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Color and COD retention by nanofiltration membranes

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Abstract

In the present study the application of the nanofiltration process was investigated mainly in the retention of color and chemical oxygen demand (COD) present in textile industry wastewater. Nanofiltration experiments were carried out in a pilot unit, operating in crossflow. Three different types of spiral wound membranes, DK 1073, NF 45 and MPS 31 were used simultaneously in the same unit. The results of the tests showed that for color retention, the values were around 99% for the DK 1073 and NF 45 membranes and the 87% for COD retention for the DK 1073. The permeate flux for the different wastewaters varied from 30.5 to 70 L/h.m^2. Fouling was observed in all membranes due to the accumulation of molecular species close to the filtering surface. The process was efficient and promising for the reuse of wastewater from this type of industry.

Keywords: Textile wastewater; Nanofiltration membranes; Color and COD removal; Fouling; Water reuse

1. Introduction

Nanofiltration is a process of separation with membrane and performance characteristics between reverse osmosis and ultrafiltration, in which pressure is the main driving force responsible for the separation. The rejection mechanisms of nanofiltration membranes have not yet been clearly identified [1]. The electrostatic repulsion of coions by fixed membrane charge (Donnan exclusion) is considered a part of a complex rejection mechanism [2]. Nanofiltration membranes present an asymmetric structure which consists of a filtering skin supported by a sub-layer of high porosity with thickness varying from 100 to 300 μm. Usually, these membranes have medium-sized pores ranging from 5 to 10 Å, and they are used mainly when one wants to retain solutes with molecular weights between 200 and 1000 Da. The application of this process has been investigated in the removal of organic compounds of low molecular weight [3], in pesticides [4], in the treatment of surface waters [5], in the treatment of effluents from the paper and cellulose in-

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dustries [6] and also in the removal of color from textile effluents [7].

The potential use of membrane technology in the textile industry seems to be as large as the volume of water consumed by this industry. Typically 200–400L are needed to produce 1 Kg of fabric [8].

Research has been carried out with the objective of defining an appropriate treatment for the textile industries effluents, which contain dyes or gums. Trial-and-error is generally used to test the applicability of nanofiltration and to select the membrane.

The main objective of this study was to investigate the application of the nanofiltration process, using three different membranes, to the retention of textile dye and COD in "real process wastewater", using a pilot unit.

2. Material and methods

2.1. Pilot unit and nanofiltration membranes

The experiments were performed with a nanofiltration pilot plant, as shown in Fig. 1, without recycling of the permeate. The non-circulation of the permeate simulates an industrial process in which the permeate is reused in the bathing rinse process or the dye process after the addition of dye and adjustment of salt concentration. In the textile industry, the reuse of process water offers considerable advantages in terms of the environment, economy, and industrial management of nanofiltration membranes [9].

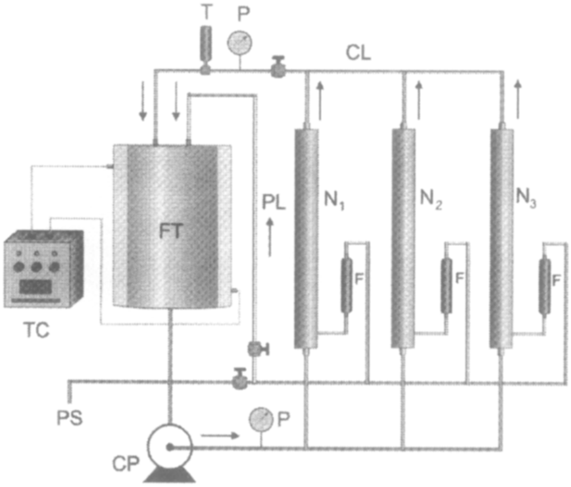

Fig. 1. Nanofiltration pilot plant schematic diagram: FT—feed tank – 550 L capacity; CP—centrifugal pump; P—pressure gauge; N_1, N_2, N_3—nanofiltration modules; F—flowmeters; CL—concentrate line; PL—permeate line; T—thermometer; TC—temperature control; PS—permeate.

In this work, three different nanofiltration membranes in the spiral wound configuration were used simultaneously in the same unit.

