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Treatment and reuse of reactive dyeing effluents

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Abstract

Industrial textile processing comprises the operations of pretreatment, dyeing, printing and finishing. These production processes are not only heavy consumers of energy and water; they also produce a substantial amount of chemical pollution. Of all dyed textile fibres, cotton occupies the number-one position, and more than 50% of its production is dyed with reactive dyes, owing to their technical characteristics. Unfortunately, this class of dyes is also the most unfavorable one from the ecological point of view, as the effluents produced are relatively heavily colored, contain high concentrations of salt and exhibit high BOD/COD values. Dyeing 1 kg of cotton with reactive dyes requires an average of 70–150 L water, 0.6 kg NaCl and 40 g reactive dye. The composition of the dye bath which we propose to treat contains solid particles (cotton fibres), dyeing auxiliaries (organic compounds), hydrolyzed reactive dyes, substantial quantities of alkalis (sodium carbonate and soda ash) and very high concentration of sodium chloride or sodium sulfate. This paper presented the state of the art of the different processes currently used for the treatment of dye house wastewaters and evaluated a four-step process [1] to recover the water and the mineral salts, while leaving the spent dyes in the reject stream. Processes evaluated included (1) cartridge filtration to remove textile fibres, (2) acidification to make the brine recovered, suitable for reuse and further dyeing operations, (3) nanofiltration (NF) to concentrate the hydrolyzed dyes and (4) reverse osmosis (RO) to further concentrate the salts for reuse in the dyeing process. A cut-off of 100 μm is sufficient to trap textile fibres, regardless of the type of effluent and the texture of the textile dyed. The hydrolyzed reactive dyes present in the treated effluents comprise the entire range of possible types of reactive dyes. For this acidification, we studied the influence of the concentration of sodium chloride, the influence of the temperature and we verified that the volume neither depends on the concentrations of reactive hydrolyzed dyes nor sodium chloride. After defining the nanofiltration membrane, we studied the effect of the pH, temperature, pressure and velocity as well as the experimental procedure on the permeate flux, recovery of the salt and removal of the color. An increase of either of the parameters temperature and pressure leads to an increase of the permeate flux. On the other hand, a rise in the pH leads to a decrease of the permeate flux. The retention factor of the sodium chloride is low when the concentration of sodium chloride is high in the retentate. Our aim was to recover 80–90% of the sodium chloride, but our experiments showed that the recovery went as high as 99%. Depending on the dyes used, the experimental procedure can be carried out in one, two or three steps. The dye retention level was always higher than 98%. After studying the operating variables, experiments with the recycled brines in new dyeing operations were carried out with specimen dyeings prepared with usual water using different classes of reactive dyes. There was no difference in the results in terms of depth, shade or fastness properties, whichever type of water was used. These last results therefore validate our process and its special innovative feature: recycling not only the water but also the mineral salts.

Keywords: Nanofiltration; Dye effluents; Elimination of dyes; Mineral salts; Operating conditions

1. Introduction

Even though it appears to be in plentiful supply on the earth's surface, water is a rare and precious commodity, and only an infinitesimal part of the earth's water reserves

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(approximately 0.03%) constitutes the water resource which is available for human activities. The growth of the world's population and industry has given rise to a constantly growing demand for water in proportion to the supply available, which remains constant. According to the data of the I.F.E.N (Institut Français de l'ENvironnement), the amount of water taken from the natural environment in France was estimated at about 40 billion m^3 (1995). On the global level, the question of the supply of fresh water is becoming more acute every day. In the dyeing of textile materials, water is used firstly in the form of steam to heat the treatment baths, and secondly to enable the transfer of dyes to the fibers. Cotton, which is the world's most widely used fiber, is also the substrate that requires the most water in its processing. The dyeing of one kilogram of cotton with reactive dyes demands from 70 to 150 L [2] water, 0.6 to 0.8 kg NaCl and anywhere from 30 to 60 g dyestuff. More than 80,000 tonnes of reactive dyes are produced and consumed each year, making it possible to estimate the total pollution caused by their use. After the dyeing is completed, the various treatment baths are drained out, including the first dye bath, which has a very high salt concentration, is heavily colored and contains a substantial load of organic substances. One solution to this problem consists in mixing together all the different aqueous effluents, then concentrating the pollution and reusing the water either has rinsing water or as processing water, depending on the treatment selected (either nanofiltration or reverse osmosis for the membrane processes). These treatments concern only very dilute dye baths. This is generally not the case of the first dye baths recovered which are the most heavily polluted ones. The wastewater produced by a reactive dyeing contains:

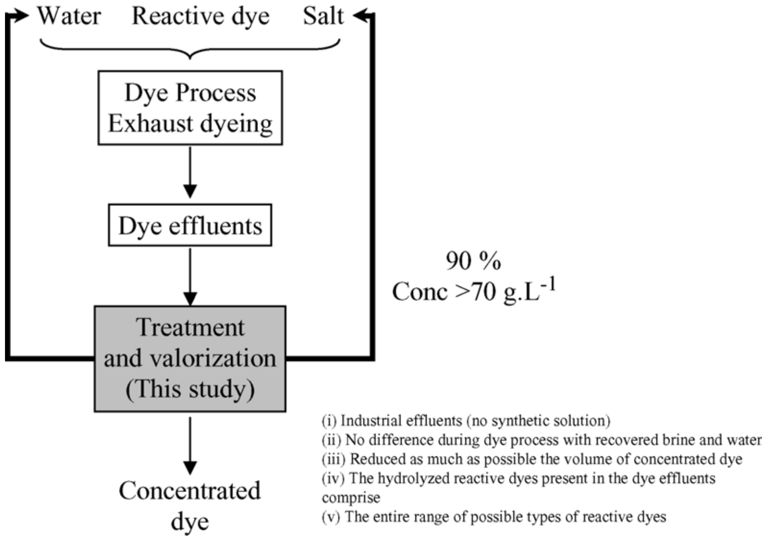
- Hydrolyzed reactive dyes not fixed on the substrate, representing 20–30% of the reactive dyes applied (on average $2\,g\,L^{-1}$). This residual amount is responsible for the coloration of the effluents and cannot be recycled.
- Dyeing auxiliaries or organic substances, which are non-recyclable and responsible for the high BOD/COD of the effluents.
- Textile fibres.
- Sixty to one hundred gram per liter electrolyte, essentially sodium chloride and sodium carbonate, which is responsible for the very high saline content of the wastewater.

In addition, these effluents exhibit a pH of 10–11 and a high temperature (50–70 °C). The legal regulations respecting the limit values for the release of wastewater are changing and are becoming increasingly severe, including the limits with respect to salinity. In France, the activities of installations subjected to authorization are delimited by a decree of 2 February 1998.

The objectives of this study were (a) to removal cotton fibres and to control the carbonate concentration which might strongly influence the nanofiltration, (b) the treatment of dye baths by nanofiltration in order to recover and reuse the sodium chloride and the water, (c) to select the NF membranes that were able to operate at high temperatures (50–70 °C), allowed for passage of monovalent salts, while retaining the hydrolyzed reactive dyes and (d) evaluate a RO process that was robust in terms of operating at elevated temperature (40–50 °C), able to operate at 80×10^5 Pa (80 bar) transmembrane pressure (TMP), and achieve greater than 90% of sodium chloride was reused. The simplified Fig. 1 presents the challenges of this study.

The process proposed by this study [1] has the following simultaneous advantages:

- compact: the place available in the dye houses is small;
- progressive: fashions and colors change; treatment must take place at the outlet of the dyeing machine, regardless of the bath, yet be capable of recycling a maximum amount of water and mineral salts;



(i) Industrial effluents (no synthetic solution)
(ii) No difference during dye process with recovered brine and water
(iii) Reduced as much as possible the volume of concentrated dye
(iv) The hydrolyzed reactive dyes present in the dye effluents comprise
(v) The entire range of possible types of reactive dyes

Fig. 1. Schematic representation of the challenges associated with this study.

- flexible: widely variable volumes must be capable of being treated;
- feasible: the quality of the water and of the brine must be constant, so as to be reusable for a new dyeing.

This paper presented the different methods currently used for the treatment of dye house effluents and those which are in the course of development. Then, it evaluated a four-step process to recover only the water and salts, while leaving the spent dyes in the reject stream. Processes evaluated included (1) cartridge filtration to remove textile fibres, (2) acidification to make the brine recovered, suitable for reuse and further dyeing operations, (3) nanofiltration (NF) to concentrate the hydrolyzed dyes and (4) reverse osmosis (RO) to further concentrate the salts for reuse in the dyeing process.

2. Review of current treatment methods of treating dyeing effluents

Owing to their high BOD/COD, their coloration and their salt load, the wastewaters resulting from dyeing cotton with reactive dyes are very polluted. For example, for Drimaren HF, this ratio is constant and around 0.35 for each dyeing step (bleaching step BOD = 1850 mg L^{-1}, COD = 5700 mg L^{-1}; neutralization step BOD = 290 mg L^{-1}, COD = 830 mg L^{-1}; dyeing step BOD = 500 mg L^{-1}, COD = 1440 mg L^{-1}; soaping step BOD = 310 mg L^{-1}, COD = 960 mg L^{-1}). As aquatic organisms need light in order to develop, any deficit in this respect caused by colored water leads to an imbalance of the ecosystem. Moreover, the water of rivers that are to be used for drinking water must not be colored, as otherwise the treatment costs will be increased. Obviously, when legal limits exist (not in all the countries) these should be taken as justification. Studies concerning the feasibility of treating dye house wastewater are very numerous. Groff [3] and more recently Marrot and Roche [4] give more than 100 references in a bibliographical review. After a study of the classic treatments of textile effluents, we shall take a more detailed look at membrane processes. The physical methods include different methods of precipitation (coagulation, flocculation, sedimentation) [5–8], adsorption (on activated carbon, biological sludges) [9,10], filtration, or membrane processes as reverse osmosis [11–13].

