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Response surface methodological approach for optimizing nitrate removal by nanofiltration and reverse osmosis processes

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ABSTRACT

The nitrate levels in many regions of Morocco, particularly agricultural areas like the Gharb region (Mnasra), often exceed acceptable standards. In some wells of this region, nitrate concentrations surpass 400 ppm, primarily due to the overuse of fertilizers. In Morocco, the maximum permissible nitrate concentration in drinking water is set at 50 mg/L. Against this backdrop, the primary objective of this study is to compare the efficacy of nanofiltration (NF) and reverse osmosis (RO) in reducing nitrate ions in three wells in the Mnasra region. This research involves two commercial membranes: NE90 for NF and RE-BN for RO. The second objective is to develop predictive models and optimize the process using a customized design based on response surface methodology (RSM). The independent variables in the RSM are transmembrane pressure (TMP, X_1) and volumetric concentration factor (VCF, X_2), while permeate flux (PF) and nitrate rejection (TR) are the response variables. Notably, the nitrate levels in the permeate from the NE90 membrane exceeded the standards at an initial concentration of 400 ppm, whereas the RE-BN membrane consistently adhered to the standards. An analysis of variance for both models revealed significant results with very low probability values ($p < 0.0001$). Specifically, TMP significantly influences PF, while VCF has a more moderate impact. Conversely, TR is more affected by VCF than TMP. The model's predictive capability is further analyzed through graphical representation. Under optimized conditions, the TR and PF achieved with the RE-BN membrane were 97% and 70 L/m^2·h, respectively.

Keywords: Nitrate removal; Nanofiltration; Reverse osmosis; Modeling; Response surface methodology (RSM); Custom design (CD)

1. Introduction

Groundwater represents the most important source of drinking water supply in many countries around the world, including Morocco, due to its easy accessibility and absence of microbiological contamination in comparison to surface water [1]. The quality of groundwater in agricultural areas is often threatened by contamination with nitrates (through use of nitrogenous fertilizers) and residues of pesticide. In Morocco, nitrate groundwater concentrations exceeding the standards (70 mg/L) is the main reason for closure of wells in the coastal aquifer [2]. The drinking water nitrate concentration limit in Morocco and in some European countries is set at 50 mg/L. The same value limit (50 mg/L) is recommended by the World Health Organization (WHO) [3]. Moreover, an excess amount of nitrate in drinking

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water causes human health problems [4]. Several reports indicate that the use of drinking water containing a high level of nitrate could lead to some disease, like central nervous system, stomach cancer, hypertension and congenital anomalies [5,6]. Among the harmful effects of nitrates on human health, methemoglobinemia and other diseases [7]. To overcome this problem, considerable attention is applied to find effective treatment processes to reduce nitrate concentrations from drinking water, such us, physiochemical processes, ion exchange, advanced oxidation processes (AOP), biological denitrification methods and membrane processes [8]. Nanofiltration (NF) and reverse osmosis (RO) are membrane processes widely used for nitrate removal and groundwater desalination due to their high efficiency, operational flexibility and energy saving compared to conventional techniques [9]. The separation mechanisms in the NF membrane involve both steric and electrostatic partitioning effects between the membrane and solutions. NF membranes can retain molecules with a molecular weight greater than the molecular weight cut-off, which is a consequence of the steric exclusion effect whereby molecules larger than the membrane pore size are rejected by the membrane [10]. Due to the electrostatic ions interactions with the membrane charged surface, NF membranes have a high retention of polyvalent ions compared to monovalent ions [11]. Concerning RO membranes, the transfer is governed by the solute-membrane interactions which are the consequence of the physical and chemical structures of these two entities [12]. The NF membrane and the RO membrane are in competition in certain water treatment applications, NF certainly allowing lower rejects but having the advantage of using lower transmembrane pressures (TMP) and higher solvent fluxes than those used in RO [13]. Several studies using membrane processes have been carried out, including a comparison of NF and RO membranes for nitrate water treatment and the desalination of brackish groundwater, focus on the reduction of nitrates in the water without taking into account the ion transfer mechanisms involved or concentrate solely on the study of fouling. [4,6]. Alavijeh et al. [14], carried out a study of nitrate removal from synthetic and natural water using the NF90 membrane. The results obtained for nitrate removal from synthesized water revealed permeation rates ranging from 16.5 to 84.3 L/m²·h. The minimum and maximum nitrate rejection percentages were 44.1% and 78.4%, respectively. For natural water, flow rates ranged from a minimum of 7.7 to a maximum of 68.1 L/m²·h. In addition, nitrate rejection rates showed minimum values of 22.1% and maximum values of 74.8%. El-Ghzizel et al. [15] examined the removal of nitrates using a pilot nanofiltration (NF) plant coupled with renewable energy, with a production capacity of 12 m³/d equipped with two NF90 40*40 membranes in series, achieving a conversion rate of 75%. The initial nitrate concentration of 68 mg·NO_3^-/L is reduced to 18 mg·NO_3^-/L, corresponding to a retention of 67.73%. Schoeman and Steyn [16], achieved nitrate retentions of 96% to 98% using a small plant equipped with an osmotically selective membrane, featuring a capacity of 55 m³/d and a TMP of 13.75 bar. The raw water had initial nitrate concentrations ranging from 186 to 235 mg·NO_3^-/L, and the plant operated at a conversion rate of 50%.