Characteristics of the nanofiltration membranes used in this work are shown in Table 1. Nanofiltration membranes were selected according to dye molecular weight within the 700 and 1000 Da range.

2.2. Wastewater

Table 2 displays the reactive dyes present in the textile wastewater. Their concentrations va-

Table 1
Characteristics of the nanofiltration membranes used in this work

Membrane type	Manufacturer	Material	Membrane property	Filtering area	[a]MWCO, Da	Max. operating pressure, bar
MPS 31	Weizmann	[b]NA	Hydrophobic	1.60 m^2	[b]NA	45
NF 45	Dow/FilmTec	Polyamide	Hydrophilic	2.40 m^2	200	41
DK 1073	Osmonics	Polyamide	Hydrophilic	1.77 m^2	300	40

[a] Molecular weight cut-off
[b] Not available

Table 2
Dyes present in the wastewaters

Waste water	Types of dyes, industrial names	pH wastewater
1	Remazol Yellow 3 RS Remazol BTE Red 3 BS	10.1
2	Remazol BTE Blue RN Special Remazol BTE Red 3 BS	4.6
3	Remazol Black Remazol BTE Red 3 BS	10.8

ried between 400 and 450 mg/L. Sodium chloride (10 g/L), calcium chloride (10 g/L) and sodium sulfate (15 g/L) were added to the solutions by industry to increase the fixation rate of dye to fiber. The wastewater originated from dyeing process, characterized by salts contents, typically varies between 30–80 g/L, COD deriving from additives such as acetic acid, detergents and complexing agents, suspended solids including cotton fibres, high temperature (over 60° C) and very often high pH [10].

2.3. Physical-chemical analyses

The chemical oxygen demand (COD), one of the most important parameters for the reuse of water, was determined through spectrophotometric tests, with readings performed in a DR-2000 model Hatch equipment at 620 nm, after sample oxidation with acid solution at 150° C for 2 h. The color was also determined spectrophotometrically at a wavelength of 436 nm, and the concentration was determined through standard curves of absorbance vs. concentration, using the same dyes. For pH measurements a DIGIMED DMPH2 model pHmeter was used.

2.4. Filtration tests

We carried out filtration tests using pure and wastewater produced by the fiber rinse bathing, normally performed at temperatures between 60 and 70° C. In this sense, all filtration tests were performed at 60° C. This temperature observes the maximum temperature limit for membranes, and results in low viscous solutions and better solution diffusion through the membranes. This favors higher permeate flux, and the system of water and energy reuse in the form of a membrane filtration plant allows for energy savings [10]. To maintain thermal conditions during the experiments, the processing temperature was maintained by using a thermal control device, shown in Fig. 1. A pressure of 25 bar was applied to all experiments.

2.4.1. Pure water flux

Pure water flux (PWF) was measured with distilled water. PWF tests were carried out at the beginning and the end of the run (before cleaning the membranes), to verify the intensity of the fouling.

2.4.2. Nanofiltration tests

In the nanofiltration tests, carried out in duplicate, the wastewater from the first rinse bathings (wastewater 1 and 2) and from the "washing machine" (wastewater 3) was used without recirculation of the permeate. Immediately before the nanofiltration tests, the wastewaters were passed through screen filters, with an average opening of 50 μm, for the elimination of particles that could cause damage to the membranes. For conditioning of the membranes and complete stabilization of the process conditions, the system was operated with recirculation of the permeate for at least 30 min.

In each experiment, 500 L of every wastewater were used separately. The permeate fluxes and COD retention were only determined for wastewater 3, in each reduction of 50 L in the feed tank. During the experiments raw wastewater, permeate, and concentrate samples were collected for analysis. The membranes were chemically cleaned after each run in agreement with the manufacturer's recommendations.

3. Results and discussion

A variation was observed in the parameters assessed, especially the color (we used all three wastewaters), COD, and permeate flux (only wastewater No. 3) parameters due to the type of membrane used and to the volume reduction in the feed tank.

3.1. Color retention

As shown in Table 3, all membranes, except for the poorly performing NF 45 in relation to wastewater 2, presented a good performance in the color retention analysis, varying from 85.2 to 99.8%.

