo blue rinsing water. This result confirms the difference previously observed between the two studied rinsing waters in terms of their permeate fluxes and their rejection rates obtained.

This result is also in relation with the interactions between the NF HL membrane and the wastewater substance charges. For charged organic compounds, electrostatic attraction, or repulsion forces between the component and the membrane influence the degree of fouling.

From the same Table 4, we find that the irreversible fouling of the HL NF membrane is more important than the reversible one and this in the case of both studied samples. In the case of indigo blue rinsing water, the resistance due to reversible fouling (R_{rf}) was in the range of $0.08 \times 10^{13}\,m^{-1}$ and the one caused by irreversible fouling (R_{if}) was in order of $0.2 \times 10^{13}\,m^{-1}$. In the case of sulfur black rinsing water, these two resistances were, respectively, equal to $0.12 \times 10^{13}\,m^{-1}$ and $0.18 \times 10^{13}\,m^{-1}$, which caused an irreversible pore blocking.

This result is very important showing that a simple cleaning membrane with pure water is not sufficient to eliminate these molecules clogging and subsequently to obtain a water permeability value nearly equal to the initial water permeability value ($L_{o\ average}$ (HL) $= 14.233\,L\,h^{-1}\,m^{-2}\,bar^{-1}$), after many cycles of water cleaning. Therefore, it is necessary to perform a chemical cleaning of the membrane with sodium hydroxide and hydrochloride acid.

The irreversible fouling is mainly caused by the presence of dye molecules, salts, and auxiliary chemical used in the two rinsing water samples. These molecules, not eliminated, cause the blocking membrane HL pores [21,65].

Pore blocking result in rapid decline of flux and severe performance reduction in membrane. The condition may turn out to be critical, if necessary membrane cleaning is not performed. Other than membrane cleaning, the membrane fouling due to pore blocking can be reduced by increasing the particle size of feed. It was emphasized that pore blocking would be higher and dominant in fouling mechanism when most of the particle in the feed has the size close to the membrane pore [75].

Recognizing the fouling propensity of a feed on membranes is very important, as it will not only deepen the understanding of the fouling behavior but also the method of preventing and controlling the fouling through early diagnosis. Tang et al. [76] grouped the factors affecting the colloidal fouling propensity

Table 4
Determination of resistances in series of the membrane NF HL after rinsing dye waters treatments

Indigo blue dye rinsing water					
ΔP (bar)	2	4	6	8	10
$R_{\mathrm{m}} \times 10^{-13}$($\mathrm{m}^{-1}$)	2.71	2.71	2.71	2.71	2.71
$R_{\mathrm{tot}} \times 10^{-13}$ (m^{-1})	3.40	3.50	3.60	3.63	3.64
$R_{\mathrm{cp}} \times 10^{-13}$ (m^{-1})	0.41	0.59	0.61	0.64	0.65
$R_{\mathrm{f}} \times 10^{-13}$($\mathrm{m}^{-1}$)	0.28	0.28	0.28	0.28	0.28
$R_{\mathrm{rf}} \times 10^{-13}$ (m^{-1})	0.08	0.08	0.08	0.08	0.08
$R_{\mathrm{if}} \times 10^{-13}$ (m^{-1})	0.20	0.20	0.20	0.20	0.20
$R_{\mathrm{m}}/R_{\mathrm{tot}}$ (%)	80.40	76.58	75.40	74.80	74.50
$R_{\mathrm{cp}}/R_{\mathrm{tot}}$ (%)	11.40	15.60	16.90	17.60	17.90
$R_{\mathrm{f}}/R_{\mathrm{tot}}$ (%)	8.20	7.82	7.70	7.60	7.60
Sulfur black dye rinsing water					
ΔP (bar)	2	4	6	8	10
$R_{\mathrm{m}} \times 10^{-13}$($\mathrm{m}^{-1}$)	2.59	2.59	2.59	2.59	2.59
$R_{\mathrm{tot}} \times 10^{-13}$ (m^{-1})	3.00	3.30	3.50	3.60	3.60
$R_{\mathrm{cp}} \times 10^{-13}$($\mathrm{m}^{-1}$)	0.07	0.41	0.58	0.67	0.72
$R_{\mathrm{f}} \times 10^{-13}$ (m^{-1})	0.30	0.30	0.30	0.30	0.30
$R_{\mathrm{rf}} \times 10^{-13}$ (m^{-1})	0.12	0.12	0.12	0.12	0.12
$R_{\mathrm{if}} \times 10^{-13}$ (m^{-1})	0.18	0.18	0.18	0.18	0.18
$R_{\mathrm{m}}/R_{\mathrm{tot}}$ (%)	87.64	78.60	74.63	72.81	71.76
$R_{\mathrm{cp}}/R_{\mathrm{tot}}$ (%)	2.22	12.30	16.70	18.80	19.90
$R_{\mathrm{f}}/R_{\mathrm{tot}}$ (%)	10.10	9.09	8.63	8.42	8.30

