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Membrane separation process for the treatment and reuse of bath dye effluents

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ABSTRACT

The main purpose of this work is to study the effect of sodium chloride concentration on the removal by nanofiltration of anionic dyes in synthetic colored wastewaters and to characterise some main performances and properties of nanofiltration membranes of different properties. Membranes Sepa DK and NF90 were used for the study and were operated at constant trans-membrane pressure. The anionic dyes, Direct Red 80 (1373 g/mol) and Acid Orange G (452 g/mol), were used at a fixed dye concentration for different salt concentrations. Results indicated that effects of pH, concentrations of salt have a role on the permeate flux and dye retention for single and mixed salt dye solution. An interesting result is that retention of Orange G is enhanced and becomes high (96%) in the presence of salt. NF 90 shows a better salt rejection than Sepa DK, for the same salt and dye concentrations. The Orange G retention increases when the pH decreases from 9 to 3. For NF90, Orange G retention is about 98%, whatever the pH. NF90 achieves the higher salt retention than Sepa DK, however, a great loss in the permeate fluxes is observed as the concentration of NaCl increased.

Keywords: Nanofiltration membrane; Dye removal; Water reuse; Mineral salt

1. Introduction

Textile processing industry generally requires significant amount of process water for cleaning, rinsing and dyeing purposes. This industry generates a very variable wastewater quality that depends on process step and on dye and textile material (cotton, synthetic fabric, silk etc). Effluents from printing and dyeing industry are characterized by high content of dye stuff, of salts and high concentration of dissolved solids (organic and inorganic). Source of the inorganic pollutants in the dye houses are the auxiliary chemicals which are used to increase the fixation rate of the dye to fiber. Cotton, which is the most widely used fiber, is a substrate that requires a large amount of water for processing. For example, to dye 1 kg of cotton with dye, 30–60 g of dyestuff, and 70–150 L of water are required [1, 3]. Therefore textile industry is a prime candidate for the development of intensive water recycling and minimization of related polluting emissions.

Many processes have been studied to treat textile wastewaters [4]. Biological treatment by activated sludge offers high efficiencies in chemical oxygen demand (COD) removal, but does not completely eliminate the colour of the water, and frequently operational problems such as bulking appear. Chemical oxidation by ozone or a combination of UV-radiation and ozone or O_3-H_2O_2 has a great interest, but decolorization of wastewater by ozone alone is not always accompanied by a significant reduction of the COD [4, 5].

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Membrane processes have the potential to remove the dyestuff and allow reuse of the auxiliary chemicals used for dyeing and to concentrate the dyestuffs and auxiliaries and produce purified water [6]. Ultrafiltration (UF) can be applied to recover auxiliary chemicals and sizing agents from the desizing effluents or high molecular weight substances and insoluble dyes from dyeing effluents. Nevertheless, UF does not remove low molecular weight and soluble dyes [7–9]. Nanofiltration (NF) allows the separation of low molecular weight organic components (200–1000 molecular weight) such as acid and direct dyes textiles and divalent ions. NF can also be used for desalination and the concentration of aqueous dye solutions in textile dye manufacturing. For membrane processes, the major problem is the decline of permeate flux due to the accumulation of molecules on the membrane surface. This accumulation, known as concentration polarisation, leads to an increase of membrane fouling [10–12]. Noel et al. [7] have evaluated the performance of two types of membrane (NF45 and BQ01) for direct dye solution. Electro-nanofiltration performance was quantified for different potentials and concentrations. An electric field was found to be efficient in reducing fouling for both membranes studied. They also noticed that direct dye solution-fouling changes the NF45 membrane into a reverse osmosis membrane, while the permeability of the second membrane was enhanced.

Ratana et al. [13] have studied three nanofiltration membranes for the treatment of effluents containing salt and reactive dye. ES20, LES90 are negatively charged membranes and NTR729HF is neutral. It was observed that the ES20 and LES90 membranes can effectively retain colour, producing a suitable permeate for reuse. They also noted that for feed containing salt and dye, the transmembrane pressure difference is enhanced, resulting in a substantial flux decline.