2.1. Usual treatments

2.1.1. Biological treatments

Biological treatments reproduce, artificially or otherwise, the phenomena of self-purification that exist in nature. Self-purification comprises the whole process by which an aquatic environment achieves the re-establishment of its original quality after pollution. Biological treatments differ according to the presence or absence of oxygen. In France, the process of “activated sludge”, the most commonly used treatment [9,10] makes it possible to obtain rates of elimination by oxidizable substances of the order of 90%. As a result of the low biodegradability of most of the dyes and chemicals used in the textile industry, their biological treatment by activated sludge does not always meet with great success: in fact most of these dyes resist aerobic biological treatment. The addition of adsorbents, such as bentonite or powdered activated carbon to biological treatment systems is necessary in order to obtain good elimination of non-biodegradable or microorganism-toxic organic substances produced by the textile industry, particularly by dye houses [9,14,15], thus reducing the harmful effect on microorganisms. Other methods consist in combining oxidative chemical treatments following the biological treatment [16], including the possibility of using organic flocculants [9]. However, these methods, which only treat the effluents in order to be able to release them to the environment in accordance with legal requirements, are very costly (around €2.5 kg^{-1} for polyamide coagulant: a factor 10 with mineral coagulants).

2.1.2. Coagulation–flocculation

Coagulation–flocculation treatments are generally used to eliminate organic substances. The products normally used have no effect on the elimination of soluble dyestuffs. Even though this process, which is widely used in Germany [17], makes it possible to effectively eliminate insoluble dyes [18], it is of doubtful value owing to the cost of treating the sludges and the increasing number of restrictions concerning their disposal.

2.1.3. Adsorption on powdered activated carbon

Adsorption on activated carbon (C^*) without pretreatment is impossible [18] because the suspended solids rapidly clog the filter. This procedure is therefore only feasible combined with a flocculation–decantation treatment or a biological treatment. This combination permits a reduction of suspended solids and organic substances as well as a slight influence on the color [19,20]. However, the cost of activated carbon is still high [10].

2.2. Electrochemical processes

The dye house wastewater is circulated in an electrolytic cell containing iron electrodes [21,22]. Even though the advantage of this process seems to be its capacity of adaptation to different volumes and pollution loads, its main disadvantage is that it generates the formation of iron hydroxide sludges, thus limiting its use.

2.3. Ozone treatment

Widely used in the water treatment, ozone is now used (either alone or in combination with other treatments, such as O_3-UV or O_3-H_2O_2) in the treatment of industrial effluents [23]. Ozone especially attacks the double bonds which are responsible for coloration. For this reason, decolorization of wastewater by ozone alone is not always accompanied by a significant reduction of the COD [24–26]. Moreover, the installation of an ozonation process involves additional costs [27].

2.4. *Membrane processes*

The increasing cost of water and its wasteful consumption have now induced a treatment process which is integrated in in-plant water circuits rather than as a subsequent treatment [28]. From this standpoint, membrane filtration offers potential applications. Processes using membranes provide very interesting possibilities of separating hydrolyzed dyestuffs and dyeing auxiliaries, thus simultaneously reducing coloration and the BOD/COD of the wastewater. In the current studies, it is difficult to recommend a particular membrane process (MF, UF, NF and RO), and the choice is guided by the desired quality of the permeation results.

2.4.1. *Reverse osmosis*

Reverse osmosis membranes have a retention rate of 90% or more for most types of ionic compounds and produce a high quality of permeate [11–13]. Decoloration and the elimination of chemical auxiliaries in dye house wastewater can be carried out in a single step. Reverse osmosis permits the removal of all mineral salts, hydrolyzed reactive dyes and chemical auxiliaries. The problem involved is that the higher the concentration of salt, the more important the osmotic pressure becomes and therefore the greater the energy required.

2.4.2. *Nanofiltration*

Nanofiltration membranes retains organic compounds of low molecular weight, divalent ions or large monovalent ions, such as hydrolyzed reactive dyes as well as dyeing auxiliaries. The effect of the concentration of dyes has been frequently reported in dye house effluents as well as the concentration of salt and the pressure [29–34]. In most published studies concerning dye house effluents, the concentration of mineral salts does not exceed $20\,\mathrm{g\,L^{-1}}$ [32] and the concentration of dyestuff $1.5\,\mathrm{g\,L^{-1}}$ [32]. The effluents are reconstituted [32,33,35] with generally only one dye and the volume studied is low [35]. The treatment of dyeing wastewater by nanofiltration thus represents one of the rate applications possible for the treatment of solutions with highly concentrated and complex solutions [36–40].

2.4.3. *Ultrafiltration (UF)*

Ultrafiltration enables the elimination of macromolecules and particles but the elimination of polluting substances, such as color is never complete (between 31% and 76%) [41]. And even in the best of cases, the quality of the treated wastewater does not permit its reuse for feeding sensitive processes, such as the dyeing of textile. Rott and Minke [42] emphasize that 40% of the water treated by ultrafiltration can be recycled to feed processes termed “minor” in the textile industry (rinsing, washing) in which salinity is not a problem. Ultrafiltration can only be used as a pretreatment for reverse osmosis [43] or in combination with a biological reactor [44].

2.4.4. *Microfiltration (MF)*

Microfiltration is suitable for treating dye baths containing pigment dyes [45] as well as subsequent rinsing baths. The auxiliaries remain in the retentate. Microfiltration can also be used as a pretreatment for nanofiltration or reverse osmosis [13].

Table 1
Possible treatments and references

Processes	Advantages	Disadvantages	References
Biodegradation	Rates of elimination by oxidizable substances about 90%	Low biodegradability of dyes Costs	[9,10,14–16,59,60]
Coagulation–flocculation	Elimination of insoluble dyes	Production of sludges Costs	[17,25,61]
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Blocking filter Cost of activated carbon	[10,20,58]
Ozone treatment	Good decolorization	No reduction of the COD Additional costs	[23–27]
Electrochemical processes	Capacity of adaptation to different volumes and pollution loads	Iron hydroxide sludges	[21,22]
Reverse osmosis	Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	High pressure	[11–13]
Nanofiltration	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts Treatment of high concentrations	/	[30–33,35–40,54]
Ultrafiltration–microfiltration	Low pressure	Insufficient quality of the treated wastewater	[13,41–45,57]

2.5. Review: conclusion

In Table 1, we present all the current processes used which have been studied for treating dye house effluents. It is clear that an overall treatment cannot be carried out in one step, because the waste compounds contained is very complex. In view of the water shortage which is developing in many countries, the increasingly severe regulations and the release thresholds which are being established, it is becoming increasingly necessary to treat wastewater essentially in view of its reuse. Only membrane filtration can permit solving these problems while also upgrading dye house effluents. These effluents are complex and always present high salinity. A review of the state of the art reveals the lack of published. A few number of references concern wastewater which only contain one dyestuff and then is no proposal for upgrading real effluents. The process that we present, including pretreatments takes into account the industrial requirements (release norms, temperature, time, etc.) and the complexity of the effluent: the result is extremely flexible.

3. Experimental part

3.1. Solutions

The effluents which constitute the object of this study result from the dyeing of cotton with reactive dyes by the exhaust process. The reactive dyes used are of the following types: vinyl sulfone, monochlorodifluoropyrimidine, monochlorotriazine, trichloropyrimidine and monofluorotriazine. The hydrolyzed reactive dyes present in the treated effluents comprise the entire range of possible types of reactive dyes. Diagrammatically, a reactive dye has the form of a complex molecule which is constituted by a chromophore responsible for the adsorption and re-emission of light rays possessing solubilizing groups, onto which a reactive group is grafted which is fixed to the cellulose by means of a covalent bond. The type of reaction can be either one of substitution or addition:

- *Mechanism of reaction by esterification:* In the case of a substitution-type bond, the reactive groups are carried by heterocycles comprised of nitrogen atoms [2]. The electronegativity of the fluorine or chlorine present on the reactive group increases the electrophilic character of the dyestuff. In an alkaline solution, there is a dissociation of the cellulose, which possesses a pronounced nucleophilic character which permits a reaction with the electrophilic sites carried by the dyestuff. There is a reaction between the cellulose and the dyestuff. The chlorine or fluorine ion is substituted by a cellulose ion (Fig. 2) while the dyestuff reacts with water (hydrolysis reaction).
- *Mechanism of reaction by etherification:* In this group of dyestuffs, use is made of the particular characteristic of the sulfatoethylsulfone group which in an alkaline solution is transformed into a vinylsulfone group capable of reacting with the cellulose [2]. There is a transformation and addition of the cellulose–O$^-$ ion. Vinylsulfone dyes follow the law of addition known as the Michael Reaction.

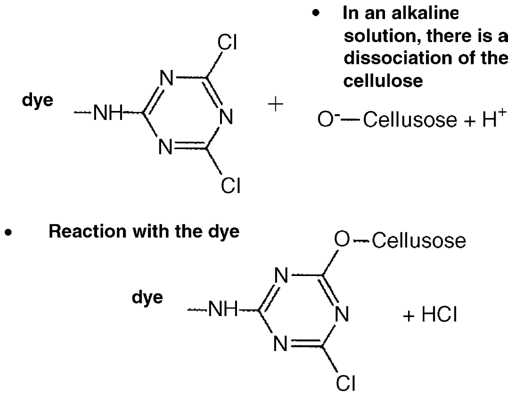


Fig. 2. Dyeing by esterification [2].

The effluents were composed on average of approximately 3 g L^{-1} of a mixture of hydrolyzed reactive dyes and 80 g L^{-1} of salts (sodium chloride). The rate of flow of dye bath to be treated, 250 L h^{-1} per machine, was imposed by the time taken to dye a textile substrate (4 h for a machine of 1000 L). These effluents were directly recovered after use at the dyehouse PETIT BATEAU in Troyes (Table 2). Thus, actual industrial effluents and not reconstituted ones were used in this study. For the diafiltration steps we used distilled and municipal water in order to study the influence of the solvent. The characteristics of municipal water used are pH 8.2, conductivity = 500 μ S cm^{-1}, hardness = 16 °F, [Ca^{2+}] = 70 mg L^{-1}, [Mg^{2+}] < 10 mg L^{-1}.

