IMPROVEMENT OF TEXTILE WASTE WATERS TREATMENT BY COMBINATION OF ULTRAFITRATION AND NANOFILTRATION MEMBRAPROCESSES

K. Ksontini [a], E. Ferjani [b *], M. S. Roudesli [a]

[a] *Département de Chimie, Faculté des Sciences de Monastir, Bd de l'Environnement, 5000 Monastir, Tunisle*
[b] *Institut Supérieur des Sciences et Technologies de l'Environnement de Borj Cedria*

(Reçu le 16 Novembre 2004, accepté le 3 Février 2006)

ABSTRACT: The present work deals with the preparation and the characterization of cellulose acetate membranes for the textile water treatment by ultra (UF) and nanofiltration (NF). The evolution of flow was analyzed and treated by a comparative study of the pH and time effects on the performances regeneration of prepared membranes. The carried out study made it possible to follow the pollution indicators during UF-NF. Indeed, we contributed to the elimination of 95% of the CDO.The proportions obtained after treatments are in conformity with the imposed standards.

RESUME : Ce travail est en rapport avec la prèparation et la caractérisation de membranes en acétate de cellulose pour le traitement de rejets textiles par ultra (UF) et nanofiltration (NF). La variation du flux a été analysée et traitée par étude comparative des effets du pH et du temps sur la régénération des performances des membranes préparées .L'étude menée a permis de suivre les indicateurs de pollution par traitement UF-NF. 95 % de la DCO a pu être éliminée. Les proportions obtenues, après traitement, sont en accord avec les normes en vigueur.

Key words: textile waste water, membrane, cellulose acetate, ultrafiltration, nanofiltration

1. Introduction

The textile industry is consuming nowadays a great quantity of water and chemicals. The compounds used are generally resistant to the climatic conditions and to the environmental influences. They fulfil a certain function on the textile articles and then they are eliminated. The major part of these chemicals is found in the aqueous rejections which have to be purified to eliminate toxic and harmful substances.

Water pollution may be caused by the concentration modification of given elements in the aqueous medium or by the introduction of new elements [1]. The most important polluting indicators are pH, conductivity, chemical oxygen demand (COD), biological oxygen demand (BOD_5), turbidity and colour.

The waste textile water may contain dyes, salts, softeners, acids, alkalis and even heavy metals (Cd, Hg, Zn, Co). [2].The suspended solids generally have an organic nature and can be decayed, during their decantation, aerobically or anaerobically. Hydrocarbons are mainly brought during the oiling operation or from the impressing residues. The adsorbable halogenic organic compounds have various ecological and toxicological behaviours. Surfactants represent a polluting load.

The usual techniques of water treatment have not the necessary capability of adaptation to face the continual changes of the effluent's contaminants and require, in general, much time, energ
y and financial resources.

Having been used for a long time in chemical, food and pharmaceutical industries, the membrane

* corresponding author, tel:21698952410, e-mail: ferjani@yahoo.fr

technology is actually one of the promising techniques employed for the textile water treatment in order to respect the increasingly demanding standards of rejection and also in the aim of a re-use of this water [3-6]. Particularly, the cellulose acetate membranes are subject to several intense researches in the purification and the desalination of water [7-11], and a beginning of use in the treatment of the textile waste waters. This material generally presents a high hydrophilicity responsible for its weak tendency towards fouling. Ultrafiltration, widely used for macrosolutes elimination, is well adapted for retention of polymers and colloids. Nanofiltration allows the separation of solutes with a molar weight reaching 200-250 $g.mol^{-1}$. The combination of these two processes can be a versatile choice for a sequential separation permitting to prevent the membrane fouling [12-14].
This study deals with the treatment of waste water samples of the Tunisian textile industry. The latter is concentrated in the Sahel region. The aim of the present work is to determine the potential use of a combined membrane technology for this application. A series of CA membrane materials having a pore size distribution of UF and NF range were prepared by phase inversion process, characterized by pure water permeability determination and then tested for the treatment of textile wastewater.

2. Experimental

2.1. Materials

Cellulose acetate (CA) (M_w ca. 30 000 $g.mol^{-1}$, 39.8 wt.-% acetyl content, degree of substitution 2.5), acetone and formamide were used as received from Aldrich. Deionised water (18 MΩ. cm, Milli Q) was used in the preparation of aqueous solutions.

2.2. Preparation of cellulose acetate membranes

A series of asymmetric CA membranes were prepared by immersion into a water coagulation bath from a dope solution made of 20 - 22 wt-% CA acetone: formamide (2: 1) mixture. After casting on a glass plate a wet film of 250 µm in thickness, the film forming system was immersed without further time of evaporation into distilled water at 4°C for 1 h. The phase inversion immediately started and the films peeled off the glass plate after some time. The membranes were then annealed for 10 min in a water bath at the desired temperature varying from 60 to 80°C. The obtained materials were named Rx-y where x denotes the polymer concentration in the dope solution and y- the annealing temperature of the membrane.

2.5 Effluent characteristics

Effluents for this study were provided from a textile unit from the region of Monastir in the center of Tunisia, which has an average consumption of drilling water of about 250 m^3/day^{-1}. The wastewaters are of a dark colour due to the presence of different agents for dyeing and impression. An average effluent whose composition is presented in table 2 was considered to prevent the daily fluctuation of chemical effluent quality.