The objective of this work is to study the effect of NaCl concentration on the removal by Nanofiltration of anionic dyes in synthetic colored wastewaters and to evaluate performances of two nanofiltration membranes in terms of flux permeate, dye/salt retention and membrane fouling. To simulate textile, wastewater we considered fairly high concentrations of salt.

2. Materials and methods

2.1. Materials

2.1.1. Membranes

Two types of flat-sheet nanofiltration membranes were used: Sepa DK (GE Water and Tech) with an approximate molecular weight cut-off of 150–300 Da, and NF 90 (Filmtech) with a molecular weight cut-off of 200 Da. These membranes are both thin-film composite with an active layer made of polyamide.

Membranes permeability was determined through filtration tests with pure water at various pressures (Table 1).

2.1.2. Dye aqueous solutions

Two different anionic dyes were chosen for this study. They present different molecular weight and charge properties. The anionic dyes, Direct Red 80 (1373 g/mol) and Acid Orange G (452 g/mol) provided from Sigma Aldrich were used in this study. Model dye solutions of different properties were prepared by dissolving dyes in pure water without adding any auxiliary compounds. Sodium chloride (NaCl) and pure water were also used in the preparation of different dyes and NaCl concentrations. The characteristics of these dyes are shown in Table 2.

2.2. Experimental system

Fig.1 presents the diagram of the batch cell operation. Experiments were performed at constant transmembrane pressure in a cylindrical stirred cell of 500 mL total capacity, provided by Polymem. The nitrogen gas was applied as a pressure source**.** The active membrane area was 44.2 cm^2. Permeates were collected every ten minutes at the outlet. The dye solutions were prepared at a fixed dye concentration for different salt (NaCl) concentrations ranging from 3 to 30 g/L.

2.3. Analytical methods

The concentration of dye in feed, permeate and retentate was determined by visible-UV spectrophotometry (V 530) for the dye solution at the maximum absorption wavelength.

The concentrations of dyes were calculated from calibration curves established previously at wavelengths of 475 and 502 nm respectively for dyes Orange G and Direct Red 80.

Sodium chloride concentration was obtained by measuring conductivity of the aqueous solution by a conductivity Meter (LF 358). The pH Meter is of type pH 539.

Table 1
Permeability of the nanofiltration membranes.

Membrane	Permeability [L/m^2.h.bar]	Isoelectric pH
Sepa DK	5–6.5	4
NF90	11–12	4

Table 2
Characteristics of dyes.

Dye (C.I.)	M.W. (g/mole)	Structure	Characteristics	Chemical formula	Charge
Direct Red 80	1375	Polyazo	Anionic, soluble	$C_{45}H_{26}N_{10}Na_6O_{21}S_6$	–6
Orange G	496	Monoazo	Anionic, soluble	$C_{16}H_{10}N_2Na_2O_7S_2$	–2