3.2. Prefiltration and acidification

A Polygard CR filter and a Rigimesh filter [46] supplied, respectively, by Millipore and Pall Exekia were used. There average cut-off was 100 μm. The Rigimesh filter was used for the validation experiments under industrial conditions. The Rigimesh filters are made of stainless steel 304 L for the media and steel 316 for the support materials. This type of filter can withstand high temperatures and high differential pressures. Thus, the prefiltration can be carried out at 70 °C (dye bath temperature at the outlet of the dyeing machine) and – what is most important – rapidly, so as not to immobilize the dyeing machine too long during drainage (1000 L/5 min). A similar prefilter but with 70 μm cut-off located downstream was used as a safety prefilter: the experiment consisted in releasing the effluent at the outlet of the dyeing machine into the prefilter. The pre-filtered effluent was then fed to the retention tank for acidification and the textile fibres trapped by the prefilter were afterwards removed. The amount of textile fibres contained in the prefilter is determined by weight and the pressure drop was controlled and found constant.

Table 2
Characteristics of dyeing bath which generated effluents treated in the laboratory and prefiltered with the polygard CR prefilter or prefiltered with the RIGIMESH industrial prefilter

Volume filtered (L)	Reactive dyes (material dyed)	Dye bath recipes
Dyeing bath which generated effluents treated in the laboratory and prefiltered with the Polygard CR prefilter		
60	Drimaren SN	15 g L^{-1} Black Drimaren SN 150 powder 100 g L^{-1} NaCl 3 g L^{-1} Na_2CO_3 4 g L^{-1} NaOH 30.5%
60	Drimaren HF	1.9% Orange Drimaren HF-2GL 3.67% Red Drimaren HF-2B 80 g L^{-1} NaCl 15 g L^{-1} Soda ash
60	Drimaren HF	0.11 g L^{-1} Drimaren yellow HF-R 0.72 g L^{-1} Drimaren red HF-G 1.22 g L^{-1} Drimaren blue HF-RL 65 g L^{-1} NaCl 10 g L^{-1} Na_2CO_3
200	Drimaren HF	1.9% Orange Drimaren HF-2GL 3.67% Red Drimaren HF-2B 80 g L^{-1} NaCl 15 g L^{-1} Soda ash
300	Drimaren HF	1 g L^{-1} Blue Drimaren HFRL 0.39 g L^{-1} Red Drimaren HFG 0.65 g L^{-1} Yellow Drimaren HFR 80 g L^{-1} NaCl 12 g L^{-1} Na_2CO_3
300	Drimaren HF	0.59% Yellow Drimaren HF-R 1.4% Red Drimaren HF-G 0.94% Blue marine Drimaren HF-B 50 g L^{-1} NaCl 15 g L^{-1} Na_2CO_3
60	Drimaren K	3.93 g L^{-1} Drimaren yellow K-2R 4.14 g L^{-1} Drimaren red K-8B 0.076 g L^{-1} Drimaren blue K-2LR 80 g L^{-1} NaCl 8 g L^{-1} Na_2CO_3
60	Drimaren K	1.09 g L^{-1} Drimaren orange K-GL 0.58 g L^{-1} Drimaren red K-8B 0.89 g L^{-1} Drimaren blue K-2LR 60 g L^{-1} NaCl 5 g L^{-1} Soda ash
60	Drimaren K	2.2% Orange Drimaren K-3R 2.2% Red Drimaren K-8B 0.073% Blue Drimaren K-2LR 80 g L^{-1} NaCl 7 g L^{-1} Soda ash
60	Drimaren K	1 g L^{-1} Tanartege INF 0.675% Orange Drimaren KGL 0.363% Red Drimaren K8B 0.563% Blue Drimaren K2LR 40 g L^{-1} NaCl 5 g L^{-1} Na_2CO_3
60	Drimaren K	0.3 g L^{-1} Tanaterge INF 0.11% Yellow Drimarene K4G 0.24% Yellow Drimaren KR 0.0275% Blue Drimaren K2LR 30 g L^{-1} NaCl 4 g L^{-1} Na_2CO_3
200	Drimaren K	2.2% Orange Drimaren K-3R 2.2% Red Drimaren K-8B

Table 2 (*Continued*)

Volume filtered (L)	Reactive dyes (material dyed)	Dye bath recipes
		0.073% Blue Drimaren K-2LR 80 g L^{-1} NaCl 7 g L^{-1} Soda ash
300	Drimaren K	1% Yellow Drimaren K-2R CDG 1.95% Red Drimaren K-8B CDG 50 g L^{-1} NaCl 5 g L^{-1} Soda ash
60	Drimaren X	1.13 g L^{-1} Drimaren Yellow X-4RN 2.435 g L^{-1} Drimaren Red X-6BN 0.508 g L^{-1} Drimaren blue X-3LR 80 g L^{-1} NaCl 20 g L^{-1} Na_2CO_3
Effluents prefiltered with the Rigimesh industrial prefilter		
1500	Remazol (cotton)	0.715% Black remazol N150 0.57% Blue remazol GG 133% 0.354% Red remazol RB 133% 70 g L^{-1} NaCl 15 g L^{-1} Soda ash
4500	Remazol (cotton, polyamide (Bouclette))	0.631% Black remazol N150 0.679% Blue remazol GG 133% 0.451% Red remazol RB 133% 80 g L^{-1} NaCl 20 g L^{-1} Soda ash
1500	Remazol (cotton)	1% Black remazol N150 1.015% Blue remazol GG 133% 0.693% Red remazol RB 133% 80 g L^{-1} NaCl 20 g L^{-1} Soda ash
1500	Drimaren K (cotton)	1.168% Orange Drimaren KGL 0.407% Red Drimaren K8B CDG 1.35% Blue Drimaren K2LR CDG 50 g L^{-1} NaCl 5 g L^{-1} Soda ash
3000	Drimaren K (cotton (Molleton grate))	0.97% Orange Drimaren KGL 0.3% Red Drimaren K8B CDG 1.123% blue Drimaren K2LR CDG 50 g L^{-1} NaCl 5 g L^{-1} Soda ash

Textile fibres are no detected after prefiltration.

The acidification of the dye bath in order to precondition it for the passage through the membrane and its reuse for a new dyeing, is based on the use of hydrochloric acid (technical grade, 30%). By experiment, we know that for a re-dyeing, it is necessary to have the following characteristics:

- T_{AC} lower than 20 °F (1 °F = 0.2 meq L^{-1} = 0.1 mmol L^{-1} of Ca^{2+});
- pH 5.5–6.0.

so as to permit an efficient separation of the salt by nanofiltration and to obtain as permeate a brine with suitable pH and T_{AC}. The introduction of hydrochloric acid was carried out by means of a universal titrator (Titroline easy, Schott, Mainz) which consists of a metering pump for injecting the amount of acid desired, a metric pH sensor and an agitator. The plotting of the pH versus V_{HCl} permitted obtaining the minimum hydrochloric acid amount sufficient to remove the bicarbonates. A sufficient degassing, to remove free CO_2, was ensured by injecting compressed air into the solution in the form of fine bubbles.

3.3. Membranes

After a screening, the nanofiltration membrane use was DESAL 5DL–OSMONICS membrane, of the spiral wound type. Characteristic molecular weight cut-off is given as 200–300 Da and the filtrating area is 2.5 m^2. The membrane use must allow the salts to pass through but retain the hydrolyzed reactive dyes and dye auxiliaries, be as inexpensive as possible and be capable of withstanding relatively high temperatures ($\cong$50 °C).

For the reverse osmosis, the membrane use was AD 2540 (OSMONICS) with a membrane area of 2.3 m^2. The RO membrane has to fulfill several criteria: it has to be resistant to temperature about 40–50 °C, transmembrane pressures in the order of 80×10^5 Pa (80 bar) and ensure a high salt retention in order to achieve the separation aimed.

3.4. Plant and experimental procedure

The plant used, already presented [46], allows us to work with membranes having an industrial elementary surface and to collect results for easy scaling up.

3.5. Methods of analysis

During experiment, samples of the permeate and the retentate were collected for analysis. The chlorides were analyzed by three different methods: conductimetry, potentiometry, spectrophotometry and certified by an independent and external laboratory which is the SEM (Société des Eaux de Marseille).

- The conductimetry analyses were made by using a conductimeter (CDM 210 and CDC 641T Radiometer analytical SA, Villeurbanne, France). The conductimetric sensor used permits automatic and permanent correction of the conductivity value by taking account of the temperature.
- The potentiometric analyses were carried out using a silver nitrate solution 0.1N (Acros, Geel, Belgium). An electrode combined with a potentiograph is employed. A silver nitrate solution is added and the potential is measured.

For a sample of a given mass, a voltage step is produced when all the free chlorines have precipitated, which corresponds to a volume of silver nitrate solution added. The concentration of chlorine can be calculated from this volume by knowing the concentration of the silver nitrate solution and the volume of the sample.

- The spectrophotometric analyses were made with a spectrophotometer (Thermo Spectronic, Aquamate, Rochester NY, USA) and a tube test (Merck) containing mercury thiocyanate(II). We introduce 1 mL of our solution in the tube, the ions chlorides react with the mercury thiocyanate(II) to give the sparingly dissociated mercury chloride(II). The thiocyanate which is thus liberated forms, together with the ferric ions, iron(III) thiocyanate red, which is measured by photometry.

The retention factors (RF) of the different species are calculated from the concentrations of each species in the permeate and in the retentate according to the following equation:

$$\mathrm{RF} = \left(1 - \frac{C_\mathrm{p}}{C_\mathrm{r}}\right) \times 100 \qquad (1)$$

with RF is the retention factor (%), C_p the concentration in the permeate ($\mathrm{g\,L^{-1}}$) and C_r is the concentration in the retentate ($\mathrm{g\,L^{-1}}$).

The color is measured by absorbance particularly in the initial solution, the first permeate and the last permeate. These absorbance measurements were carried out with a spectrophotometer (Thermo Spectronic, Aquamate). A spectrum is plotted over the entire visible band and the absorbance of the solution is measured at the wavelength of the higher peak corresponding to the color of the solution.

4. Results and discussion

The results are normalized with respect to temperature.

4.1. Prefiltration step

Experiments with the Polygard CR filter and with the Polygard Rigimesh were already presented [46]. For laboratory and industrial scales, all textile fibres had been trapped in the selected prefilter.

4.2. Nanofiltration step

4.2.1. Membranes

The DESAL 5 DL membrane used allow the salts to pass through but retain the hydrolyzed reactive dyes and dye auxiliaries and resists has high temperatures (≅50 °C).