Table 1 : Characteristics of the average textile processing wastewater

indicator	Effluent
pH	4.35
Conductivity ($mS.cm^{-1}$)	7.9
TH (°F)	46
COD (mg $O_2.L^{-1}$)	960
Turbidity (TNU)	1.17

2.3. Permeation experiments

The permeation tests were carried out at 25°C under an operating pressure (ΔP) up to 16 bar using a conventional cross-flow Amicon type cell having a total feed solution capacity of 350 mL. Dimensions and characteristics of the used cell were previously described [9]. The effective surface membrane area was of 38.5 cm^2. During all experiments, the solutions were stirred with a velocity of 180 rpm. As the effluent was concentrated during the experiments, a linear law was considered to estimate the variation of concentration versus the permeate volume. Every experiment was replicated 3 times and an average value was considered for concentration calculation. Membranes were first conditioned in the test cell with pure water by gradually increasing the pressure till 16 bars for at least 1 h.

Physico-chemical parameters of effluents and of permeates were determined by using the following techniques: turbidity (turbidimeter, HACH RATIO 2100A), conductivity (conductimeter, Taeussel model 123) and COD (HACH DR/2010)

In each experiment, the volume flow (J_v) of permeate was determined and the solute retention rate (R) defined as $R\ (\%) = (1 - C_p / C_f) * 100$ where C_p is relative to permeate concentration and C_f denotes the feed concentration.

3. Results and discussion

3.1 Pure water permeability

Permeability (L_p) is considered as an intrinsic characteristic of membrane. According to the DARCY law, this study was performed for a 2-16 bar pressure range. The obtained results showed a linear variation of flows. On the other hand, we observe that the values of pure water permeability coefficient vary in an inversely proportional way with the annealing temperature (table 2). The obtained L_p are clearly characteristics of a UF range behaviour.

Table 2 : Pure water permeability for UF membranes

Membrane	$L_p(L.m^{-2}.h^{-1}.bar^{-1})$
R 20—60	6.25
R 20—65	4.16

The two other samples were tested in the same conditions. The obtained results showed the same kind of curves. Registered values of flows and L_p (table 3) are, thus, lower than that of UF membranes and denote a NF range behaviour. It clearly appears that acting on polymer concentration in the dope solution and annealing temperature make possible the tailoring of samples well responding to specific needs [8].

Table 3 : Pure water permeability for NF membranes

Membrane	$L_p(L.m^{-2}.h^{-1}.bar^{-1})$
R 20—80	0.76
R 22—80	0.66

3.2 Effluent permeabilities

The textile waste water permeability was determined from flow calculation under given pressure. This was performed after a preliminary neutralization of effluent pH from 4,35 to 7 by mean of 1M

NaOH solution . In the aim of a sequential realization of the separation, we carried out the following procedure according to which the UF membranes are used for a first step separation. The obtained permeates (1 for R20-60 and 2 for R20-65) are then submitted to NF purification. The permeation rates were calculated from 15 mL obtained volumes, 38,5 cm^2 membrane area and registrated time for each operation.

The flow registration versus the applied pressure for UF membranes reported in figure 1clearly shows a perfect linear variation. At equal pressures, the higher is annealing temperature, the lower is resulting flow. This behaviour is related with the pore narrowing and the densification of obtained membranes. The same phenomenon is put in evidence by the growth of the straight slope from 3.10 to 3.50 for a 5 °C diminution of annealing temperature.

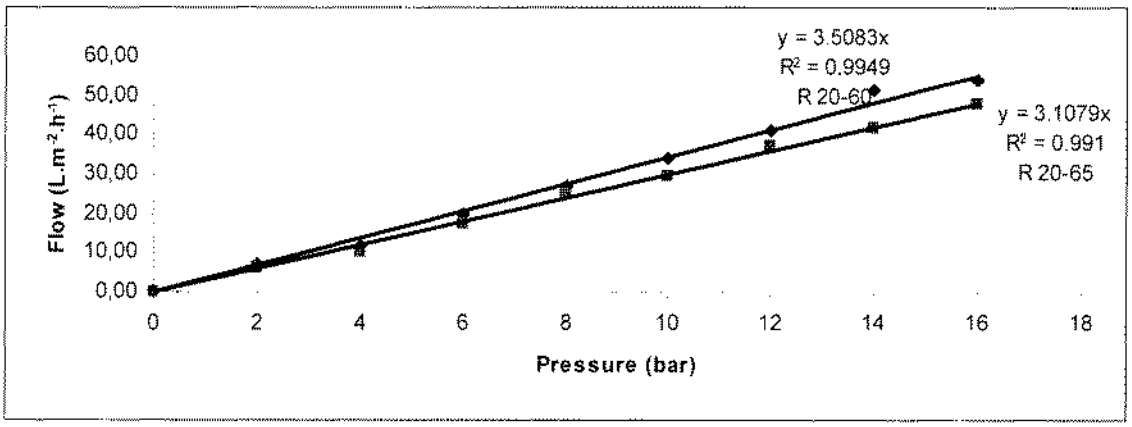

Figure 1: Effluent flow variation versus applied pressure for UF (R20-60 (♦)and R20-65(■))membranes.

These curves pass by the origin in accordance with UF mechanisms for which the effect of solution osmotic pressure may be neglected.