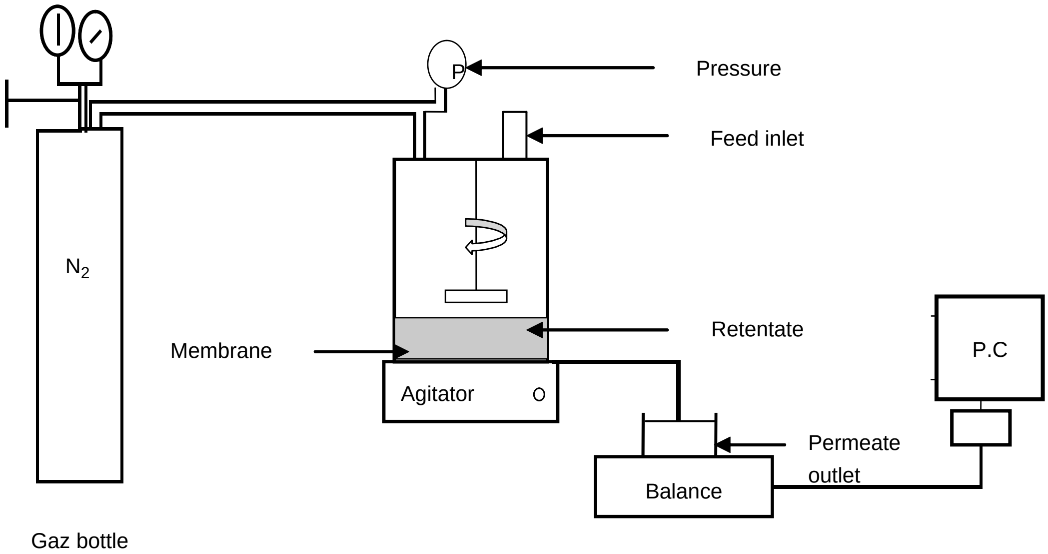

Fig. 1. Schematic diagram of nanofiltration set-up.

3. Results and discussion

3.1. Calculations

The apparent dye retention is defined as: $R = 1 - \frac{C_{per}}{C_{ret}}$, With, C_{per}: permeate concentration [mg/L.], C_{ret}: retentate concentration [mg/L.], retentate concentration [mg/L.], The concentration factor is given by: $FC = \frac{C_{ret}}{C_0}$, with C_{ret}: concentration of retentate [mg/L], C_0: Initial concentration [mg/L]

3.2. Effect of pH

3. 2. 1. Effect of the pH on the dye retention

pH is a very important factor for the NF permeation for a dye bath. The pH values of 3, 6 and 9 were studied. The effect of initial solution pH on the retention of Orange G and Direct Red 80 are presented for operation at fixed and identical pressure and stirring rate for the two membranes. According to Fig 2(a), Orange G retention by Sepa DK is significantly higher at pH3 (between 98% and 99%) and decreases slightly when the pH increases from 3 to 9. The polyamide membrane Sepa DK has a cut-off of around 150–300 Da and an isoelectric point (I.P) of 4.

The occurrence of an isoelectric point means that at lower pH than the I.P., the membrane is positively charged and vice-versa. Hence, in the case of membrane Sepa DK, the membrane carries positives charges (NH_3^+) at pH = 3 and negatives charges (COO^-) at pH = 6. Thus flux decline and high retention for Orange G at pH = 3 can be attributed to the high affinity of the anionic dye for the polyamide active layer and electrostatic interactions between the membrane surface and solution dye which lead to surface modification of the membrane.

At pH = 6 and 9, negative charges have a repulsive effect on dyes, retention declines slightly, the surface membrane becomes more hydrophilic. For NF90 (Fig.2(b)), Orange G retention is about 98%, whatever the pH. The structure of the active layer of this membrane is different from that of the Sepa although with the same polyamide thin composite. NF90 consists of a fully aromatic polyamide active layer [14]. Nghiem et al. [14] reported that the pore radius of NF90 is very smaller. The membranes Sepa DK and NF90 retain totally the Direct red 80 (1372 Da) at the three pH, because molecules are bigger than the pore size.