4.2.2. Variation in the concentration of NaCl

For each test, we used conductimetry to follow the evolution of the concentration of sodium chloride in the retentate and in the permeate versus time (Fig. 3). Concentrations (i.e. conductivities) varied in a similar way in retentate and in permeate; it decreased during the diafiltration. It increased in the course of the concentration step (some ionic compounds are still present in the retentate). We compared the concentration values obtained by conductimetry with those obtained by spectrophotometry and potentiometry (Figs. 4 and 5). For the retentate, the results gained with spectrophotometry are different than those obtained with the other analysis methods and are not satisfactory. This discrepancy is due to the presence of parasite compounds, such as hydrolyzed reactive dyes or dyeing auxiliaries in the retentate, which falsified the analysis. In the case of the permeate, the spectrophotometry results are in agreement with other results and confirm that the hydrolyzed reactive dyes and the dyeing auxiliaries present in the retentate were totally retained by the membrane.

The results obtained by SEM (Figs. 4 and 5) validate those obtained by conductimetry, potentiometry and spectrophotometry and therefore confirm the separation by nanofiltration. Measurement of the concentration of salts by means of conductimetry can be easily carried out under industrial conditions.

4.2.3. Variation of the retention factor

4.2.3.1. Sodium chloride. The evolution of the retention factor for various effluents according to the NaCl concentration

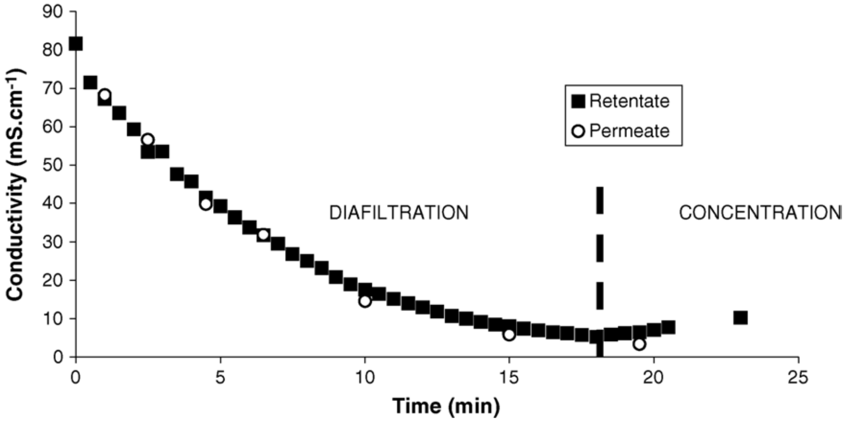


Fig. 3. Variation of the conductivity in the retentate and the permeate vs. time (dye: Drimaren K, [NaCl] = 80 g L^{-1}, T = 50 °C, TMP = 1 × 10^6 Pa (10 bar), Q = 300 L h^{-1}, V_0 = 9 L, pH 5.5, solvent = distilled water).

in the feed solution was presented [46]. The retention factor increases as the concentration of NaCl decreases [47]. When the concentration of NaCl is high, electrostatic repulsions at the membrane wall are weak and the salts pass easily through the membrane. 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 salts are retained. It can therefore be seen that it is easy to eliminate the salts when their concentration in the solution is high, but this is appreciably more difficult when the concentration is lower than 10 g L^{-1}. As a regard with the energy costs, recovering only 85–90% of the salt present in the effluent is sufficient.

4.2.3.2. Hydrolyzed reactive dyes. In all cases, the absorbance of the permeate was very weak, i.e. virtually nil, showing that as all the hydrolyzed reactive dyes were retained by the membrane. The absorbance of the retentate permits quantification of the concentration factor (it is the ratio of the final retentate absorbance on initial retentate absorbance) and to check the mass balance. The absorbance values obtained for each of the hydrolyzed reactive dyes are given in Table 3. Without further improvement of the operating conditions, it can already be stated that the hydrolyzed reactive dyes and the dyeing auxiliaries were retained by the nanofiltration membrane and that the salts pass through, thus being recoverable. We shall now see what the effects of the operating variables are, in order to optimize the process.

4.2.4. Variation of the permeate flux

When the evolution of the permeate flux is considered versus time (Fig. 6), it can be seen that during the diafiltration step it increases as the concentration of NaCl decreases. More, the flux strongly decreases during the concentration step with increase of the concentration of hydrolyzed reactive dyes and dyeing auxiliaries.

4.2.5. Variation of the operating parameters

4.2.5.1. Effect of the pH. Due to the presence of carbonate species, we verified that for variable salinities and temperatures, the pH value fixed at 5.5 remained efficient. From the

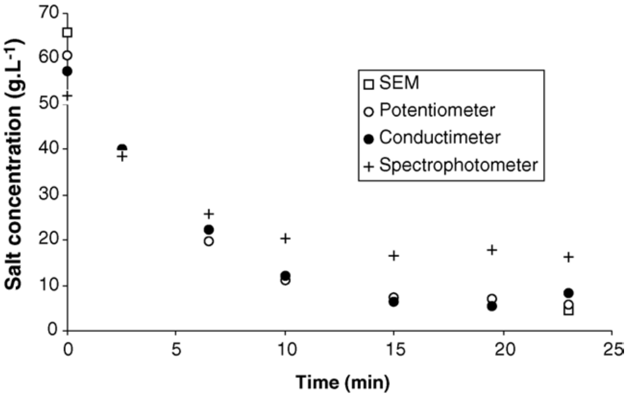


Fig. 4. Variation of sodium chloride concentration in the retentate vs. time from different analytical methods (dye: Drimaren K, [NaCl] = 80 g L^{-1}, T = 50 °C, TMP = 1 × 10^6 Pa (10 bar), Q = 300 L h^{-1}, V_0 = 9 L, pH 5.5, solvent = distilled water).

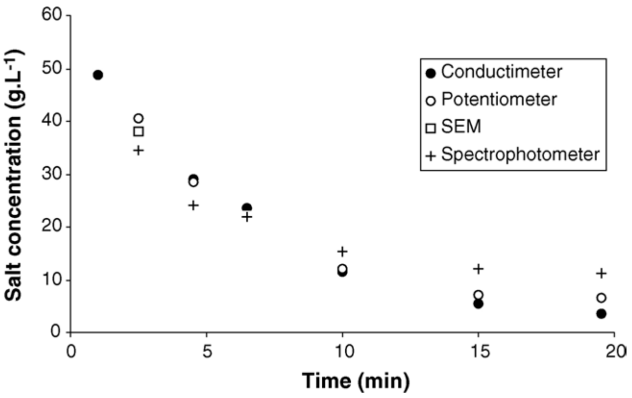


Fig. 5. Variation of sodium chloride concentration in the permeate vs. time from different analytical methods (dye: Drimaren K, [NaCl] = 80 g L^{-1}, T = 50 °C, TMP = 1 × 10^6 Pa (10 bar), Q = 300 L h^{-1}, V_0 = 9 L, pH 5.5, solvent = distilled water).

Table 3
Absorbance of the effluent, permeate and retentate flux

Reactive dyes	Color	Initial absorbance	Final absorbance	Permeate absorbance	Concentration factor	Concentration factor obtains by the mass balance
Drimaren K-NaCl	Red	0.46	1.13	0	2.5	3
Drimaren K-NaCl	Red	0.41	1.08	0	2.7	3
Drimaren K-NaCl	Red	0.82	5.18	0	6.3	6.2
Drimaren K-NaCl	Orange	1.78	6.82	0.01	3.8	4.1
Drimaren HF-NaCl	Green	0.42	1.16	0	2.8	2.8
Drimaren HF-NaCl	Brown	0.47	1.52	0	3.3	3.2
Drimaren HF-NaCl	Black	0.24	1.34	0	5.7	5.6
Drimaren X-NaCl	Red	1.51	4.1	0.01	2.7	2.6

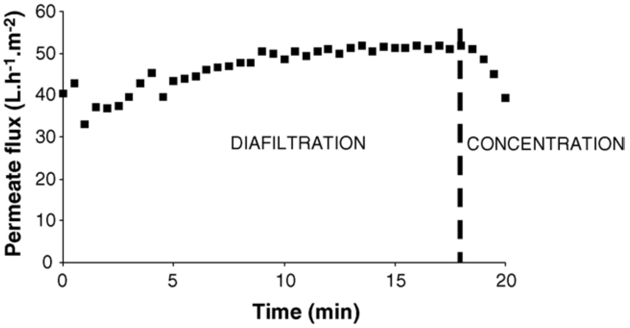


Fig. 6. Variation of the permeate flux vs. time (dye: Drimaren K, [NaCl] = 80 g L^{-1}, T = 50 °C, TMP = 1×10^6 Pa (10 bar), Q = 300 L h^{-1}, V_0 = 9 L, pH 5.5, solvent = distilled water).

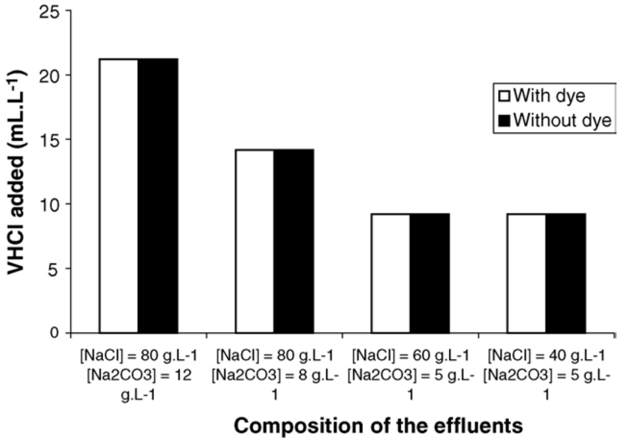


Fig. 8. Evolution of hydrochloric acid volume added as a function of effluents compositions.

variation of acidity constants with the temperature and the salinity [48–50], we calculated the concentrations of the various species carbonated for a sodium chloride concentration of 0, 40 and 50 g L^{-1} in order to examine at the influence of the salinity on the distribution of the carbonated species. For higher concentration values, it was impossible to calculate and to predict the salt concentrations for each species (no ideal solution) and so we have realised some experiments. In view of these results and in the industrial concentration range (40–80 g L^{-1}) it can be concluded that the carbonate ion concentrations remain low at pH 5.5. We can keep a pH at 5.5 for the acidification. Dyeing experiments are in agreement with this conclusion. The temperature effect is presented in Fig. 7 showing that the increase of the temperature involves a very small variation of the concentrations at pH 5.5.

