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Removal of textile-based dyes by nanofiltration: study of physicochemical parameters' effect on the retention by experimental designs methodology

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ABSTRACT

This paper focuses on nanofiltration (NF) process mainly in the retention of colored effluents chemicals and dyes as they are rejected from textile plants. The purpose of this work is to study the effect of initial dye concentration, pH, salt presence, conversion rate, and transmembrane pressure (PTM) on Basic Green 4 and Basic Yellow 2 retention by NF. Tangential filtration mode through a composite membrane NF270 type Dow FILMTEC was used in the experiments. Experimental designs such as full factorial design and Box–Behnken matrix were used. Tests have shown that the pH, the conversion rate, and salt concentration have a negative influence on Basic Green 4 and Basic Yellow 2 retention. By comparison, the PTM and initial dye concentration have a positive effect on the retention of these dyes. Finally, the retention rate for Basic Yellow 2 and Basic Green 4 was higher than 90% in our study.

Keywords: Membrane; Textile dye; Nanofiltration; Retention; Experimental design; Modeling

1. Introduction

The studies have well shown that the colored effluents rejected without suitable treatment can bring about a certain number of undesirable changes in the receiving media. These rejections cause concentration of color, an increase in turbidity and stench, which makes not only water unsuitable for domestic or industrial use, but also can reduce the transmission of light, thus limiting the growth of aquatic plants and their self-purification process. Moreover, these dyes exert a negative effect on the life of fish. Color removal by traditional methods of treatment (e.g. ozonization, bleaching, the hydrogen peroxide/UV, electrochemical techniques) is inadequate because the majority of the textile dyes have complex aromatic molecular structures, which resist degradation. The need for more effective remedial measures drew the attention of specialists in the environment and engineers towards different membrane techniques [1]. The application of membrane filtration processes not only allows high removal efficiency, but also allows re-use of water and some of the invaluable waste components (in particular, the dyes). For a few years, technical and economic improvements have made the industrial liquid waste processing using the

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membrane systems even more advantageous. Membrane separation processes have been demonstrated to be a practical alternative [2–8] for the removal of a variety of dyes.

Among the various membrane separation processes, nanofiltration (NF) is considered as the most efficient process in the treatment of wastewater from the textile industry since the 1990s [9–11]. This can be attributed to two unique characteristics of NF membranes: (1) the molecular weight cut-off of NF membrane varies from 200 to 1,000 daltons (g mol^{-1}) with pore size ranging from 0.5 to 2.0 nm and (2) most the NF membranes are negatively charged or positively charged. The steric hindrance is the main separation mechanism of uncharged solutes, while the electrostatic effect is the determining factor for the charged solutes removal [12,13]. It is a process, which makes it possible to concentrate and to demineralize the treated liquid.

Our study was to determine in the first instance the electric charge of the membrane NF270 that was used in the experiments and this in the context of analyzing the behavior of cationic dyes Basic Green 4 and Basic Yellow 2 with respect to the membrane. Then our work was to evaluate the influence of some physicochemical parameters, namely pH, salinity, conversion rate, and the dye concentration on dye removal. To quantify the effect of each parameter, the experimental design methodology was used.

2. Materials and methods

2.1. NF pilot

A flat sheet laboratory-scale NF/RO setup consisting of a planar cross-flow module (Osmonics, Module SEPA CFII, USA), with a membrane area of 138 cm^2, was used in total recycle mode. The total volume of the system was 5 l. The feed tank was equipped with a temperature control system. A gear pump (Wanner GP, USA) with variable speed has been used to circulate the feed solution through the module. Two valves were installed at the concentrate outlet and at the feed inlet to adjust the transmembrane pressure (PTM) and the volumetric flow rate. A schematic representation of the equipment is illustrated in Fig. 1.

2.2. Membrane

Membrane NF270, provided by the Dow/Filmtec Company, is a NF composite type membrane whose active layer is made up of polyamide while the microporous layer and the layer ensuring the mechanical stand are made of polysulfone, where permeability is stable enough for a broad range of the pressures of operation [14].

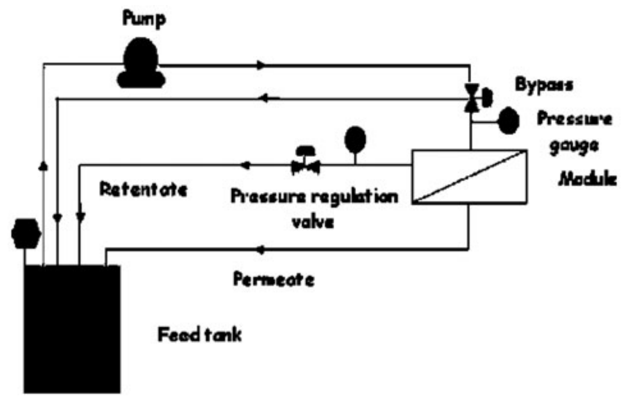


Fig. 1. Schematic representation of the module NF/RO.

The membrane samples NF270 were received in the form of sheets and conditioned. Membrane coupons were cut out in these sheets progressively of the needs. Once wet, the membrane coupons were kept at 4°C in the demineralized water during 24 h.