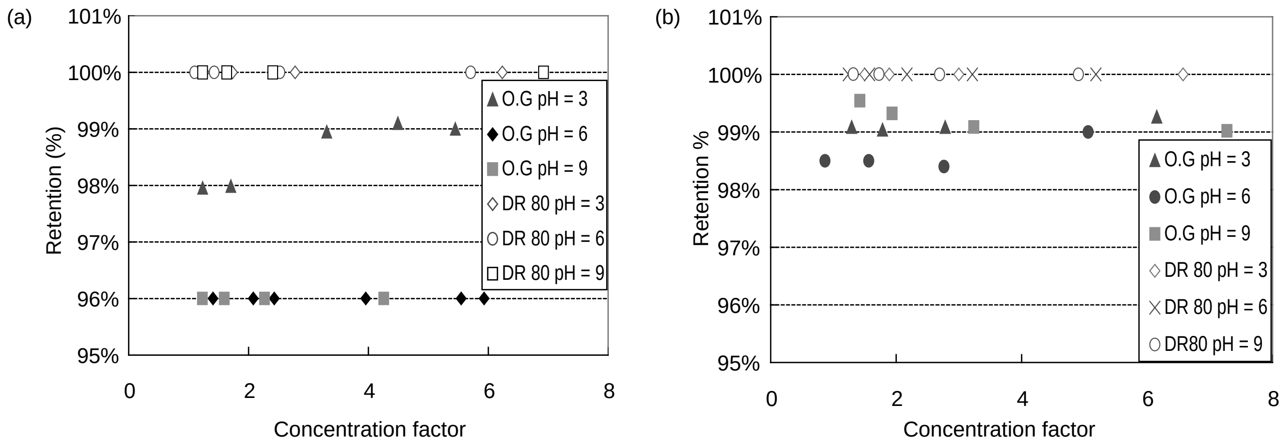

Fig. 2. Effect of pH on the dye retention versus concentration factor: (a) Sepa DK, (b) NF90, ([dye] = 100 mg/L, ΔP = 6 bars, T = 25°C).

3.2.2. Effect of the pH on relative flux

The effect of initial pH of the solution on relative flux (J/J_0) versus cumulative volume of Orange G is given in Figs. 3(a) and (b) for Sepa DK and N

Figures 3(a) and (b) show that the relative flux declines slightly when pH decreases from 9 to 3.

For the same filtrated volume, the relative flux was 85% at pH = 3 and about 89 and 93% at pH 6 and 9 respectively, for the Sepa DK. For the NF90 the relative flux was about 75% at pH = 3 and 85 at 90% at pH = 9 and 6 respectively. The increase in relative flux at pH = 9 is most likely caused by the increasing negative charge of the membrane repulsing the negative charged Orange G. The increase hydrophilic sites would cause the increase of permeate flux. Similary, Qin et al. [15] reported that feed pH significantly affected the flux permeate pH and ion retention due to change of membrane surface.

3.3. Effect of salt

3.3.1. Effect of concentration salt on the salt retention

Filtration was then operated with solutions containing 3, 10 and 30 g/L of NaCl at a constant pressure of 6 bars. For each test, conductimetry measurements were used to follow the evolution of the concentration of NaCl in the permeate and in the retentate versus time.

As showed in Figs. 4 (a) and (b), relative permeate flux is directly related to the osmotic pressure differences. Osmotic pressure differences increase with increasing salt concentration which decrease the driving pressure and thus the permeate flux. The permeate flux reductions after 2 h of filtration were about 80%, 85% and 90% for 3, 10 and 30g/L of NaCl respectively for NF90. Whereas for the Sepa DK, the permeate flux reductions were only of 15%, 20% and 40% respectively corresponding to 3, 10 and 30 g/L.