This variation in the retention values obtained for wastewater 2 in relation to the membranes used, might be attributable to the fact that they present distinct cut-off values, or it may be a consequence of the different interactions among the membrane dye material. Retention levels of similar textile dyes, by nanofiltration membranes, have been reported in the literature [11,12].

Studies by Stoyko and Pencho [13] on the purification of water contaminated with reactive dye, using nanofiltration, considered a dye retention of 85–90%, and a permeate flux of 30–45 L/h.m^2, satisfactory for the reuse of the water.

Higher retention values of 97–99% were obtained in studies by Ismail [14] using nanofiltration membranes. The author observed that the use of higher transmembrane pressure values resulted in better dye retention, and that the permeate was practically colorless. Moreover, studies by A. Akbari et al. [15] showed that a wastewater pH variation from 6 to 10.3 did not affect dye retention significantly. However, it did affect the permeate flux in relation to the type of membrane used. Thus, a dye retention of over 90% can be considered satisfactory for the reuse of wastewater in textile industry processes.

3.2. COD retention

It is known that the effects related to the concentration polarization can be reduced but not avoided. As a result, a deposition of particles/macromolecules occurs on the surface of the membrane, which can lead to the formation of a “gel”, usually denominated “seconddary membrane”, with adverse effects in relation to the permeate flux due to an increase in the hydraulic resistance of the system. Depending on the membrane, particles size and superficial pores distribution profiles, a total blocking of these membranes can occur. On the other hand, the formation of this “secondary membrane” frequently results in a gradual increase in the retention of solutes during the filtration time, as can be observed in Table 3.

Despite the occurrence of a more gradual retention of COD for the NF 45 membrane, the

Table 3
Color and COD retention by nanofiltration membrane: color as a function of wastewater type and COD as a function of volume reduction in the feed tank — wastewater 3

Membrane type	[a]Color retention, %; wastewater			[b]COD retention wastewater 3, %; volume reduction in the feed tank, %			
	1	2	3	20	40	60	80
MPS 31	97.3	90.1	97.3	78	76	75	73
NF 45	99.2	78.5	98.4	45	63	70	80
DK 1073	98.6	85.2	99.8	74	78	83	87

[a] Initial concentration of dye was 450–500 mg/L
[b] Initial COD was 700 mg/L

performance of the membranes can be considered satisfactory after a reduction of 80% in the volume of wastewater 3 in the feed tank, where the COD retention ranged from 73 to 87%, which corresponded to a final COD of 189 and 91 mg/L, respectively. The COD that remained in the filtrate was possibly produced by the solutes and other oxidizable, low molecular weight materials that permeated the membrane.

A. Bes-Piá et al. [16] considered a 76–83% COD reduction in textile industry wastewater satisfactory values. The wastewater was submitted to nanofiltration combined with physical and chemical treatment, allowing for a final COD below 100 mg/L.

Guohua et al. [17] used nanofiltration membranes to show that COD retention in textile industry wastewater increased with higher pH values but was also dependent on the type of membrane.

It is also important to consider that the retention of COD may be influenced by a transmembrane pressure drop, operating temperature, concentration, and contribution of pollutants to COD [18].

Regarding the concentrate, even with a larger pollutant load in relation to the initial wastewater its later chemical or biological treatment is facilitated because it is, in general, more practical and economical to work with smaller volumes.

3.3. PWF - Pure water flux

A substantial difference was observed in the PWF before the wastewater nanofiltration (clean membrane) through the different membranes, as shown in Table 4. This difference can be attributed either to a larger or smaller hydrophilicity of the membranes (unknown factor) or to a difference in the medium diameter of its superficial pores. The obtained fluxes can be considered normal when compared with those obtained from other nanofiltration membranes available on the market.

3.4. Membrane permeate flux (wastewater)

The permeate flux is one of the most important parameters in the evaluation of the performance of a filtration system. When the level of solute retention is met, the permeate flux becomes a fundamental factor in the optimization of the process. It is also fundamental to make it compatible with the industrial reality. The higher the permeate flux, the lower the filtration area necessary for a certain amount of solution to be processed.