2.3. Solutions

The basics dyes used are the Basic Green 4 and Basic Yellow 2. They are cationic dyes. The cationic dyes contain a quaternary amine group, which generally forms the integral part of the formula, but it is not systematic. Sometimes, a positively charged sulfur or oxygen atom replaces nitrogen. Their characteristics are given in Table 1. However, being cationic dyes, we supposed for our study that their chemical formula should be in the shape of $D–N^+$ and X^- ($D–N^+$ indicates the organic part and X^- the Co-ion).

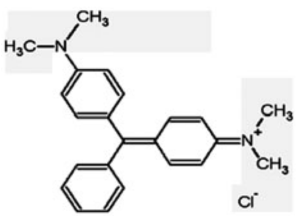
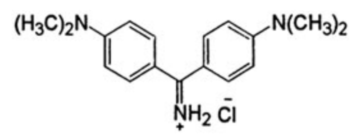
Salts used during the experiment are KCl and NaCl (Aldrich). The pH of the solutions was adjusted from 3 to 9 using hydrochloride acid (HCl, 1 N) and sodium hydroxide (NaOH, 1 N).

2.4. Analytical method

The pH was determined using a pH-meter (Ecoscan Ion6) equipped with a double-junction electrode with Ag/AgCl reference cell. A conductivity meter (Hach 2000) was used to determine the ionic conductivity of the synthetic effluent.

Initial and residual dye concentrations were established by spectrophotometric method after preparing calibration curves. The dyes used for this purposes were Basic Yellow 2 (λ_{max} = 431 nm) and Basic Green 4 (λ_{max} = 620 nm).

Table 1
Dyes characteristics

	Textiles dyes	
Characteristics	Basic Green 4	Basic Yellow 2
Nom IUPAC	4-[(4-dimethylaminophenyl)-phenyl-methyl]-N,N-dimethyl-aniline	4,4´-carbonimidoylbis(N,N-dimethylaniline) hydrochloride
Name	Malachite green	Auramine O
Appearance	Green crystalline powder	Yellow powder
Molecular formula	$C_{23}H_{25}N_2Cl$	$C_{17}H_{21}N_3HCl$
Molecular weight g/mol	365	304
Molecular structure		
λ_{max}	620 nm	431 nm
pH	7.4	7.5

2.5. Experimental procedure

The experiments were conducted in a tangential mode during the entire study. All experiments were performed at a temperature of 20˚C. During the experiments, the permeate (Q_p) and concentrate (Q_c) flow were calculated by measuring in each test the time required to have 10 ml of permeate volume and 50 ml of concentrate volume. In addition, from the two flows, the conversion rate (Y) is calculated as shown in Eq. (1):

$$Y\ (\%) = \frac{Q_P}{Q_P + Q_C} \times 100 \tag{1}$$

The parameter that was determined in this study is the observed retention R_{obs}, which is calculated as shown in Eq. (2):

$$R_{obs}\ (\%) = \left(1 - \frac{C_p}{C_0}\right) \times 100 \tag{2}$$

C_0, and C_p, respectively, stand for initial concentration and permeate concentration.

2.6. Streaming potential measurements

The streaming potential (SP) measurement makes it possible to determine the membrane load. The membrane NF270 load was evaluated by means of a measuring device SP house. In this work, SP measurements are made by the flow through the membrane pores. The apparatus used is a cell impasse 8050 model Amicon whose schematic is shown in Fig. 2. The filtration cell that has a capacity of 50 ml was used with a flat membrane NF270 (for a work surface of 14.52 cm^2). The unit was operated at pressure differentials up to 5 bars using nitrogen gas pressure as a driving force. A pair of Ag/AgCl electrodes inserted into the device was used to measure the potential difference between the two sides of the membrane in relation to the PTM. The electrodes were connected to a voltmeter (Radiometer Analytic PH250, France) having a high impedance (10 MΩ). SP measurements were made at the room temperature of 20˚C. The membrane samples were cut out to adapt to

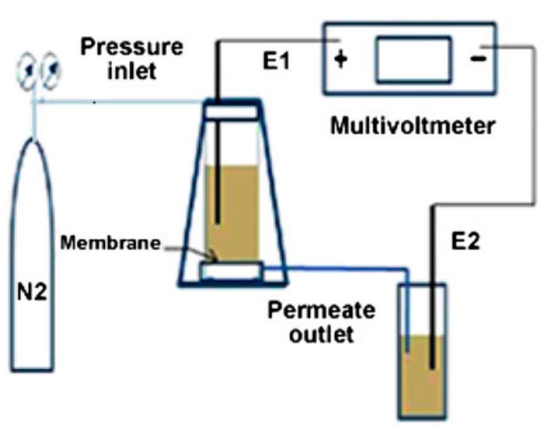


Fig. 2. Schematic representation of the measuring device PE.

the measuring cell, then humidified with pure water, and stored in a refrigerator at 4°C during 24 h.

The SP measurement allows the characterization of the membrane's active layer due to a decrease in the PTM occurring in the micropores of the active layer. Moreover, these experiments are planned for the qualification of the pore walls charge and not their quantifications.

The SP was measured using the electrolytic solution KCl with a concentration of 10^{-3} M.

In order to consider the membrane isoelectric point (IEP), the SP was determined as a function of pH in a KCl solution of 10^{-3} M. The pH was adjusted by the addition of HCl (1 M) or NaOH (1 M) to the solutions and the pH was varied in range from 2 to 10.