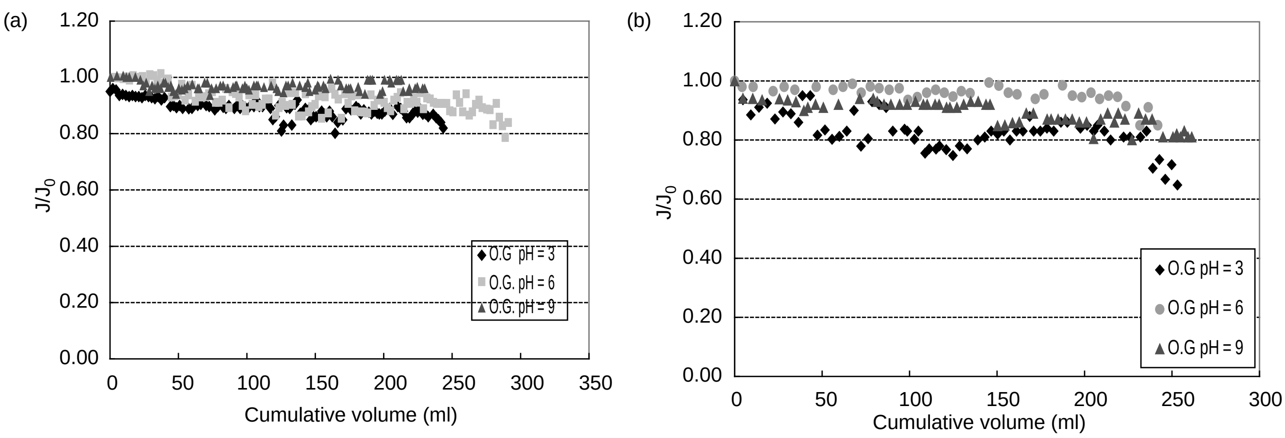

Fig. 3. Effect of pH on the relative flux (J/J_0) versus cumulative volume: (a) Sepa DK, (b) NF90 ([O.G] = 100 mg/L, ΔP = 6 bars, T = 25°C).

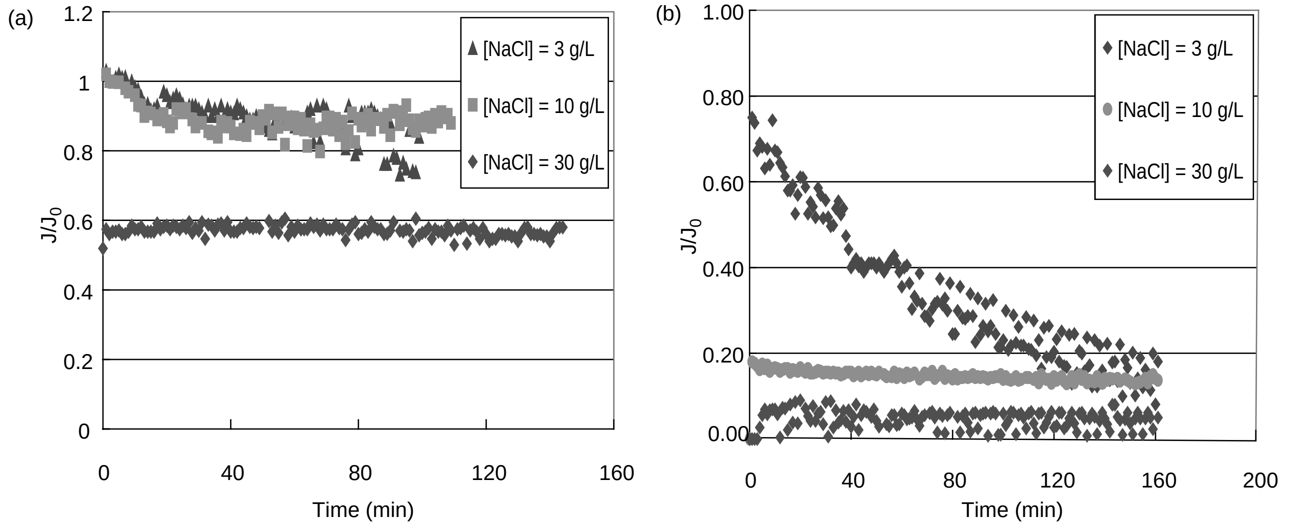

Fig. 4. Effect of concentration NaCl on the NaCl retention versus time: (a) Sepa DK, (b) NF90, ΔP = 6 bars, T = 25°C, pH = 6.