In order to investigate the influence of the hydrolyzed reactive dyes, we compared the results obtained with the real effluents and synthetic solutions without hydrolyzed reactive dyes. It can be seen that the hydrolyzed reactive dyes have no influence on the hydrochloric acid amount necessary for sufficient elimination of carbonates (Fig. 8). However, it

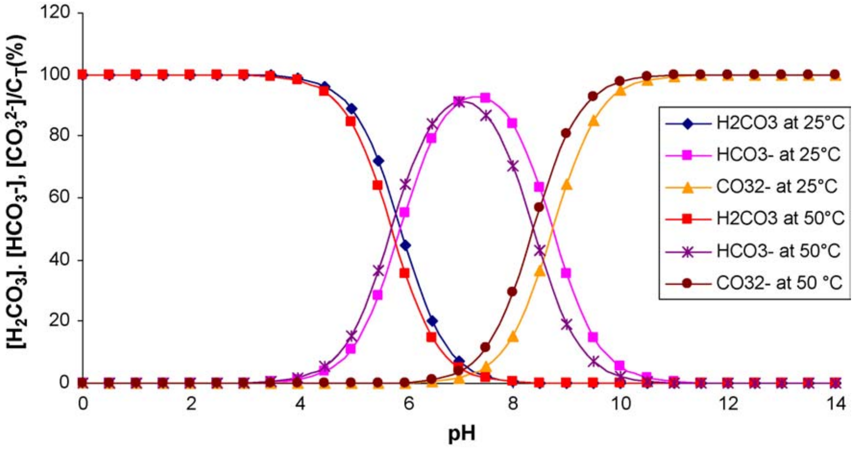


Fig. 7. Influence of the temperature between 25 and 50 °C on the species carbonated according to the pH.

was observed that CO_2 formed may produce a slow variation of the pH (Table 4) if it is not removed from the solution. Removal of CO_2 achieved by injection of fine bubbles of compressed air into the solution. The course of the pH indicates a pronounced enhancement of the pH value followed by its stabilization. Measurements of the complete alkali metric titer and of the different concentrations are given in Table 4. Considering these results, CLARIANT society (manufacturer of reactive dyestuffs) suggested to change sodium carbonate by a sodium carbonate–NaOH 30.5% mixture in the dyeing process. The experimental results are given in Table 5. Finally, this dyeing modification appears to be very advantageous. It induces a considerable reduction of the amounts of hydrochloric acid. Neither the final dye yield nor the leveling time of the dyeing process are affected by the modification suggested. But the question may be asked: would it be more advantageous to remove the carbonates after the nanofiltration step? We filtered two effluents, one carbonated and the other decarbonated (Fig. 9). As expected, the permeate flux is much higher when there are no more bicarbonates and carbonates present. The effect of the pH has been studied by a large number of authors [51–54]. The isoelectric point of the membrane used is in the vicinity of 4.2 [55]. Below this value, membrane is positively charged, and above it, the membrane is negatively charged. When the pH is high, the carbonate solution contains monovalent Cl^- ions and a substantial concentration of bivalent ${CO_3}^{2-}$ ions, and we thus have strong repulsions between the membrane and the solution. At pH 5.5 the membrane is still negatively charged but as the isoelectric point is approached and the solution now contains only monovalent Cl^- ions and a low concentration of ${HCO_3}^-$, the repulsions between the membrane and the solution are therefore less strong and the permeate flux higher. The pretreatments are now described: prefiltration to remove the textile fibres and acidification to remove carbonate species.

4.2.5.2. Effect of the temperature. Although the temperature of the effluents at inlet of the nanofiltration step is variable but close to 50 °C, two experiments were undertaken in order to investigate the influence on permeate flux. Normally, an increasing of the temperature entails an increase of the permeate flux (Fig. 10). The variation of permeate flux with temperature is usually explained by the variation in the viscosity of the effluent. In the range of temperature (24–50 °C), the viscosity of the effluents treated (0.98–0.62 mPa s) is approximately that of water (0.91–0.55 mPa s) and in agreement with the permeate flux variation.

4.2.5.3. Effect of the transmembrane pressure. The higher the transmembrane pressure, the higher the permeate flux and two cases were observed. For a solution slightly concentrated in hydrolyzed reactive dyes, flow increases linearly with the transmembrane pressure. The hydrolyzed reactive dyes in weak concentration do not induce any fouling of the membrane: we found the water permeability

Table 4
Variation of the hydrochloric acid volume as a function of carbonate concentration

$[Na_2CO_3]$ ($g\,L^{-1}$)	V_{HCl} added ($mL\,L^{-1}$)	Initial pH of solution	Without degassing				With degassing				After 24 h without degassing			
			pH	T_{AC} (°F)	$[CO_2]$ free ($\times10^{-5}$ mol L^{-1})	$[{HCO_3}^-]$ ($\times10^{-3}$ mol L^{-1})	pH	T_{AC} (°F)	$[CO_2]$ free ($\times10^{-5}$ mol L^{-1})	$[{HCO_3}^-]$ ($\times10^{-3}$ mol L^{-1})	pH	T_{AC} (°F)	$[CO_2]$ free ($\times10^{-5}$ mol L^{-1})	$[{HCO_3}^-]$ ($\times10^{-3}$ mol L^{-1})
5	9.2	10.3	5.3	3	726	0.6	8.1	2.5	1.03	0.5	6.1	3	110	0.6
7	12.2	10.3	5.5	6	1000	1.2	8.2	5	1.52	1	6	7.5	346	1.5
8	14.2	10.5	5.4	5.5	987	1.1	8.1	5.5	1.75	1.1	6	2.5	113	0.5
12	21.2	10.6	5.4	11.5	1920	2.3	8.2	5.5	1.53	1.1	6.6	10.5	106	2.1
15	27.2	10.5	5.4	11	1680	2.2	8	3.5	1.69	0.7	6.1	10.5	335	2.1
20	37.2	10.7	5.3	12	2770	2.4	8.1	6	2.3	1.2	5.9	6	365	1.2

Effect of the degassing on the concentrations.

Table 5
Influence of sodium carbonate–NaOH 30.5% mixture on volume of hydrochloric acid

Na_2CO_3 ($g\,L^{-1}$)	HCl 9.55N or 35% ($ml\,L^{-1}$)	Na_2CO_3 ($g\,L^{-1}$)	NaOH 36°B ($ml\,L^{-1}$)	HCl 9.55N or 35% ($ml\,L^{-1}$)	Gain (%)
20[a]	32	10[a]	2[a]	18	43.7
15	24	8	1.5	15	37.5
10	16	6	1	11	31.2
5	8	3	0.5	5.5	31.2

[a] A solution of 20 $g\,L^{-1}$ carbonate represents the same solution for producing a dyeing as a solution of 10 $g\,L^{-1}$ carbonate with 2 $mL\,L^{-1}$ soda 36°B. It was observed that in the second case, less hydrochloric acid is required for acidification.

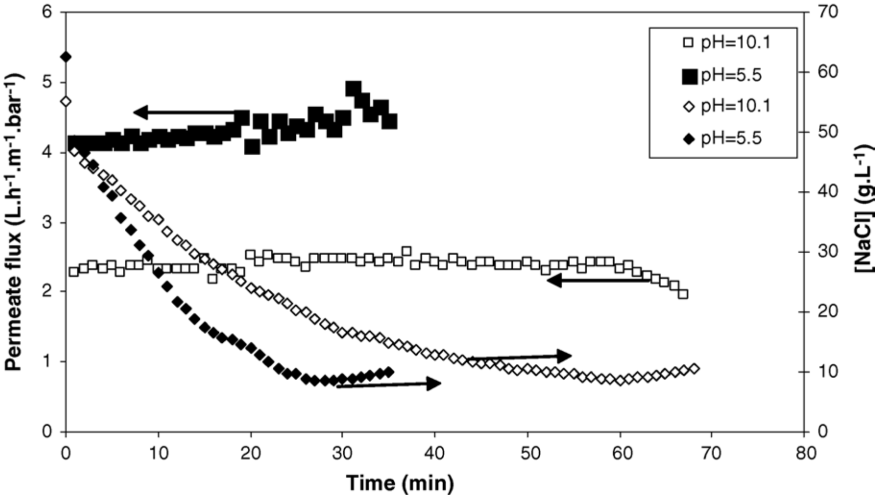


Fig. 9. Variation of the permeate flux and variation of the retentate concentration vs. time for different pH (dye: Drimaren HF, [NaCl] = 80 $g\,L^{-1}$, [Na_2CO_3] = 15 $g\,L^{-1}$, T = 50 °C, TMP = 1×10^6 Pa (10 bar), Q = 350 $L\,h^{-1}$, V_0 = 20 L, solvent = distilled water).

values. In the case of strongly colored effluents, a limiting flux is observed due to the fouling of the membrane by the hydrolyzed reactive dyes. The limiting flux is reached obtained for a transmembrane pressure higher than 20×10^5 Pa (20 bar), so that it is necessary to work with a lower transmembrane pressure. Transmembrane pressure around 1×10^6 Pa (10 bar) for all effluents appears to be efficient and prevents fouling whether they are clear or strongly colored.

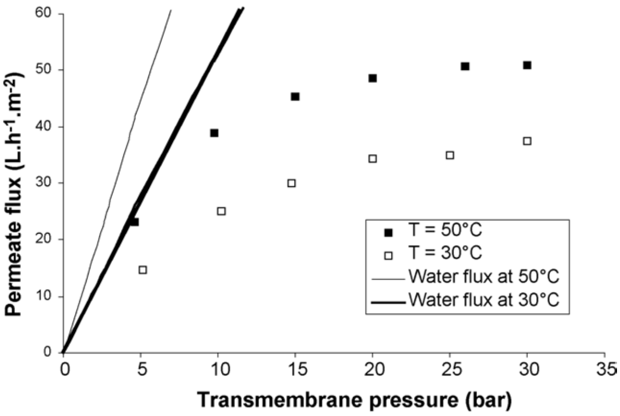


Fig. 10. Variation of the permeate flux vs. transmembrane pressure for different temperatures (dye: Drimaren K, [NaCl] = 40 $g\,L^{-1}$, Q = 350 $L\,h^{-1}$, V_0 = 10 L, pH 5.5, solvent = distilled water).