2.7. Experimental design

2.7.1. Design structures

The purpose of the experimental designs is to choose the best experience for discovering the evolution rules of an interest quantity in terms of operating variables. These rules generally result from a mathematical formula or operating instructions. The found formulas are primarily practical, that is they lay bare an approximate mathematical representation of the phenomenon in a limited area of experimental space.

The experimental designs carried out during our study are of two kinds: a full factorial design and Box–Behnken design.

- The full factorial designs on two levels are simplest; they are also most useful because they form the base of all the study beginnings. The first results obtained, thanks to these plans which can always be supplemented by new experiments, making it possible to reach the required information and the degree of accuracy. The experiences number in this case is equal to 2^k, k the factors (parameters) number and "2" the level (maximum and minimal value of the experimental field) number. In our study, we have three factors (parameters), which gives us eight experiments (in order to be able to validate the model statistically, the experiments were doubled, which gives us 16 experiments) [15]. The plan was applied to the NF of Basic Yellow 2 and Basic Green 4. The three parameters are the dye concentration [Dye], the salt concentration [NaCl], and the PTM.
- Box–Behnken designs meet a particular criterion of optimization: Box–Behnken designs [16–18] are rotatable second-order designs based on three-level incomplete factorial designs. The special arrangement of the Box–Behnken design levels allows the number of design points to increase at the same rate as the number of polynomial coefficients. For three factors, for example, the design can be constructed as three blocks of four experiments consisting of a full two-factor factorial design with the level of the third factor set at zero [16]. Box–Behnken design requires an experiment number according to $N = k^2 + k + cp$, where (k) is the factor number and (cp) is the replicate number of the central point [18]. Box–Behnken is a spherical, revolving design. The advantage of this plan is the small number of experiments needed for its realization: in our case, that is to say three factors, the tests number performed are 15. The factors used in this plan are the dye concentration, pH, and the conversion rate. The experiment list is reported in Table 6.

2.7.2. Typical model used

2.7.2.1. Full factorial design with three factors. The mathematical model associated with the full factorial designs is a first-degree polynomial compared to each variable. It is assumed that the factors effects are additive and that there may be interactions between factors. The model, which makes it possible to connect the retention (R) for our plan to the three factors [Dye]; [NaCl] and PTM as shown in Eq. (3):

$$R\ (\%) = a_0 + a_1[\mathrm{Col}] + a_2[\mathrm{NaCl}] + a_3\mathrm{PTM} + b_1[\mathrm{Dye}] \times [\mathrm{NaCl}] + b_2[\mathrm{Dye}] \times \mathrm{PTM} + b_3\mathrm{PTM} \times [\mathrm{NaCl}] + b_4\,\mathrm{PTM} \times [\mathrm{Dye}] \times [\mathrm{NaCl}] \tag{3}$$

where a_0 is the factorial effect average of the response on the field considered, a_i have the linear effects of each factor, and b_i the interaction factorial effects.

Table 2 shows the parameter values that are used for the full factorial design

2.7.2.2. Surface design from Box–Behnken. The mathematical model associated with the Box–Behnken design is the second degree with the interaction of order 2. In this study, there is a model of three factors: Dye, Y (conversion rate), and pH. The parameter followed during the tests is the dye retention (R). The model can be written as shown in Eq. (4) [16]:

Table 2
Correspondence between levels coded and actual levels of factors (parameters) for full factorial design

		Levels		
Variables coded	Factors	Min. −1	Centre 0	Max. +1
X1	[Dye] (mg/l)	20	60	100
X2	[NaCl] (g/l)	0.0	2.5	5.0
X3	PTM (bar)	4.0	8.0	12

Table 3
Correspondence between levels coded and actual levels of factors (parameters) for a plan Box–Behnken

		Levels		
Variable coded	Factors	Min. −1	Center 0	Max. +1
X1	[Dye] (mg/l)	20	60	100
X2	Y (%)	10	40	70
X3	pH	3.0	6.0	9

$$R\ (\%) = a_0 + a_1\,[\text{Dye}] + a_2\,Y + a_3\,\text{pH} + b_1[\text{Dye}] \times Y + b_2[\text{Col}] \times \text{pH} + b_3 Y \times \text{pH} + c_1[\text{Dye}]^2 + c_2 Y^2 + c_3\text{pH}^2 \tag{4}$$

where a_0 is the factorial effect average of the response on the field considered, a_i have the linear effects of each factor, b_i the factorial effects of the interactions, and c_i the quadratic effects of each factor.

Table 3 shows the parameter values used for Box–Behnken.

From the results obtained, the statistical processing was made using the software of experimental design Nemrodw (2007) in order to determine the mathematical model coefficients connecting the retention to the various studied parameters. The model coefficients are significant if the confidence thresholds are lower than 5%. The confidence thresholds are given by calculating the probability on the Fisher test of each coefficient.

The model validity is obtained by making the variance analysis.