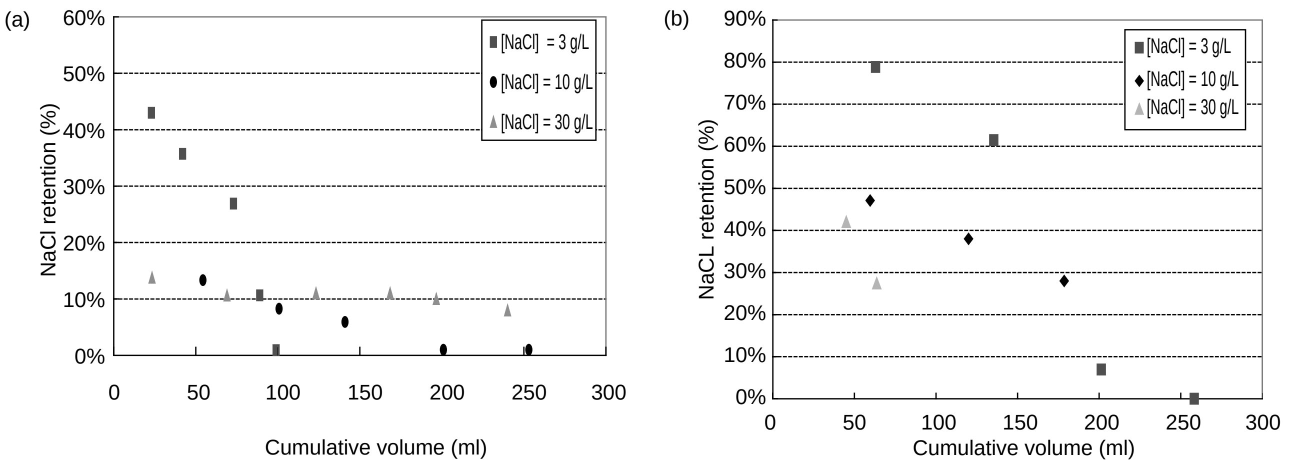

Fig. 5. Effect of concentration NaCl on the NaCl retention versus cumulative volume: (a) Sepa DK, (b) NF90, ΔP = 6 bars, T = 25°C, pH = 6.

The evolution of the NaCl retention for different salt concentrations is presented in Fig. 5(a) and (b) for Sepa DK and NF90 respectively. As expected, the NaCl retention decreases as the concentration of salt increases, for the two membranes. When the concentration of NaCl is high, electrostatic repulsions at the membrane wall are weak and the salt passes easily through the membrane. Given a fixed charge density of the membranes, the Donnan exclusion, however, becomes less effective with increasing salt concentration in the feed. In contrast a decrease in salt concentration induces an increase in the retention. When the concentration of NaCl is low, strong electrostatic repulsions occur near the membrane and whence salt is retained. The same phenomena have also been observed by Van Der Bruggen et al [16].

NaCl was almost totally retained by NF 90, retentions varying in the range 50–80%, when the salt concentration was lower than 10 g/L. The smallest salt retentions were noticed for the Sepa DK, retentions varying of 35%, 10% and 7% when the NaCl concentration increases from 3 to 30 g/L.

3.3.2. Effect of salt concentration on the permeate fluxes and dye retention

Experiments were then carried to determine the performance of the membranes for the mixture salt-dye. The concentration of dye in the feed was 100 ppm for the three concentration of NaCl considered. The permeate fluxes are lower than those obtained from the feeds