4.2.5.4. Effect of the velocity. A variation of permeate flux by varying this parameter can be noted only in case of fouling (dark effluents). For a TMP of 1×10^6 Pa (10 bar), even for the dark effluents, fouling is not encountered (Fig. 11). For the process we selected a circulating flow rate at 350 $L\,h^{-1}$ as regard as the flow rate recommended by the supplier but it is obviously possible to work below.

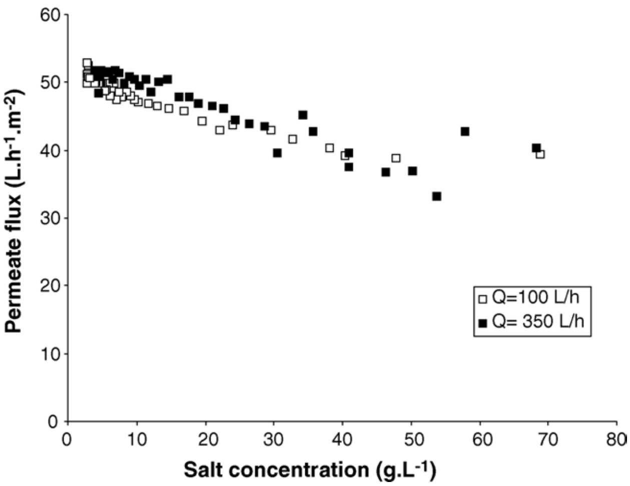


Fig. 11. Variation of the permeate flux vs. concentration in the retentate for different velocities (dye: Drimaren K, [NaCl] = 80 $g\,L^{-1}$, TMP = 1×10^6 Pa (10 bar), T = 50 °C, V_0 = 9 L, pH 5.5, solvent = distilled water).

4.2.5.5. Regulating the nanofiltration step. All the experiments described above were carried out in two steps, a diafiltration step during which the sodium chloride is recovered while keeping a constant concentration of hydrolyzed reactive dyes and dyeing auxiliaries, and a concentration step where the minimum volume of hydrolyzed reactive dyes and dyeing auxiliaries is aimed. Fig. 6 shows off the diafiltration step of a dark effluent and the permeate flux increases due to the elimination of the sodium chloride, and then during the concentration phase the permeate flux strongly decreases when the major part of salts is recovered: the hydrolyzed reactive dyes and the dyeing auxiliaries are concentrated. Due to their fouling effect it seems impossible to concentrate the initial effluent directly. Different situations can be encountered depending of the nature of the effluent and they can be easily distinguished. So, three processes are used [46]:

1. If the initial effluent contained diluted hydrolyzed reactive dyes (pale shade and/or high rate of fixation) (Fig. 12), the nanofiltration can be carried out in one single step, called the preconcentration step. In such a case, the decrease in permeate flux is not pronounced, due to the concentration of hydrolyzed reactive dyes and there is no need of reverse osmosis, because the recovered permeate contains the same high salt concentration as the effluent treated.
2. If the effluent has a low concentration of hydrolyzed reactive dyes (medium shade), it is possible to carry out the nanofiltration in three steps: preconcentration, diafiltration and concentration (Fig. 13). The diafiltration takes place when the permeate flux becomes too low to continue the preconcentration and if the amount of salt already recovered is not yet sufficient (Fig. 14).
3. If the effluent has a high concentration of hydrolyzed reactive dyes (deep shade), the nanofiltration is carried out in two steps, namely diafiltration and concentration (Fig. 6).

4.2.5.6. Effect of the water quality used in the diafiltration step. The water used in the diafiltration step was distilled water, available in the laboratory. However, municipal water or groundwater which has been softened is of course preferred for industrial uses. Fig. 15 shows the evolution of the permeate flux versus the sodium chloride concentration obtained with distilled water and municipal water (pH 8.2, conductivity = 500 μ S cm^{-1}, hardness = 16 °F, [Ca^{2+}] = 70 mg L^{-1}, [Mg^{2+}] < 10 mg L^{-1}). The permeate flux are found identical. Municipal water causes no problems for the diafiltration step. However, caution is advisable because this is not true for all effluents. In fact, Fig. 16, which was obtained with an effluent having a high concentration of hydrolyzed reactive dyes, shows that the flows with two different solvents are not at all identical or capable of being superimposed. With municipal water there is a rapid decline of the flux. It should be noted, however, that the purpose of the reverse osmosis step is to recover not only a brine but also pure water which is capa-

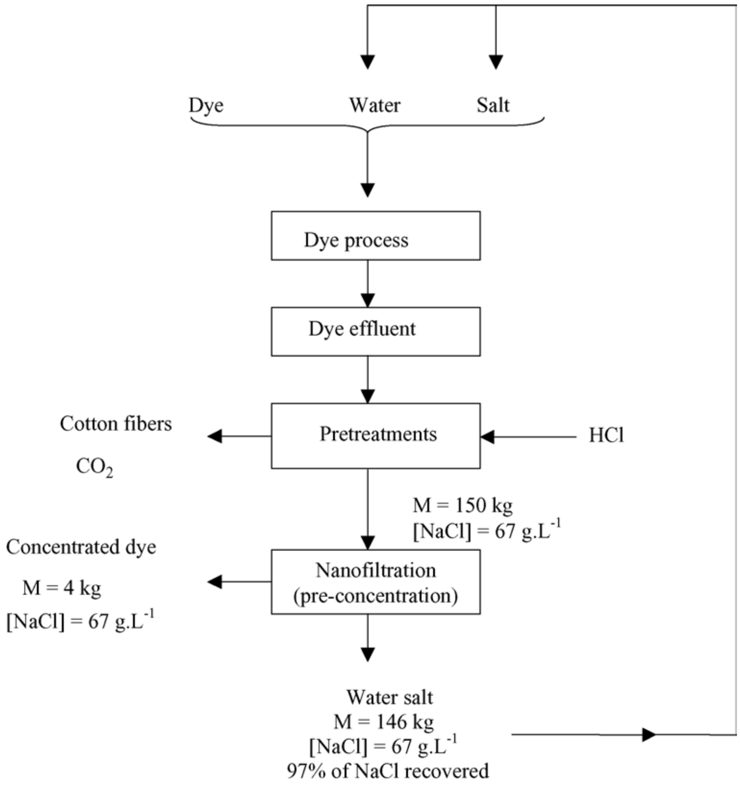


Fig. 12. Mass balance for a treatment by direct preconcentration (dye: Drimaren HF, [NaCl] = 65 g L^{-1}, TMP = 20 × 10^5 Pa (20 bar), Q = 350 L h^{-1}, T = 50 °C, V_0 = 150 L, pH 5.5, solvent = distilled water).

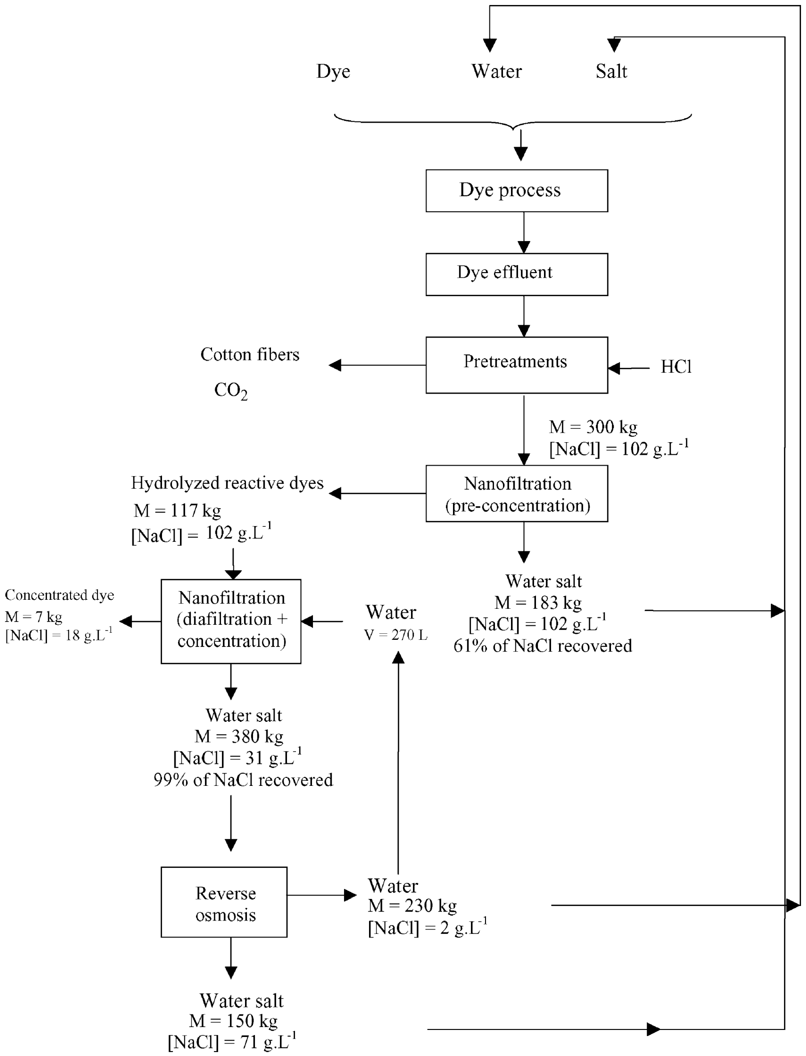


Fig. 13. Mass balance for a treatment by preconcentration, diafiltration and concentration (dye: Drimaren K, [NaCl] = 100 g L^{-1}, TMP = 20 × 10^5 Pa (20 bar), Q = 350 L h^{-1}, T = 45 °C, V_0 = 300 L, pH 5.5, solvent = distilled water).