3. Results and discussion

3.1. Determination of IEP

Fig. 3 shows SP variation according to the pH of the KCl solution for membrane NF270. The pH for which the SP is zero corresponds to the IEP of the system membrane-solution. Thus for our membrane NF270 of polyamide type, the IEP found is 2.9 (Fig. 3). For the pH lower than this value, the membrane is positively charged (this corresponds to the protonation of the amine functional groups present on the membrane: R–NH → R–NH_2^+); while it is negatively charged for pH above the IEP (in this case it is about deprotonation of the carboxylic groups: R–COOH → R–COO^-) [19–21].

3.2. Removal optimization of BG4 and BY2 through NF by using the factorial designs methodology

Table 4 shows the experimental design with the factors values and the response that is in our study the dye retention. Table 4 gives each factor effects and their interaction that will allow us to model and quantify each parameter influence on the dye retention.

In view of the values given by the Nemrodw software (2007) tests, we can say that all the coefficients are significant and may be involved in the model equation.

The interaction effects values are very low (Table 5), we had only kept the each factor effects.

We can write the relationship between the dye retention and the different parameters as shown in formulas (5) and (6).

$$R_J\ (\%) = 90.96 + 2.27 \times [\text{Dye}] - 0.19 \times [\text{NaCl}] + 0.61 \times \text{PT} \tag{5}$$

$$R_V\ (\%) = 90.35 + 5.26 \times [\text{Dye}] - 0.28 \times [\text{NaCl}] + 0.37 \times \text{PT} \tag{6}$$

Eqs. (5) and (6) represent, respectively, the retention of the BG4 and BY2.

The positive sign in front of the terms indicates a positive effect on the process, while a negative sign indicates an antagonistic effect.

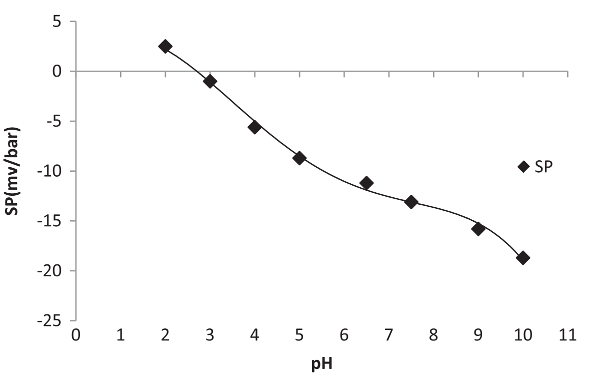


Fig. 3. Behavior of the SP as a function of pH for NF270 (KCl = 10–3 M, T = 20˚C).

Table 4
Experiment design for the full factorial design dye BY2 and BG4

				Retention (%)	
N° experience	[Dye] (mg/l)	[NaCl] (mg/l)	PTM (bar)	BY2	BG4
1	20	0	4	88.015 ± 0.048	84.978 ± 0.303
2	100	0	4	94.34 ± 0.057	95.824 ± 0.163
3	20	5	4	87.85 ± 0.024	84.101 ± 0.304
4	100	5	4	92.685 ± 0.029	95.000 ± 0.326
5	20	0	12	89.875 ± 0.024	86.075 ± 0.304
6	100	0	12	93.89 ± 0.029	95.647 ± 0.163
7	20	5	12	89.005 ± 0.48	85.197 ± 0.304
8	100	5	12	93.56 ± 0.014	95.971 ± 0.082

Table 5
Values of the effects the full factorial design

		Coefficient		Signif. (%)	
Factors	Name	BY2	BG4	BY2	BG4
	a_0	90.964	90.34901	<0.01***	<0.01***
[Dye]	a_1	2.279	5.26129	<0.01***	<0.01***
[Sel]	a_2	−0.190	−0.28180	<0.01***	<0.01***
PTM	a_3	0.617	0.37339	<0.01***	<0.01***
[Dye] × [Sel]	b_1	0.067	0.15680	1.63*	0.144**
[Dye] × PTM	b_2	−0.135	−0.17486	0.0302***	0.0730***
[Sel] × PTM	b_3	−0.109	0.14338	0.122**	0.246**
[Dye] × [Sel] × PTM	b_4	0.2153	0.14338	1.96*	0.246**

*<5%; **<1%; ***<0.1%.

The model of full factorial design was used with three process variables ([Dye], [NaCl], and PTM) to evaluate their impact and their interaction on the retention of two basic dyes.

The equations obtained allow us to relate the retention with these three factors. Referring to the results obtained (Table 5) from the Nemrodw software, we can say that all the factors have a more or less significant effect while the interaction effect is very weak. The most significant factor is the dye concentration that has a positive effect on the dyes retention, that is to say, when the dye concentration increases the retention increases significantly. Salinity has a negative effect, but very low on the dye elimination, with increasing salt concentration, the dye retention declines slightly. We can also say that the PTM has a positive effect but very low on retention, and it increases slightly with increasing pressure.

Figs. 4–6 show the different effects of interactions between factors. These figures represent the average retentions obtained taking into account the variation of two factors while keeping the third fixed factor.

3.3. Removal optimization of BG4 and BY2 by the response surface methodology: plan of Box–Behnken

Using the response surface methodology (RSM) approach, tests were carried out based on the Box–Behnken model for the experiments design to see the effect of independently factors and the interaction between the factors.

For the execution of this plan, we had fixed the PTM at 8 bars and we repeated the experiment in the center of the field three times. The parameters studied during optimization are dye concentration [Dye], conversion rate (Y), and pH. Table 6 shows the experimental design and the values of the each factors effect are consigned in Table 7.