Table 4: UF membrane permeability to effluent

Membrane	$L_p(L.m^{-2}.h^{-1}.bar^{-1})$
R 20—60	3.50
R 20—65	3.10

The behaviour of NF membranes (figure 2) gives rise to several different results. At first, concerning the influence of the polymer concentration, we observe some flows gaps up to about 30—40% (under a 16 bar applied pressure).

The variation of flows is, in general, linear but the two curves do not pass by the origin putting in evidence an osmotic pressure of 0.5-1 bar .The relatively slight values of this pressure are probably related with partial elimination of loaded charges during UF operation.

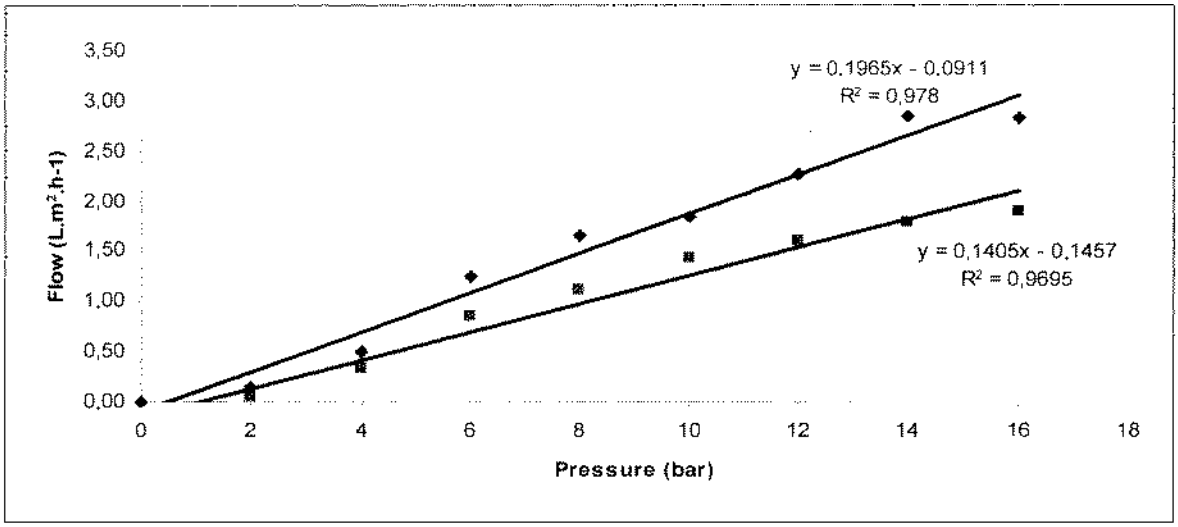

Figure 2: Effluent flow variation versus applied pressure for NF(R20-80(♦)and R22-80(■))membranes.

On another hand, it is seen that, for a same annealing temperature, the effluent permeability declines in the order of 25 % for an inerease of polymer concentration from 20 to 22 %.

Table 5: UF membrane permeability to effluent

Memhrane	L_p(L.m^{-2}.h^{-1}.bar^{-1})
R 20—80	0.19
R 22—80	0.14

3.3 Influence of filtration time

Due to the concentration polarisation and fouling phenomena, it is well established that the permeate flow declines. This behaviour is generally more pronounced in the case of frontal separation. In the aim of appraising this problem, we registered the flow variation of UF membranes under a 2 bar pressure versus time separation. The obtained results illustrated with figure 3 clearly show a first step decrease of permeate flow followed by a tendency towards stabilisation and the reaching of a plateau after12 h of separation. The R20-60 membrane flow is faster stabilised than that of R20-65. At the same time, the charge loss of the last sample is higher than that of the first (57.83% against 41.90%)

The flow decline is related to gradual pore obstruction by solid matters. This phenomenon is particularly important in the case of a frontal separation applied to a so hard loaded effluent as textile wastewaters. It may be explained in terms of a gel layer formation and a solute adsorption on the membrane surface. The matter accumulates little by little on the pore wall till forming around it a settling. Then occurs an erosion phenomenon leading to the solvent passing and to the stabilisation of flows [15].