into three categories which consisted of membrane properties (morphology), feed water composition, and hydrodynamic condition.

The parameters in these categories included particle charge, particle concentration, membrane surface charge, membrane pore size, membrane roughness, feed ionic strength, pH, temperature, feed flux, operation mode, and feed water source (dyeing wastewater itself) [75].

Due to the fact that the dye can be fixed at the fiber, accumulation of the dye molecules to the membrane then is expected. The reaction between dye and polyamides membrane was stated by Akbari et al. [1,77].

Yeung and Shang [64] found that higher charge or higher concentration of cation would enlarge the aggregates of C.I. Reactive Red 2. The authors found both acidic and alkaline conditions promote aggregation; and higher concentration of inorganic ions would result in an increase in dye aggregation. However, the dye molecules under alkaline condition are more hydrophobic [1,24].

In-depth explanations on the interactions between foulants and membranes were discussed by Dakheel et al. [1,78] and Liang et al. [1,79]. Another possible interaction for dye–membrane would be mechanical entrapment that has been mentioned by Pielesz et al. [1,80].

The dyeing bath pH also was found to affect the mechanism of fouling. Capar et al. [1,81] studied the NF of acid dyeing bath from carpet industry and found that the irreversible fouling occurs in an acidic pH of the dyeing bath. The mechanism of fouling changed to the reversible fouling in neutral pH which makes the membrane easier to clean. In another study, Koyuncu et al. [1,51] found that the cake layer formation dominated at the lower organic and inorganic compounds.

To date, there is no comprehensive investigation that has been conducted to compare the effect of all membrane materials types on the fouling potential under an equivalent study condition. Most of the researches conducted were only concentrated on a few membrane materials by selection. Thus, the understanding on the fouling potential for different types of membrane materials has yet to be explored. Hydrophobicity and permeability characteristics of membrane materials are believed to be two most important contributing factors to the fouling propensity of the membrane [75].

5. Conclusions

In the present study, the NF process was proposed for the treatment of industrial textile rinsing effluents coming from a Tunisian factory. According to the results, we can conclude that the NF process improves significantly but not sufficiently permeate quality of the studied rinsing waters. Based on permeate flux performances and pollutant rejections and regarding permeate quality in terms of color rejection, COD reduction and turbidity removal, results showed relatively high rejections and better performances were obtained for blue indigo permeate. However, salinity rejection was very low and meant poor performance as it did not exceed 35% for both studied rinsing effluents.

Though NF HL membrane exhibited greater COD and color rejections, it was still not very easy to meet the national standard values, hence this alternative was found useless in terms of parameters removal performance, especially for salt retention.

NF performance to dye aqueous solution in terms of dye retention rate and water permeability was affected by the transmembrane pressure, the feed dye concentration, as well as the presence of salts in the solution. The increase of transmembrane pressure or the feed dye concentration led to a decrease in water permeability.

When considering textile process effluents, direct NF is a feasible solution only for the most diluted effluents of rinsing operations. However, despite the low concentration of most contaminants in the investigated diluted effluents, they were not suitable for direct reuse.