The data processing was carried out with the Nemrodw 2007 and MiniTab 16 software. The variance analysis made it possible to validate the model statistically and the Student test was made for the each factors effects. The Student test is represented in Table 6 by “% sign”; the values with one, two or three (*) are those which are significant and will be taken into account in the model equation. Thus, we can

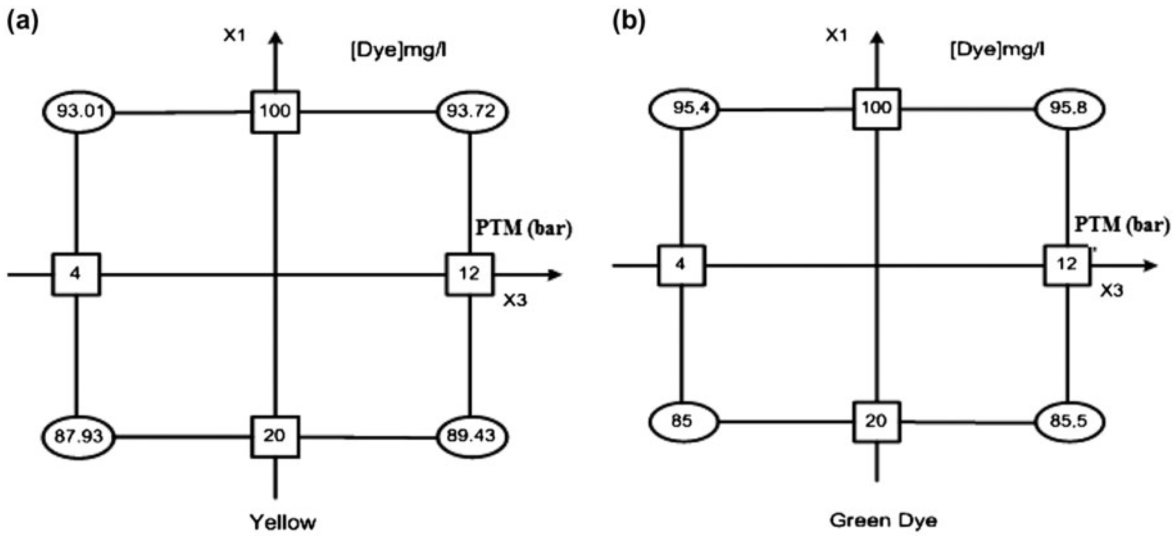


Fig. 4. Interaction between the initial dye concentration and pressure transmembrane. Retention is marked in ellipses, factors maximum and minimum in the squares. (a) For BY2 and (b) for BG4.

Table 6
Box–Behnken plan for the dye Yellow and Green

				Retention (%)	
N° experience	[Dye]	*Y*	pH	BY2	BG4
1	20.0000	10.0000	6.0000	87.240	81.140
2	100.0000	10.0000	6.0000	91.310	90.530
3	20.0000	70.0000	6.0000	87.030	80.710
4	100.0000	70.0000	6.0000	91.250	90.150
5	20.0000	40.0000	3.0000	79.530	81.330
6	100.0000	40.0000	3.0000	91.590	90.960
7	20.0000	40.0000	9.0000	84.140	81.100
8	100.0000	40.0000	9.0000	86.230	90.790
9	60.0000	10.0000	3.0000	88.340	87.610
10	60.0000	70.0000	3.0000	88.050	86.670
11	60.0000	10.0000	9.0000	85.670	85.720
12	60.0000	70.0000	9.0000	84.640	84.880
13	60.0000	40.0000	6.0000	88.370	87.480
14	60.0000	40.0000	6.0000	88.550	87.240
15	60.0000	40.0000	6.0000	88.800	87.200

write the relationship between retention and the different parameters in this way:

$$R_J\ (\%) = 88.57 + 2.805 \times [\mathrm{Col}] - 0.199 \times Y - 0.854 \times \mathrm{pH} - 2.867 \times \mathrm{pH}^2 \tag{7}$$

$$R_V\ (\%) = 87.307 + 4.769 \times [\mathrm{Col}] - 0.324 \times Y - 0.51\mathrm{pH} - 0.925 \times [\mathrm{Col}]^2 - 0.75 \times Y^2 \tag{8}$$

Eqs. (7) and (8) represent respectively the retention of the BG4 and BY2 by the membrane of NF270.

The response Eqs. (7) and (8) obtained for the retention of BY2 and BG4 were used to visualize the effect of experimental factors on the responses. The response surfaces show the removal of dyes, Basic Green 4 and Basic Yellow 2.