Table 4

Wastewater flux and PWF before and after the nanofiltration experiments; transmembrane pressure: 25 bar; temperature: 60° C

Membrane type	[a] PWF, L/h.m^2, after 2 h filtration.	[b] Wastewater permeate flux, L/h.m^2; volume reduction in the feed tank, %				[c] PWF, L/h.m^2, after 2 h filtration
		20	40	60	80	
MPS 31	70	70	67	65	63	68
NF 45	150	47	43	38	30	109
DK 1073	190	73	66	57	45	123

[a] Before wastewater nanofiltration
[b] Wastewater 3
[c] After wastewater nanofiltration

Usually, a permeate flux within the 30–60 L/hm^2 range is considered acceptable in terms of cost-effectiveness for nanofiltration processes at pressures ranging from 15 to 30 bar. Stokyo and Pencho [13] reported that a 30–45 L/hm^2 flux is viable for purifying processes of water contaminated with reactive dyes. Ismail Koyuncu et al. [19], while assessing cost-effectiveness, showed that payback for the cost of nanofiltration units for the reuse of textile industry wastewater, operating with an average permeate flux of 10 L/hm^2, can be obtained in less than 2 years.

During the nanofiltration processing of wastewater 3, a decay in the permeate flux was observed together with a reduction in wastewater volume in the feeding tank, as shown in Table 4. This permeate flux behavior is expected and is due to an increase in the solution viscosity and the total resistance of the system, represented not only by the resistance of the membrane, but also by fouling. The fouling effect is considered an additional resistance resulting from adsorption, concentration, polarization, and particles and solute deposition by convection [9].

Since the osmotic pressure is directly related to the molecular weight and the concentration of the chemical species, it needs to be considered in this case as a reducer of the permeate flux. Dyes and salts used by the textile industry have low molecular weights and during the nanofiltration process they accumulate close to the membrane surface, increasing the osmotic pressure, which reduces the effect of the mechanical pressure. In this experiment we did not measure the osmotic pressures of wastewater.

It was observed that the membranes were colored after nanofiltration. This happens because the dye molecules are intended to attach strongly to a surface, which can be disadvantageous for fouling effects [20], hence a reduction in the permeate flux is observed [11].

Regarding the performance of the nanofiltration membranes used, it can be seen from Table 4 that the MPS 31 and DK 1073 membranes showed larger permeate fluxes.

Immediately after the nanofiltration, the PWF's of the membranes were determined to verify the intensity of the fouling before the procedures of chemical cleaning. These results also are shown in Table 4. A significant increase in the permeate flux (with pure water) was observed for the NF 45 and DK 1073 membranes after the nanofiltration process. The MPS 31 membrane, in spite of presenting a smaller PWF before the nanofiltration, gave a positive performance in the wastewater nanofiltration, and it practically returned to its initial flux after just the passage of pure water. These results show that this membrane presents a larger resistance to fouling, probably due to the medium size of its superficial pores, smaller adsorption of the dyes used, and also as a consequence of a smaller physical-chemical affinity between these and the hydrophobic material used to prepare the membrane. After the chemical cleaning, the PWF of all the membranes were restored.

In general, because hot water from the reuse system is used, the time for heating it in the dyeing apparatus is reduced. Therefore, the cycle time for a dyeing can be reduced and, consequently, the capacity of the existing dyeing equipment is increased [10].

4. Conclusions

- We can consider that the nanofiltration process, with the membranes and the conditions used, proved to be efficient for the retention of dyes, COD and color present in textile wastewaters.
- The process allowed the production of a permeate with great reutilization possibilities, and the permeate fluxes can be con-

sidered compatible with the industrial reality.

- In a general sense, membrane fouling was not severe and occurred mainly due to the accumulation of dye and other organic materials on the membrane surface. This accumulation, in its turn, leads to a permeate flux reduction during the process.
- With the exception of COD removal, the membrane MPS 31 showed the best performance in terms of color removal, permeate flux, and fouling resistance.
- Taking into account the great amount of water used by textile industries and the expectations of an increase in the price of this resource in the near future, membrane technology represents a promising method that could be used by the textile industries in the reuse of wastewaters.

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