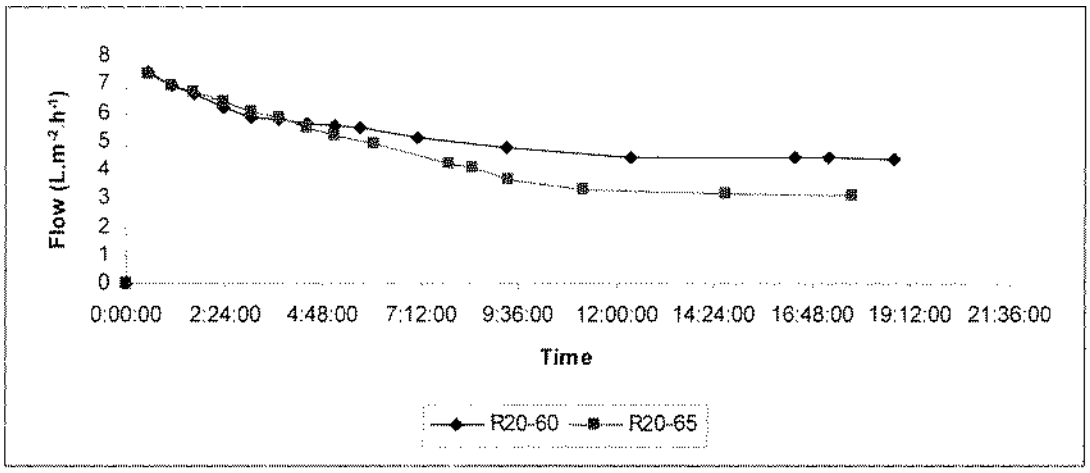

Figure 3: Flow variation under a 2 bar pressure versus time for UF membranes

The same experience was performed for NF membranes using the UF permeate under a 16 bar pressure. The obtained results are assembled in figure 4. In this case, the stabilisation is not reached after about 17 h and the charge loss is similar to that of UF membranes (54%). This may be explained by the fact that pore radii in the case of NF samples are much narrower and thus the erosion phenomena are negligible. The problem of fouling may be resolved by membrane regeneration. The next part of this study is then dedicated to comparison between different methods of CA membranes regeneration.

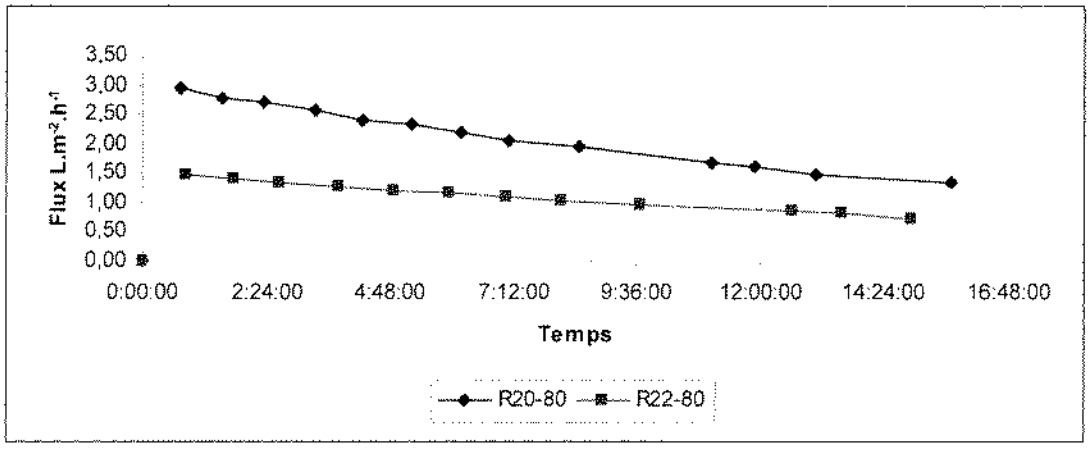

Figure 4: flow variation under a 16 bar pressure versus time for NF membranes

3.4 Membrane regeneration

According to recent works, [2-4], the efficiency of this treatment mainly depends on 4 factors: the treating agent, the regeneration pH, time of operation and temperature. In this work, we are interested in the influence of pH and time.

With regard to the Darcy law, the pure water filtration, in the absence of fouling, gives a flow variation represented by:

$$J = \frac{\Delta P}{\mu . R_m} \qquad (1)$$

Where μ (Pa·s) is the dynamic viscosity of the permeate and Rm (m^{-1}) is the hydraulic resistance of membrane.

The appearing resistance after fouling (Rc) may be calculated from water flow (J_{ep}) after cleaning with pure water according to the next relation:

$$Rc = \frac{\Delta P}{\mu \times J_{ep}} - R_m \qquad (2)$$

The remaining résistance after cleaning with pure water (Rr) was calculated from water flow (J_r) after regeneration according to:

$$Rr = \frac{\Delta P}{\mu \times J_r} - R_m \qquad (3)$$

Using these 2 relations, we can formulate 2 ratios indicating the efficiency of regeneration [6]: FE (%) - fouling or acquired resistance elimination and FR (%)-flow recuperation

$$FE\ (\%) = \frac{Rc - Rr}{Rc} \times 100 = \frac{\frac{1}{J_{ep}} - \frac{1}{J_r}}{\frac{1}{J_{ep}} - \frac{1}{J}} \times 100 \qquad (4)$$

$$RF\ (\%) = \frac{J_r - J_{ep}}{J - J_{ep}} \times 100 \qquad (5)$$

3.4.1 pH regeneration influence

After effluent filtration, R 20—65 UF membrane was cleaned and used for filtration (under 3 bar pressure) of pure water. J_{ep} Was determined and a regeneration bath was prepared according to the next procedure:

- Membrane regeneration for 20 mn at pH 4 using prepared solution from 1M HCl in deionised water
- Membrane regeneration for 20 mn at pH 8 using prepared solution from 1M NaOH in deionised water
- Membrane regeneration for 20 mn at pH 4 and then retrocleaning during 15 mn
- Membrane regeneration for 20 mn at pH 8 and then retrocleaning during 15 mn

J_r was then determined. Assembled results in figure 5 show slightly similar values of FE and FR. That's in relation with the fact that these two parameters are representative of the same phenomenon: regeneration of membrane intrinsic performances.