Based on the results obtained from Nemrodw 2007 and MiniTab 16 software, we can say that all parameters have a significant effect on the process of dye retention by the membrane NF270. The dyes concentration has a positive effect on the dyes retention as explained above. As against, the conversion rate and pH have a negative effect on the removal of two dyes by this membrane type. When the pH or conversion

Table 7
Values of factor effects for Box–Behnken design

Factors	Name	Coefficient		Signif. (%)	
		BY2	BG4	BY2	BG4
	a_0	88.573	87.307	< 0.01***	< 0.01***
[Dye]	b_1	2.805	4.769	0.0740***	0.0124***
Y	b_2	−0.199	−0.324	12.1	1.34*
pH	b_3	−0.854	−0.510	0.790**	1.08*
[Dye]	c_1	−0.334	−0.925	9.7	0.550**
Y	c_2	0.968	−0.750	1.32*	0.787**
pH	c_3	−2.867	−0.337	0.153**	12.3
[Dye] × Y	b_1	0.037	0.013	76.2	31.7
[Dye] × pH	b_2	−2.492	0.015	0.187**	86.1
Y × pH	b_3	−0.185	0.025	22.9	77.3

*<5%; **<1%; ***<0.1%.

rates increase, dyes retention decrease significantly (when increasing the pH from 3 to 9, for a dye concentration of 100 mg/l and a conversion rate of 40%, the retention rate ranges from 91 to 82% for the BY2, while for the BG4 variation is less important).

Interactions between factors are not statistically significant and are not included in the equations that relate the retention factors of influence.

4. Discussion

4.1. Effect of the dye concentration on dye retention

The dye concentration has a positive effect on their retention (Figs. 4 and 7) by NF [2,22,23] and this is explained by the positive sign of the coefficient related to the dye concentration (Table 6 and Table 7).

The dyes retention by the membrane is due to the dye molecular size and the pores size. Thus, these molecules agglomerate and form a cake on the membrane surface. At higher concentrations, the molecules adsorb easily onto the membrane, which can be observing after the filtration experiments [6]. When the dye concentrations increase, the osmotic pressure increases resulting in the emergence of concentration polarization phenomenon [24]. This phenomenon makes it possible to explain the increase in the retention when the concentration increases.

4.2. Effect of salt concentration on dye retention

The coefficient related to the salt concentration is negative (Table 5); which means that the salt concentration has a negative effect on the retention.

We can say that when one passes from a null salt concentration within the dye solution to a salt presence (5 g/l), the dye retention decreases as underlined in their study. The ionic force i.e. the salt concentration in the solution has a negative effect on the dyes retention (Figs. 5 and 6). Retention of two dyes with a charged membrane (NF270) is not only influencing by the steric effect, but also the electrostatic repulsion by a low salt concentration between the dye and the membrane surface, which thus favors the elimination of dyes [23]. The salt has no influence on the screening effect; while for high salt concentrations, the Donnan effect becomes less effective. The decrease in dye retention when the salt concentration is high is mainly due to the increase in membrane pore size. This increase is the result of pores swelling due to the electrostatic repulsion between the counter ions excess present in the electrical double layer [25–27].

4.3. Effect of the PTM on dye retention

The retention of dyes BY2 and BG4 increases slightly when going from a pressure of 4 bar to 12 bar (Fig. 6). This is confirmed by the sign of the coefficient associated with the PTM being positive (Table 5).

By observing Figs. 4 and 6, we can say that the PTM has a positive effect on the retention of dyes BY2 and BG4 and this is consistent with several studies [23,28–30]. This can be explained by the fact that when the pressure increases the solution flow also increases, yet the increase in concentration leads to an increase in retention. The increase in retention as a function of PTM can also be explained by the fact that transport of an ion (dyes are cationic ions) through the membrane due to diffusion and convection, which are, respectively, due to a concentration gradient and a pressure gradient across the membrane. At low PTM, diffusion

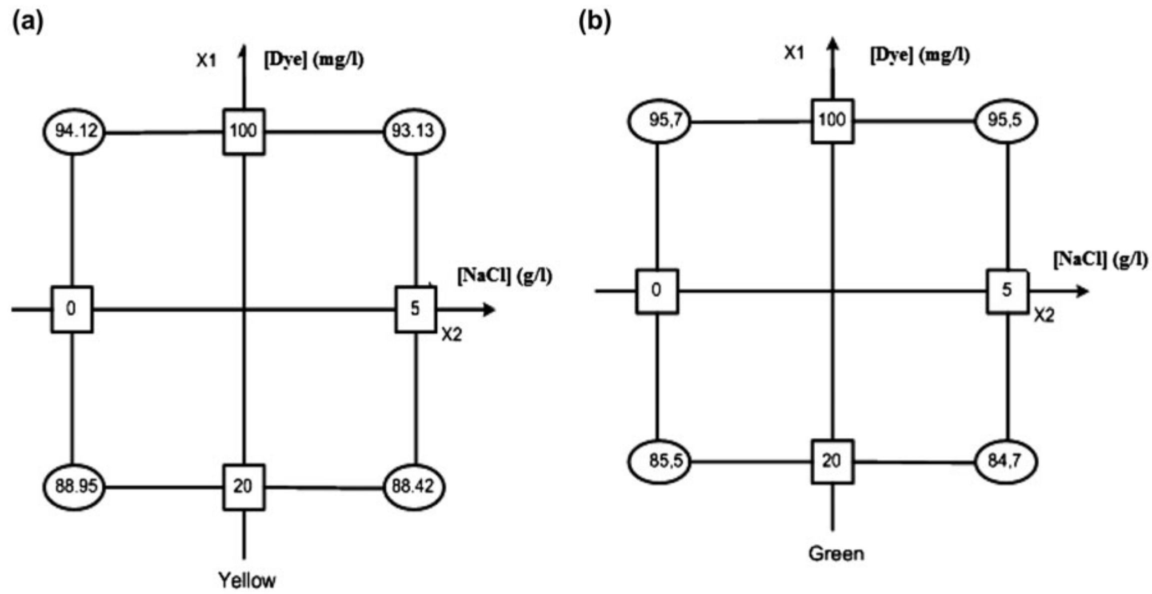


Fig. 5. Interaction between the initial dye concentration and pressure transmembrane. Retention is marked in ellipses, factors maximum and minimum values in square. (a) For BY2 and (b) for BG4.