The NF direct treatment of these diluted effluents faces a major problem which limits the performance from a technical point of view membrane permeate quality and life of the membrane used. This problem concerns membrane fouling, which is the most serious obstacle for the efficient running of membrane treatment plants. In fact, NF HL membrane showed sensitivity to fouling that was more important when treating dye sulfur black solution and it was irreversible for both studied dye solutions (indigo blue and sulfur black).

This investigation revealed that organic and inorganic fouling not only caused an immediate deterioration of permeate flux, because the reduction in permeate flux rates was related to the development of a fouling layer on the membrane, but also the permeate quality in terms of salt (for both dye effluents), COD, color, and turbidity (in case of sulfur black effluent) rejections during NF stage.

Rejection variation of conductivity might be a convenient method to indicate the membrane fouling during long-run. However, concentrations, physicochemical properties of possible membrane foulants, membrane characteristics, permeate flux, and rejection rate of the membranes, provided strong effects fouling characteristics in the membrane system which were closely related to their flux decline.

To ensure efficiency in NF operation, to yield higher permeate fluxes and to improve the treated effluent quality, proper pretreatment has to be carried out to minimize or avoid fouling membrane.

It is clear that NF still has to grow more in terms of understanding, materials, and process control. Regardless of reviewed drawbacks, NF is widely used in industry and special properties of the NF membranes make possible novel separations that are difficult or expensive to achieve with other, separation methods.

Furthermore, the potential of NF in industrial application is still underdeveloped because of these drawbacks. In anticipation of new insights and generally applicable solutions, using NF with the current knowledge will offer a considerable lead to more conservative players.

It can be stated that further implementation of NF will go hand in hand with the elaboration of the research objectives. In that sense, it can be expected that large steps forward will be made during the coming decade.

Symbols

NF — nanofiltration
VRF — volume reduction factor
COD — chemical oxygen demand ($\mathrm{mg\,L^{-1}}$)
L_o — pure water permeability coefficient ($\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$)
ΔP — transmembrane pressure (bar) or (Pa)
η_{water} — viscosity of pure water (Pa.s)
R_m — intrinsic hydraulic resistance of clean membrane ($\mathrm{m^{-1}}$)
J_o — clean water permeate flux ($\mathrm{m^3\,m^{-2}\,s^{-1}}$) or ($\mathrm{L\,h^{-1}\,m^{-2}}$)
P_i — inlet pressure (bar)
P_e — exit pressure (bar)
P_p — permeate pressure (bar)
Vi — initial volume of feed solution (ml or L)
Vr — retentate volume (ml or L)
R — rejection rate (%)
$X_{permeate}$ — measured parameter in the permeate stream

X_{feed} — measured parameter in the feed stream

$\lambda_{\max}$ — maximum wavelength (nm)

J_{p} — sample permeate flux ($\text{m}^3\,\text{m}^{-2}\,\text{s}^{-1}$) or ($\text{L}\,\text{h}^{-1}\,\text{m}^{-2}$)

σ — reflection coefficient dimensionless number (between 0 and 1)

$\Delta\Pi$ — osmotic pressure across the membrane (bar) or (Pa)

η_{sample} — viscosity of textile sample (Pa.s)

R_{tot} — total hydraulic resistance of the membrane (m^{-1})

R_{cp} — resistance due to concentration polarization (m^{-1})

R_{f} — resistance due to fouling particles (m^{-1})

R_{rf} — resistance due to reversible fouling (m^{-1})

R_{if} — resistance due to irreversible fouling (m^{-1})

J_{washing} — permeate flux after the pure water washing step ($\text{m}^3\,\text{m}^{-2}\,\text{s}^{-1}$) or ($\text{L}\,\text{h}^{-1}\,\text{m}^{-2}$)

$J_{\text{intensive washing}}$ — permeate flux after intensive washing step ($\text{m}^3\,\text{m}^{-2}\,\text{s}^{-1}$) or ($\text{L}\,\text{h}^{-1}\,\text{m}^{-2}$)

MWCO — molecular weight cut-off ($\text{g}\,\text{mol}^{-1}$)

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