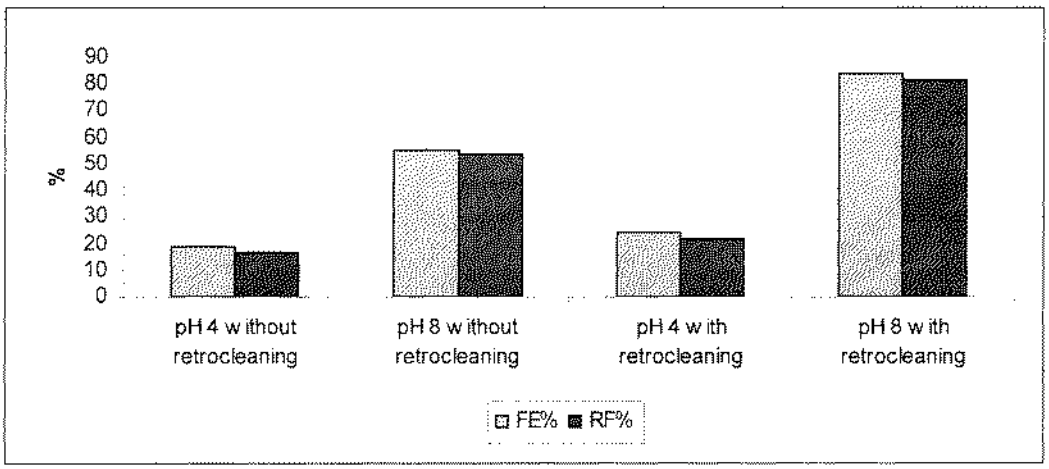

Figure 5: Influence of pH and retro-cleaning procedure on FE and RE for R 20—65 UF membrane.

Depending on pH value, we observe two kinds of behaviour: The pH 4 regeneration is less effective(20-25%) without and with retrocleaning. It is to be noted that pH8 regeneration gives rise to better results (reaching 87% of flow recuperation after retrocleaning). It is clear that the increase of pH enhances the flow recuperation and that the use of retrocleaning improves significantly the regeneration efficiency by eliminating the matter settling on the pore walls. This efficiency acts probably on the adsorbed settling at membrane surface and pore walls and, at the same time, on the gel layer.

3.4.2 Influence of the regeneration time:

For this part of the study, pH was optimised at 8 and the operation time was fixed to 5, 20 and 30 min. The obtained results of figure 6 clearly show the great influence of this parameter. Both FE and FR were initially moderate (40 % for 5 min) and reached a maximum of 97% at 30 min. This puts in evidence that one can quasi totally regenerate the initial performances of our membranes by acting only on pH and time.

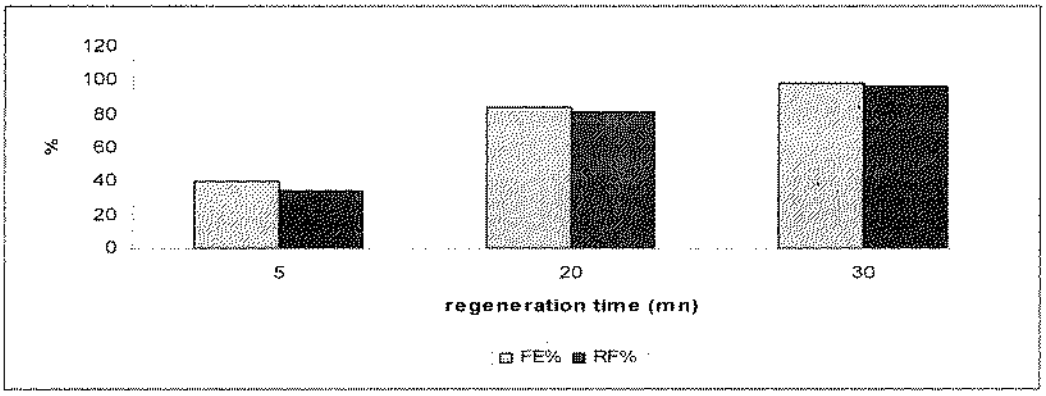

Figure 6: Influence of regeneration time on the FE and FR

3.5 Efficiency of the textile effluent treatment filtration process

In the aim of optimising the treatment efficiency, we opted for a 3 stage process which includes in the first step the R20-60 loose membrane, a UF/NF treatment as a secondary step and finally the NF R22-80dense membrane as a tertiary treatment

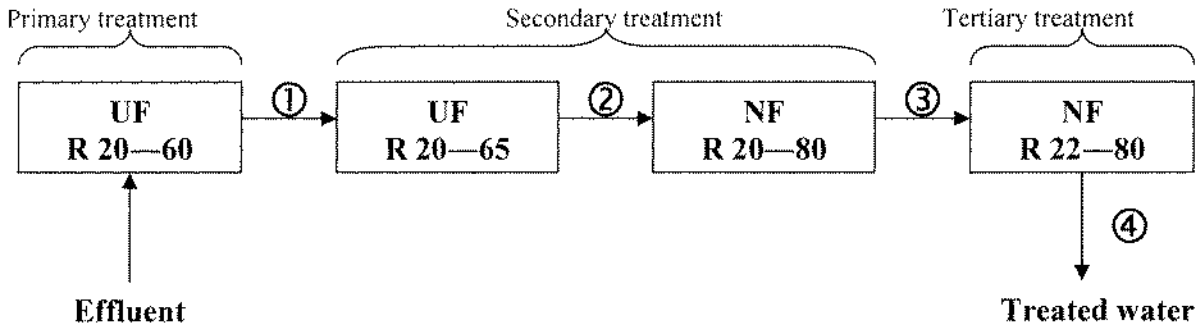

Figure 7: Filtration process for wastewater treatment

In fact, this kind of parallel and/or serial processes represents one of the most important advantages of the membrane technology since one can envisage a great number of conformations depending on the loading charge of effluent, the treated volume and the requested efficiency. COD, conductivity, turbidity and colouring were analysed after every operation.