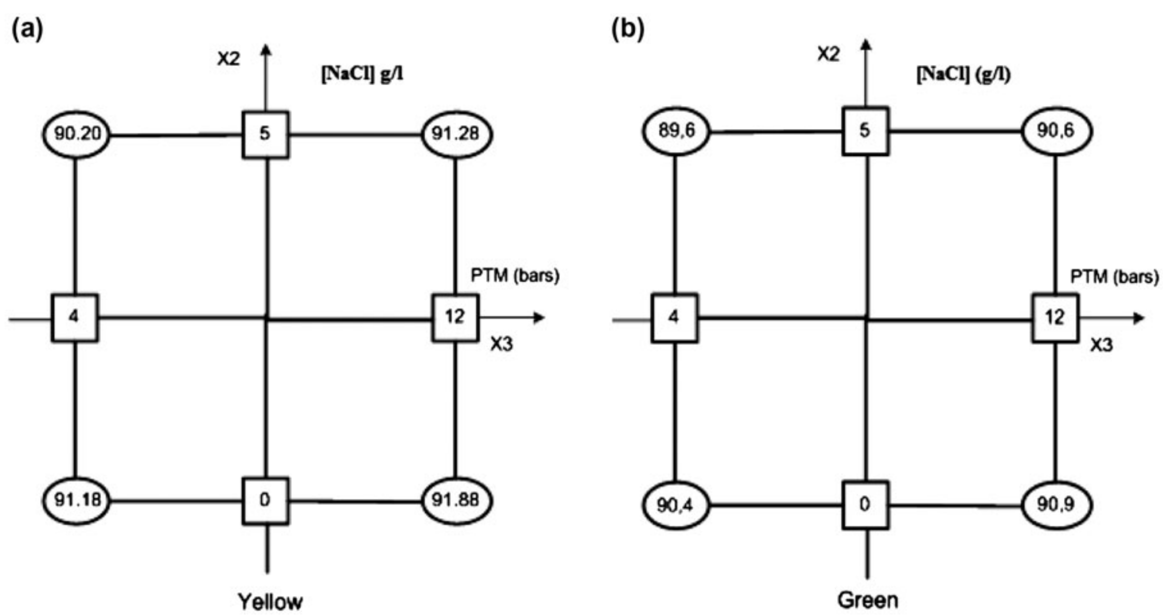


Fig. 6. Interaction between the salt concentration and pressure transmembrane. Retention is marked in ellipses, factors maximum and minimum values in square. (a) For BY2 and (b) for BG4.

contributes significantly to the ion transport leading to lower retention. With the increase in PTM, the ion transport by diffusion becomes relatively less important, so that the retention of the ion is higher [31,32].

4.4. Effect of rate conversion

The conversion rate (Y) gives the quantity of treated water compared to the amount of water sent by the water supply. The coefficients values related to the conversion rate for both BY2 and BG4 dyes are very low.

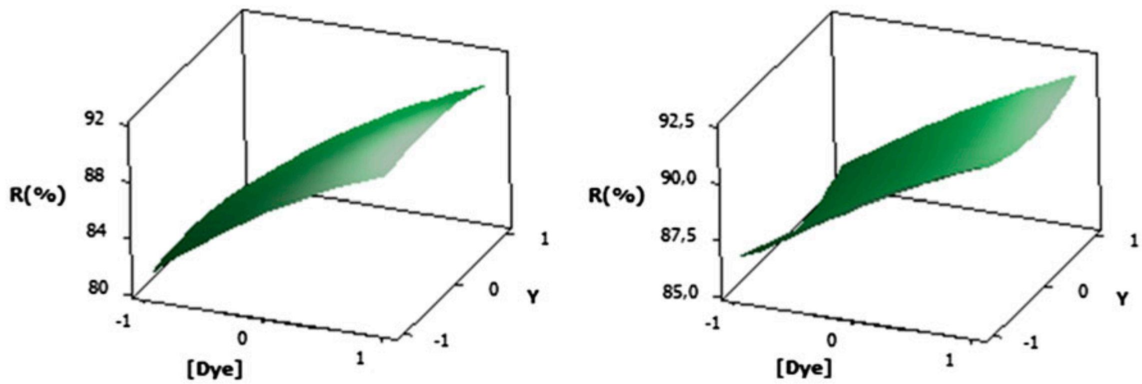


Fig. 7. Response variation—R in the plan: Y, [Dye]/fixed factors: pH = 6 [BG4 (diagram at left) and BY2 (diagram at right)].