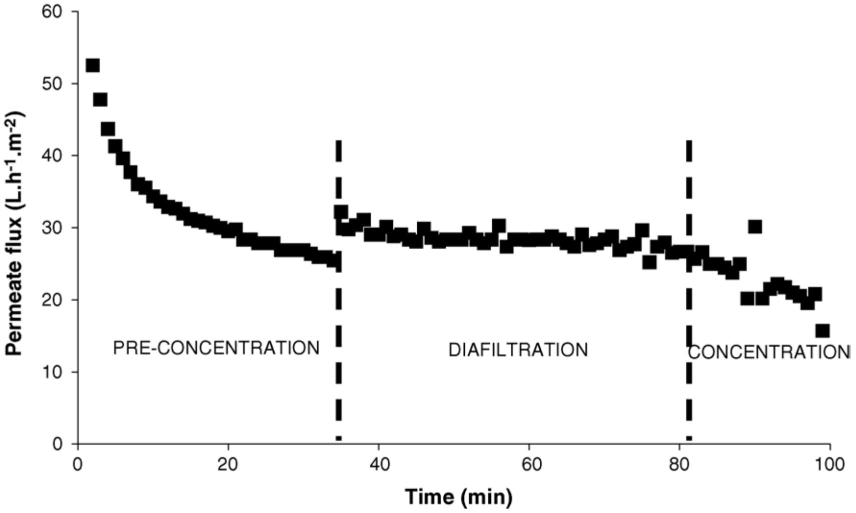


Fig. 14. Variation of the permeate flux vs. time (dye: Drimaren HF, [NaCl] = 100 g L^{-1}, TMP = 20 × 10^5 Pa (20 bar), T = 50 °C, Q = 350 L h^{-1}, V_0 = 300 L, pH 5.5).

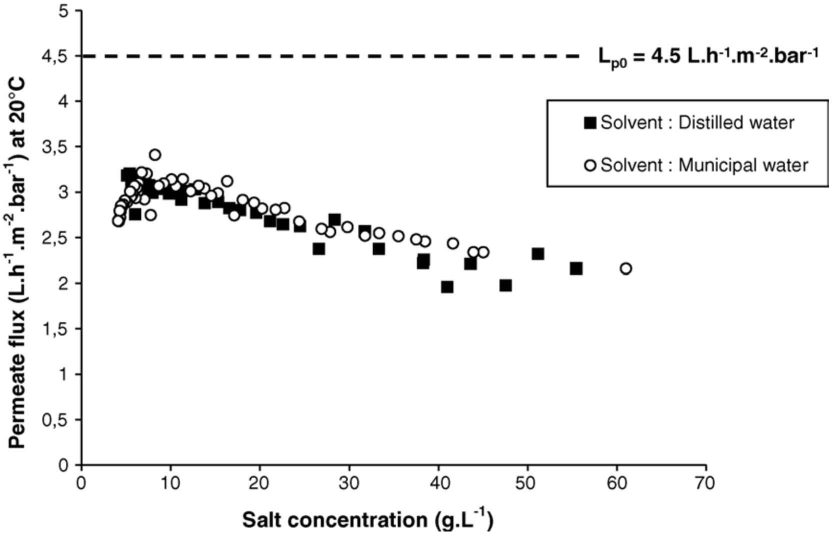


Fig. 15. Variation of the permeate flux vs. concentration of sodium chloride in the retentate for different solvents (dye: Drimaren K, [NaCl] = 80 g L^{-1}, TMP = 1 × 10^6 Pa (20 bar), Q = 350 L h^{-1}, T = 50 °C, V_0 = 10 L, pH 5.5).

ble of being reused for the diafiltration. This would permit a reduction of the use of municipal water.

4.2.6. Regeneration of the NF membrane

Fig. 17 indicates the permeability of the NF membrane after washing with water or chemicals after several successive experiments. Chemical washing was carried out at the end of each experiment: the lower permeability value obtained (before washing) during this study is 1×10^{-5} L h^{-1} m^{-2} Pa^{-1} (1 L h^{-1} m^{-2} bar^{-1}). In all these case, a total regeneration of the membrane was achieved; when the adsorption is low, washing with distilled water is sufficient, otherwise a normal industrial washing (NaOH + dodecyl sulfate, HCl) permits recovery of the initial permeability.

4.3. Reverse osmosis step

4.3.1. Membranes

For the reasons given above, we decided to use membrane AD 2540 F (OSMONICS) and to discuss the result obtain with this membrane. With membrane SC 2540, designed for briny water, the retention factor of the salt was not found high enough when the salt concentration in the feed tank increases.

4.3.2. Variation of the NaCl concentration and retention factor

The concentration (i.e. conductivity) increases slightly in the permeate and very strongly in the retentate versus time due to the retention of sodium chloride (Fig. 18) and the retention

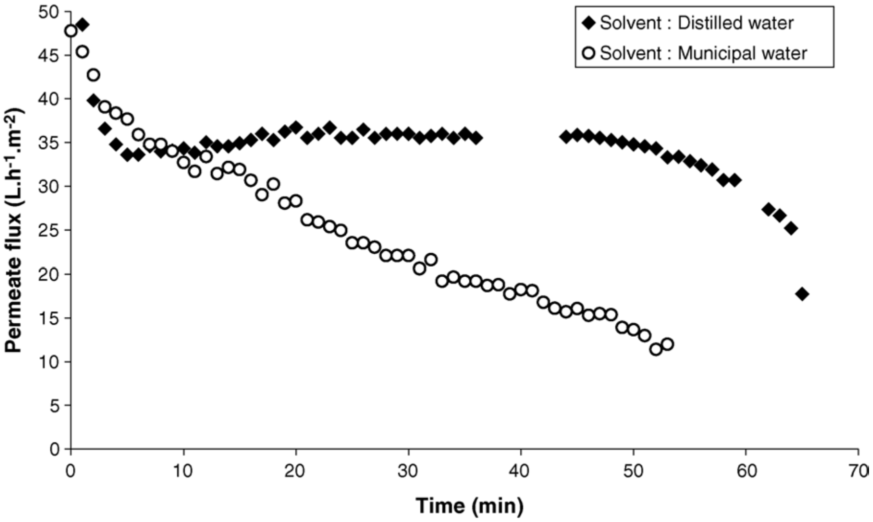


Fig. 16. Variation of the permeate flux vs. time with different solvents (dye: Drimaren HF, [NaCl] = 80 g L^{-1}, TMP = 20 × 10^5 Pa (20 bar), Q = 400 L h^{-1}, T = 50 °C, V_0 = 15 L, pH 5.5).

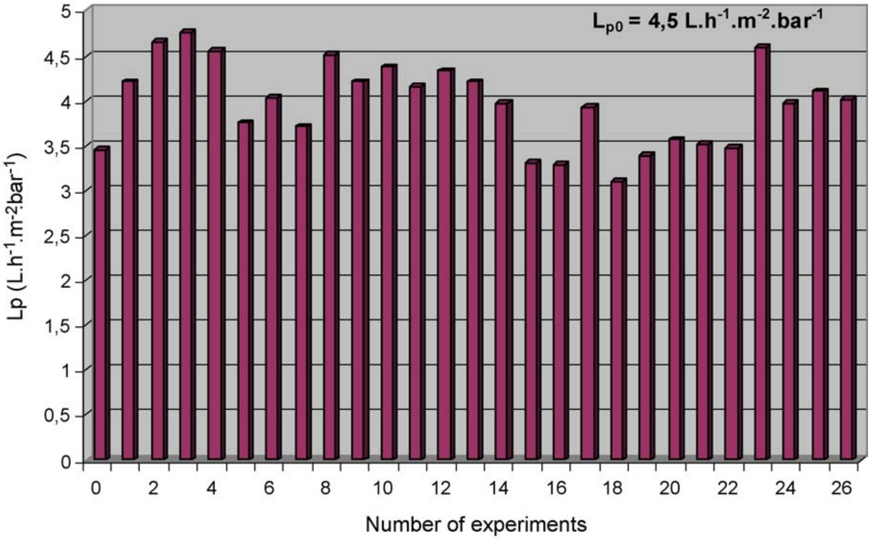


Fig. 17. Variation of the NF membrane permeability vs. number of experiments.

factor remains constant (around 90%) when the concentration of NaCl in the retentate increases (15–80 g L^{-1}).

4.3.3. *Evolution of the permeate flux*

The permeate flux decreases as the concentration of NaCl in the retentate increases. In fact, when the osmotic pressure is taken into account and the permeate flux is no expressed as a function of the transmembrane pressure but as a function of the effective pressure corresponding to the transmembrane pressure less the osmotic pressure, the permeate flux remains constant near the zone of tolerable experimental error. It is therefore not the permeate flux which decreases versus time but the effective pressure, because the osmotic pressure increases. Therefore, operating pressure only depends on the osmotic pressure: in order to reach 70 g L^{-1} as final concentration, the maximum osmotic pressure to overcome is 57×10^5 Pa (57 bar) [56] so that a transmembrane pressure around 70×10^5 Pa (70 bar) is sufficient.

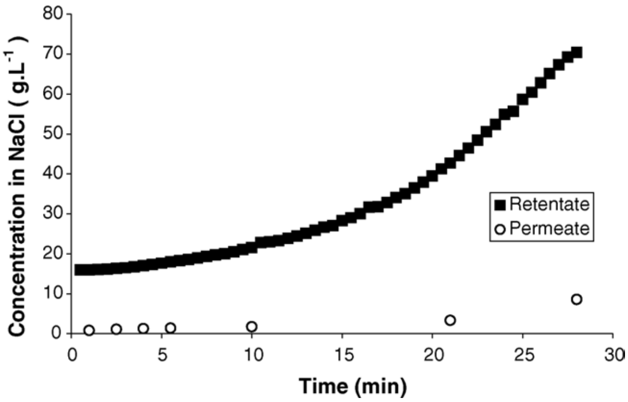


Fig. 18. Variation of the sodium chloride concentration vs. time for the permeate and the retentate (T_{moy} = 35 °C, TMP = 70×10^5 Pa (70 bar), Q = 500 L h^{-1}, V = 20 L).

4.3.4. *Variation of the operating parameters: temperature and velocity*

The variation of the permeate flux with the temperature was not studied and fixed at 35 °C, as this depends on the temperature at the outlet obtained after nanofiltration. Moreover, if it is necessary to modify this parameter, it will be possible to predict the value of the permeate flux by the large number of publication which have studied the effect of temperature on RO flux. In the range of flow rates tested, the velocity has no influence either on the permeate flux or even on the evolution of the concentration of the retentate. 500 L h^{-1} was used as operating flow rate as recommended by the membrane manufacturer.