3.5.1 COD Variation

Obtained results of permeate COD variation and calculated percentages of COD reduction after every filtration operation are reported in figure 8 and 9. It is shown , since the beginning, (after R20-60) that this parameter drastically diminishes. In fact, the reduction reaches 70 % of the total load .That really explains the fast fouling of this membrane. Moreover, it should be judicious to use a preliminary stage of microfiltration to eliminate the bulky particles and to prevent the hard fouling of UF membrane. The R 20—65 membrane which has actually some similar characteristics brings no appreciable variation of COD. In fact, all particles of this range have been stopped during the last stage. The NF stage proved to be important for the retention of small loading particles responsible of colour. The stopped COD reached, then, a maximum of 95%. The remarks done about R-20-65 are available too for R22-80. Only a weak variation of COD was obtained.

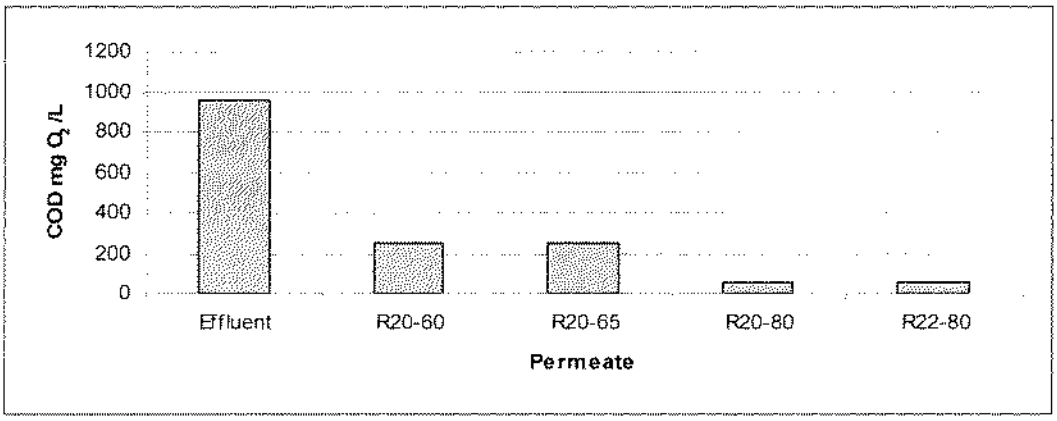

Figure 8: Effluent COD variation in the permeate during the filtration process (see Fig 7 for explanations of the filtration sequence)

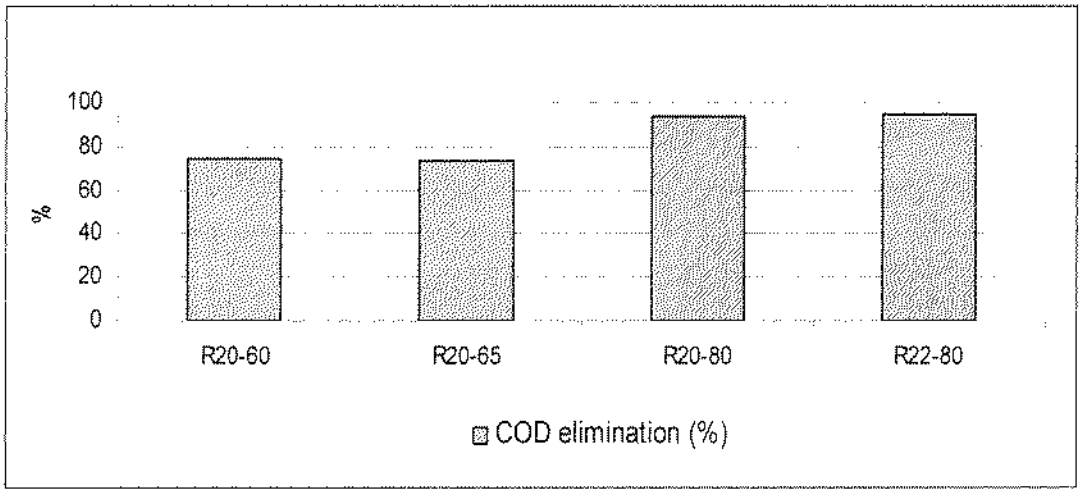

Figure 9: COD (%) reduction

It was observed, by the way, that membrane performances were slightly related to effluent pH. A variation of this parameter was performed.