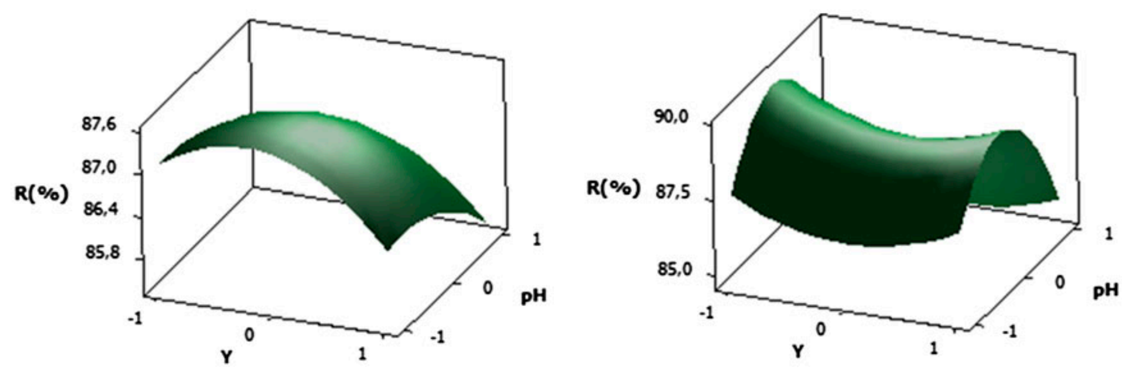


Fig. 8. Response variation—R in the plan: Y, pH/fixed factor: [dye] = 60 mg/l [BG4 (diagram at left) and BY2 (diagram at right)].

These values are in the range of experimental error. In conclusion, we can say that the conversion rate does not affect dyes retention (Fig. 8). In this case of two dyes whose size is greater than the molecular weight cut-off of the membrane, with high conversion rates, the concentration factor increases very slightly. This small increase is probably responsible for the non-influence of the conversion rate on the retention of the two dyes. It may also explain the slight decrease in retention by the fact that the diffusion through the membrane,

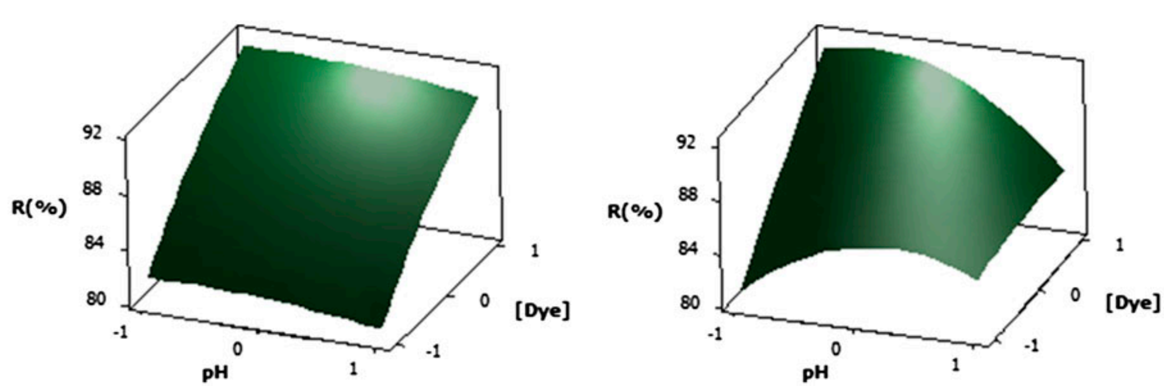


Fig. 9. Response variation—R in the plan: pH, [Dye]/fixed factor-Y = 40% [BG4 (diagram at left) and BY2 (diagram at right)].

which is a factor of solutes permeation, becomes higher with increasing the conversion rate [33].

4.5. Effect of the pH on dye retention

The solution pH varies between 3 and 9 during the tests. The pH has a negative effect on the retention and the negative sign of the coefficient related to the pH (Table 7) explain that. When the pH increases, the retention decreases in manner significant [34] (Fig. 9).

The pH variation of the solution while passing from the acidic to the basic environment modifies the active surface of the membrane. Our study was carried out in a zone of pH ranging between 3 and 9. The SP measurement shows us that in this zone membrane NF270 is negatively charged [19,20,35,36]. Indeed as the pH increases the sites negatively charged with the membrane become increasingly numerous. The dyes Basic Yellow 2 and Basic Green 4 being cationic basic dyes in the form of ($D–N^+$ and $X^−$), when the pH increases, the attraction between the dye and the membrane becomes stronger. In addition, the decrease in dye retention is related to electrostatic attraction negatively charged sites of the membrane ($R–COO^−$) and $D–N^+$ ion of the dye.

5. Conclusion

The retention of a species in NF depends on several physical and chemical parameters. The undertaken study enabled us to include certain phenomena implied in the retention of textile dyes. Modeling by the factorial designs gave us an idea on the influence of the dye concentration, the pressure and the presence of salts on dye retention. The Box–Behnken design was then used to evaluate the effect of the conversion rate and pH on the removal of BY2 and BG4. We noticed that the dye concentration, the salt concentration, and the pH influence largely the elimination of the dyes by NF.

From the models obtained, we can say that, knowing the composition of a textile effluent and according to the procedure chosen, we can make forecasts on the dyes elimination in this effluent.

The cationic dyes removal by NF depends not only on the steric hindrance, but also on the electrostatic interaction that results from the electrical charge on the surface of the membrane NF270.

The membrane NF270 can eliminate both BY2 and BG4 more than 90%.

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