4.4. *Dyeing experiments: validation of the process*

The comparative dyeing experiments were carried out with usual water (demineralized municipal water, $T_{AC} = 0$) and the brine recycled according to the process described. Four classes of dyes were tested (Table 6), the goal of these experiments being to show that a brine obtained by "pretreatments, nanofiltration and reverse osmosis" of a dyebath containing hydrolyzed reactive dyes could be reused for a new dyeing operation. The dyeing effluent obtained from the Petit Bateau dye house had the following initial composition: 0.59% Drimaren Yellow HF-R, 1.40% Drimaren Red HF-G, 0.90% Drimaren Navy HF-B, 50 g L^{-1} NaCl, 15 g L^{-1} NaCl sodium carbonate and dyeing auxiliaries. After being treated according to our process, a concentrated brine was obtained having the following characteristics: 61 g L^{-1} NaCl, pH 5.5 and T_{AC} = 6.5 °F (1 °F = 5 meq). The absorbance spectrum of this colorless brine confirms that it contains no further hydrolyzed reactive dyes or dyeing auxiliaries. The usual water used as reference had the following characteristics: permanent hardness 0 °F, $T_{AC} \leq 5$ °F, pH 7 ± 0.5.

Table 6
Dyeing parameters with usual water or recycled brine for different reactive dyes

	Drimaren K		Drimaren HF		Drimaren XN	
	Usual water	Recycled brine	Usual water	Recycled brine	Usual water	Recycled brine
Dyeing	4% Red Drimaren K-4BL	4% Red Drimaren K-4BL	2% Red Drimaren HF-2B	2% Red Drimaren HF-2B	3% Yellow Drimaren X-4RN	3% Yellow Drimaren X-4RN
Alkali (g L^{-1})	5	5	10	10	15	15
Salts added (g L^{-1})	60	0	70	9	70	10
Fixation temperature (°C)	60	60	60	60	98	98
Rapport of bath	01:10	01:10	01:10	01:10	01:10	01:10
Mass (g)	15	15	15	15	15	15

4.4.1. *Dyeing with Drimaren CL dye*

The amount of material dyed was 15 g and the dyebath volume was 150 mL. The different sequences of the dyeing recipe were:

- Substantive phase: the reactive dyes are transferred from the bath onto the material thanks to the presence of salt.
- Fixation phase: addition of alkali induce the reaction of reactive dyes with the cellulose.
- Washing: elimination of the hydrolyses reactive dyes and dyeing auxiliaries.

The recipe can thus be described according to Fig. 19 for the recycled brine and for the usual water.

4.4.1.1. Recipes with 1% Drimaren Red CL-5B. The dye bath had the following composition:

- 1% Drimaren Red CL-5B, 48 g L^{-1} NaCl added and 7 g L^{-1} sodium carbonate.

With the usual water it was necessary to add the 48 g L^{-1} NaCl, whereas with the recycled brine, a simple dilution of the recycled brine changed the concentration from 61 to 48 g L^{-1} NaCl.

4.4.1.2. Recipes with 3% Drimaren Red CL-5B. The dye bath had the following composition:

- 3% Drimaren Red CL-5B, 70 g L^{-1} NaCl and 12 g L^{-1} sodium carbonate.

Here it was necessary to add 9 g L^{-1} NaCl only in the dye bath prepared with recycled water in order to obtain the required concentration of salt (70 g L^{-1}). For the other classes of dyes (K, HF and X), the results are given in Table 6. Whatever the reactive dye selected and the type of water used, there was no difference between the dyeing carried out with usual water or with the recycled brine, whatever the strength, shade or fastness properties. The results are given in Table 7. The dyed samples, two per dyeing test have been evaluated trough the most important fastness and compared the results:

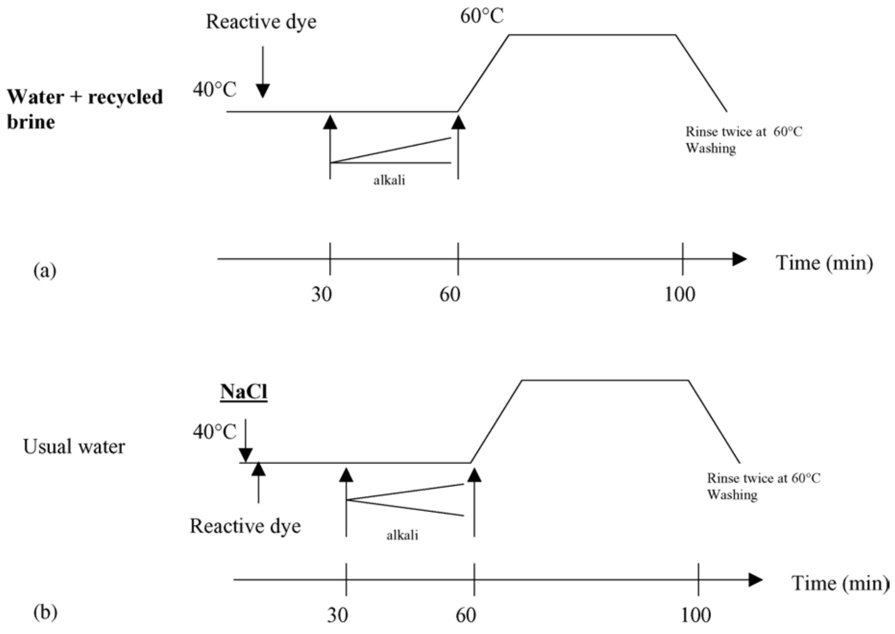


Fig. 19. Dyeing protocol with (a) recycled brine and (b) usual water.

Table 7
Strength, shade or fastness as a function of the water used (usual or recycled)

Reactive dyes	Strength (%) water + recycled brine	Shade	Fastness (%)	Strength (%) usual water
CL	99	100	100	100
X	97	100	100	100
K	98	100	100	100
HF	99	100	100	100

- Shade: same intensity, same hue.
- Domestic laundry C2S ISO CO: no difference in terms of shade degradation and bleeding on multifibres witness.
- AATCC 61: same results than C2S ISO CO6.
- Water fastness ISO E01: no difference in terms of shade degradation and bleeding on multibres witness.
- Perspiration ISO E04 (acid and alkaline) 5: same results than Water fastness ISO E01.
- Rubbing fastness X12 (wet and dry): no difference.
- Light fastness: no difference between the two dyeings in terms of degradation and hue change.

5. Conclusion

Textile process who dye cotton by the exhaust method with reactive dyes are facing by increasingly restrictive environmental problems. It consists of different steps (pretreatments, nanofiltration and reverse osmosis). The two pretreatments ensured the efficiency and strength of our process and take into account the industrial requirements. After having determined the cut-off of the prefilter on the laboratory-scale, this choice was validated on industrial site. All cotton fibres were stopped. Then, the mixture will be acidified and degassed so that it contains no more compounds likely to reform carbonates, neither before the nanofiltration step, nor even before a re-dyeing. We have demonstrated that there is no influence of the color and the high concentration of mineral salt on the acidification step. This work resulted in a re-examining of the dyeing process recommended by Clariant and it is now suggested replacing carbonates by a mixture of carbonates and soda. For the NF and RO steps, several types of dye house effluents were treated. Whatever the reactive dye-NaCl combination used, the hydrolyzed reactive dyes and dyeing auxiliaries were retained in an amount of over 98%, and the mineral salt recovery reached a rate of 98%. The different parameters studied permitted optimization of the operating conditions of the nanofiltration. The best conditions are easy to implement: a transmembrane pressure of 1×10^6 Pa (10 bar), and circulation flow rate of $350\,\mathrm{L\,h^{-1}}$ and a temperature of 50 °C, corresponding to that of the effluents at the outlet of the dyeing machine and pretreatments. The nanofiltration process can be carried out in one, two or three steps, depending on the type of effluent which can be easily determined by its color intensity. After each experiment, washing with water or chemicals allows total recovery of the initial permeability of the membrane. The recovered brine should have a sufficient concentration to be directly recycled and reused ($70\,\mathrm{g\,L^{-1}}$) so if necessary the reverse osmosis increases the concentration of mineral salts of the dilute brine obtained by the nanofiltration step. The optimal RO conditions are a transmembrane pressure of 70 bar and a circulation flow of $500\,\mathrm{L\,h^{-1}}$. We have shown that only the osmotic pressure controls the mass transfer. Concerning the validation of our process standard dyeing carried out with usual water gave the same results as those obtained with the recycled brine after readjustment of the amount of electrolyte when this was found to be necessary. The shade depth, hue and end-use fastness properties were identical, whichever type of water used.

In conclusion, dyers now have the possibility of achieving considerable savings of sodium chloride, with less pollution of the environment with salt loads and reduction in the consumption of fresh water. In addition to its innovative character, the treatment process presented in this study permits the dyer to regulate the problem of coloration of the final effluents and to reduce pollution not only of organic but also of mineral origin, as the effluents contain practically no further salt. The dyehouse will thus save 90% of its consumption of salt (€87 $\mathrm{tonnes^{-1}}$), i.e. a saving of approximately €78,300 $\mathrm{year^{-1}}$ (Petit Bateau consumption (≅1000 tonnes $\mathrm{year^{-1}}$), Petit Bateau dye house, France). It permits a shorter return on investment by only considering the cost of the primary material.

The treatment of the final waste by coagulation–flocculation–decantation was investigated and the treatment of other dyebaths, which will be the object of another published article.

List of symbols:

C_p	concentration in the permeate ($\mathrm{g\,L^{-1}}$)
C_r	concentration in the retentate ($\mathrm{g\,L^{-1}}$)
L_po	membrane permeability ($\mathrm{L\,h^{-1}\,m^{-2}\,Pa^{-1}}$ ($\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$))
ΔP	pressure drop (Pa (bar))
Q	flow rate ($\mathrm{m^3\,s^{-1}}$)
R	gas constant ($8.31\,\mathrm{J\,mol^{-1}\,K^{-1}}$)
RF	retention factor (%)
T	temperature (K)
TMP	transmembrane pressure (Pa (bar))

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