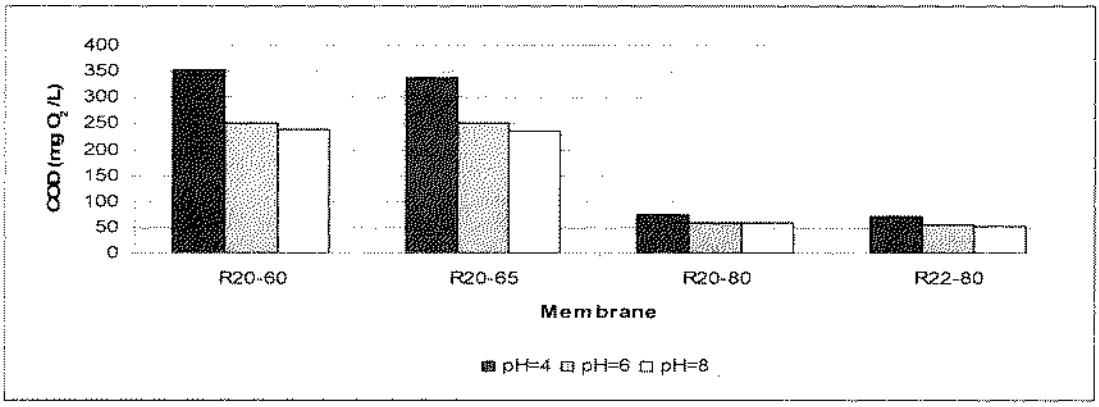

Figure 10 : COD variation versus effluent pH

It is seen (figure10) that the increasing of pH had a positive influence on the filtration performances. This might probably be related with a partial inflating of membranes which generates a pore narrowing [8].

3.5.2 Conductivity variation

Results of conductivity measurements assembled in figure11 show a variation which finally justifies our choice of the treatment scheme. Effectively, since the first UF membrane, a reduction of this parameter (18-20 %) was observed. The slight variation of annealing temperature (60 to 65 °C) meets an interest in a consequent decrease of conductivity (16-17%) after R20-65 sample. Moreover, the NF membranes contribute to 30% of reduction. The total reduction was about 50 %. This result is sufficient when compared with norms in form.

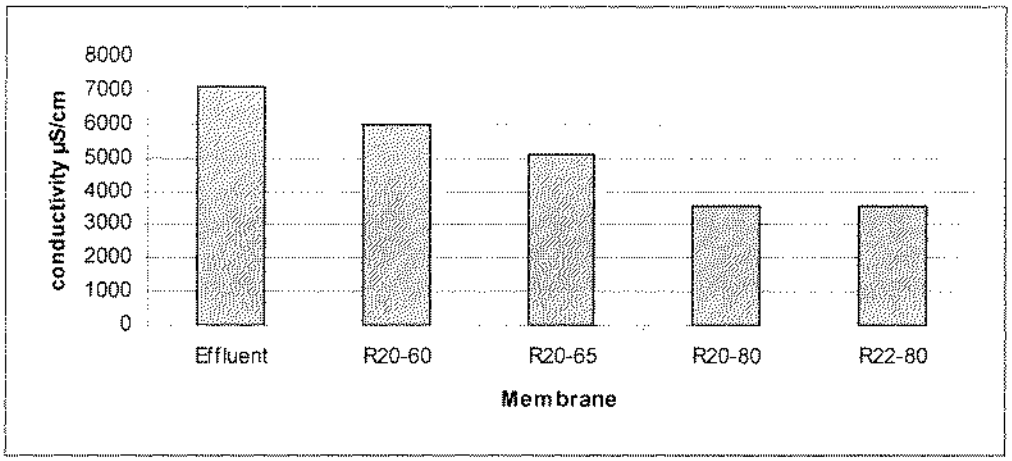

Figure 11: Variation of conductivity during filtration process

3.5.3 Turbidity and colouring variation

Turbidity is generally related to the presence of fine particles which are evenly distributed in the effluent. The results of figure 12 put in evidence a hard retention of NF R20-80 membrane and an important contribution of the denser R22-80 sample (10%).

Concerning the coloring performed by absorbance measurements at 657 nm, an important contribution was brought by UF membranes (65 to 75%). This certainly concerns particles with higher molecular weight. The major remaining colour was eliminated by NF membranes to reach 95 % of retention of this kind of pollution.