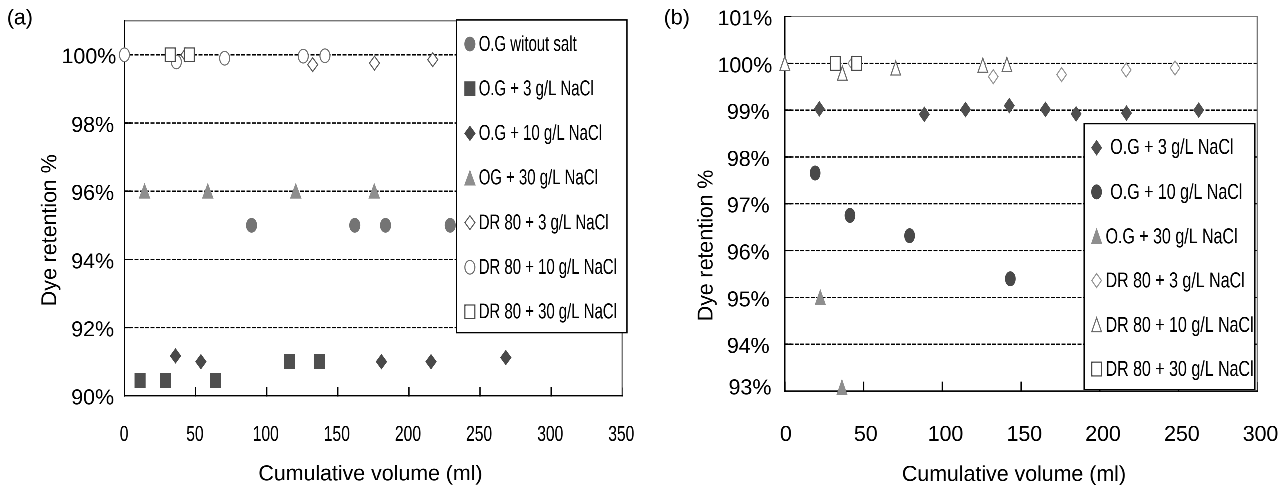

Fig. 6. Effect of NaCl concentration on the dye retention versus cumulative volume: (a) Sepa DK, (b) NF90, ΔP = 6 bars, T = 25°C, pH = 6.

containing only salt or dye. It is most likely that the Sepa DK and NF90 membranes experience the superimposition effects of transmembrane osmotic pressure and dye concentration polarization. The Direct red 80 retention (Fig. a and b) was 100% in all cases whatever the NaCl concentration. The retention is controlled by a sieving mechanism.

However concerning Orange G retention, it is interesting to observe that, in presence of salt, it varies in a different way depending on the membrane. Indeed the presence of high salt concentration has an interesting impact on the Orange G retention rate, for membrane Sepa DK. For this membrane, when salt concentration is enhanced up to 10 g/L Orange G retention decreases. But for a concentration of salt of 30 g/L this membrane exhibits the higher Orange G retention rate (96%) compared with the one observed with the salt free feed which is about 95% (Fig. 6(a)). A higher salt concentration (30 g/L) promotes dye aggregation, i.e. as the concentration of NaCl increases the degree of dye aggregation increases. Dye aggregation near the surface membrane, is promoted by a high ratio relative molecular mass to ionic group content.

For the NF90 (Fig. 6(b)), the Orange G retention rate decreases slightly when NaCl concentration increases. The retentions remain high and varied between 95% and 99% when the salt concentration decreases from 30 to 3 g/L. This might be explained by the smallest pore size of NF90 membrane [17].

4. Conclusion

In this study, the feasibility of nanofiltration of bath dye effluents was investigated. The effect of NaCl concentration and initial solution pH on removal of anionic dyes was evaluated in order to characterise some main performances of Sepa DK and NF90 nanofiltration membranes.

The evaluation of the salt at high concentration effect showed an interesting and reproducible result for Sepa DK: retention of Orange G is enhanced and becomes high (96%). Salt retention rate decreases with increasing salt concentration and when the NaCl concentration achieves 30 g/L, the salt retention rate decreases from 14% to 8% for Sepa DK membrane and from 47 to 27% for NF90 membrane. The dyes retentions remain constant at all pH for NF90. Orange G retention was affected by initial solution pH, the retention rate increases when pH decreases. Direct red 80 was 100% retained and produced a permeate which is suitable for water reuse.

The Sepa DK can effectively retain colour, producing a permeate with reuse possibility in the bath dye. At the same time, it allows to achieve a significantly higher flux in presence of salt. Although the NF90 membrane presents the high dye retentions, suffers from flux decline, caused by the transmembrane pressure.

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