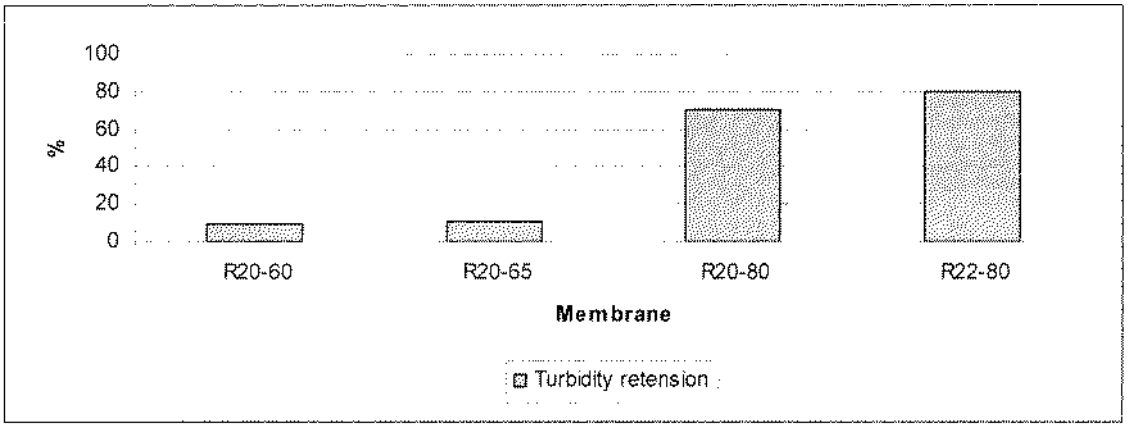

Figure 12: Turbidity retention

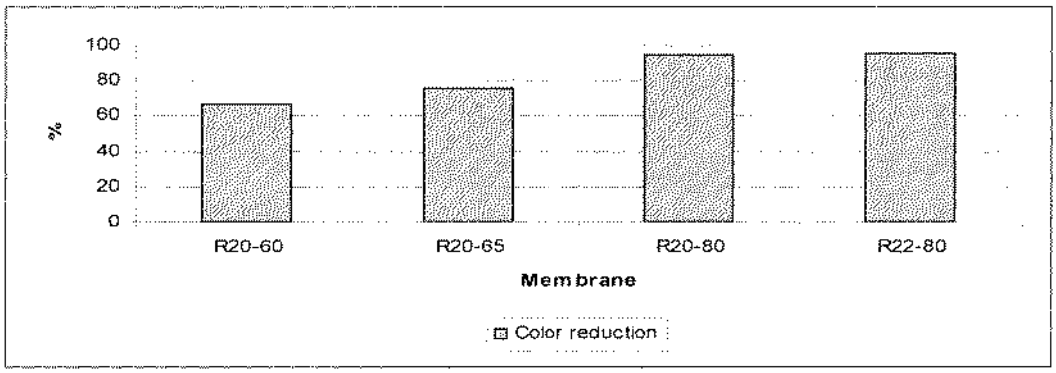

Figure 13: Elimination of coloration

3.5.4 Other parameters

Obtained results for total hardness and salt concentration are assembled in table 6. It is shown that the quasi totality of hardness was eliminated. This value is in agreement with our previous works [9-10] where it was demonstrated for NF membranes a better rejection for bivalent ions.

The total dissolved salts of permeate reached 3850 $mg.L^{-1}$. This rejection of dissolved inorganic ions was rather performed by the NF membranes.

Table 6 : Other parameters

Pollution indicator	permeate
Hardness (°F)	2
Dissolved salts (mg/L)	3850

4. CONCLUSIONS

This work dealt with the treatment of a hard loaded textile effluent from the Sahel region of Tunisia by cellulose acetate membranes prepared in our laboratory. Our attention was focused, essentially, on the preventing of the membrane fouling and the production of a permeate which could respond to the national norms.

The membranes were in the beginning characterised in terms of pure water and effluent permeability. That leads to 2 kinds of UF and NF samples.

The fouling study by a variation of pH and time treatment showed that our samples can easily regenerate their initial performances after a treatment of 30 min at pH 8. This problem is essentially

met in the case of frontal stirring treatment (concentration of the effluent) and is much weaker in the case of tangential separation (higher Reynolds and recirculation to the feed tank)
The treatment of the polluting parameters was successfully performed using a serial UF/Nf process which permitted a gradual retention of loading particles. All the reached values are in conformity with the norms in form.
This work should be continued in a pilot scale with tangential separation for more important volumes of treated effluent.

References

[1] I. Hendrickx and G. D. Boardman) ; Pollution prevention studies in the textile wet processing industry ; Blacksburg, Virginia; 24061.
[2] M. Marcucci, I. Ciabatti, A. Matteucci and G. Vernaglione; *Membrane Technologies Applied to Textile Wastewater Treatment;* **2003**;*Vol 984*; 53–64
[3] W. Rbowen and H. Mukhtar; *Journa of Membrane Science*. **1996**;*112* ; 263—274.
[4] S. Khan, A. Ghosh, Vramachandhran, J. Bellare, M.S. Hanra, M. Ktrivedi and B.M. Misra ; *Desalination*. **2000;***128* ; 57—66.
[5] B. Van Der Bruggen, B. Daems, D. Wilms and C. Vandecasteele ; *Separation and Purification Techniques*. **2001**;*22—23* ;519—258.
[6] S. S. Madaeni, T. Mohamamdi and M. K. Moghadam ; *Desalination*. **2001;***134*;77—82.
[7] E. Ferjani and M.S. Roudesli, *European Polymer Journal*: **2000**;*36* ;35—49.
[8] E. Ferjani, D. Picard, M.M Chehimi, M. Majdoub, M.S. Roudesli and M. Delamar, *Journal of. Membrane Science ;* **2000** ;*165* ;125—133.
[9] E. Ferjani, R. Haj Lajimi, A. Deratani and M.S. Roudesli, *Desalination,* **2002** ;*146* ;352—330.
[10] E. Ferjani, M.S. Roudesli and A. Deratani, *Desalination*, **2004**;*162*; 103—109.
[11] A. Maurel; techniques séparatives à membranes ; Traités de génie des procédés, Techniques de l'ingénieur J 2 790.
[12] Jacob Peter Van't Hul; Membrane separation in textile washing processes ; Twente university; The Netherlands **(2002)**
[13] Douglas L Woerner; Membrane Technology In Textile Operations;Koch Membrane Systems**(2002)**
[14] J.M. Berland and C. Juery ; Les procédés membranaires pour le traitement de l'eau, Techniques de l'Ingénieur ; **(2002).**
[15] H.Barnier and P. De Bank; International Conference on Inorganic Membranes ICIM2, Montp. France, **(1991)**.