The application of mathematical and statistical modeling proves to be an essential tool for anticipating membrane separation processes. Specific models such as those of Spiegler–Kedem and Kedem–Katchalsky play a crucial role in this modeling. Subsequently, statistical methods like response surface methodology (RSM) have been widely adopted to address regression problems, whether they involve linear or nonlinear relationships and multiple variables [17]. This approach, although it does not require an in-depth physical understanding of the system or considered process [18–20], enables establishing a relationship between design variables and the process response by conducting a limited number of experiments and optimizing this response using design variable parameters [21–23]. RSM is used for designing experiments and optimizing the effect process variables [24]. This approach based on design of experiments is a set of statistical and mathematical tool. RSM can reduce the trials number and recognizes the influence of process parameters on the removal process [25]. Indeed, RSM has been successfully used for process parameters optimization like metal ion concentration, pH values and reaction time. RSM is widely used in drinking water treatment processes such as electrochemical and AOPs [26]. RSM was used in several studies to model the removal of multiple contaminants such as fluoride, arsenic, sulfate and nitrate by two membranes (NF90 and NF270). The significance of the quadratic model is determined by the *F*-value of the model, a large *F*-value (85,189.92 for NF90 and 6,352,140.52 for NF270) is obtained indicates that the model is significant for both membranes. In addition, RSM was used to predict permeate flow, water recovery, salt rejection and specific energy consumption of the three hybrid configurations (NF and RO in parallel, NF-RO in series and RO-NF series) for groundwater. They obtained nitrate retention rates of 44.89%, 38.64% and 49.66%, respectively [27,28].

Therefore, the prime objective of the present study is to compare and evaluate the performance of two types of membrane, nanofiltration (NF = NE90) and reverse osmosis (RO = RE-BN) in nitrate reduction in the Mnasra region groundwater. This region is part of the Gharb basin and covers an area of approximately 600 km² [29]. The Mnasra coastal zone benefits of a good quality groundwater, accessible to users at relatively shallow depths. The productivity of the catchments is generally good, with the quality of the fertile soils, which explains the significant development of irrigated agriculture associated with the agricultural food industry [30]. In the second part of this study, a custom design (CD) based on RSM is implemented to develop predictive models and optimize the nitrate reduction process (RO). This approach aims to evaluate the effects of the variables of this process and their interactions on the removal of nitrate concentrations. The independent variables used in this process include the transmembrane pressure (X_1) and the volume concentration factor (X_2), with the aim of optimizing performance by maximizing the two responses considered (permeate flux, PF (Y_1) and nitrate rejection, TR (Y_2)).

2. Materials and methods

2.1. Feed water characteristics

The waters of wells 1 and 2 have fairly similar characteristics. The water from well 3 has mineral concentrations

2 to 3 times higher than the other two waters. The nitrate concentrations are well above the standards for drinking water. The three wells feed water characteristics are presented in Table 1.

2.2. Unit pilot used

The experiments were performed on an NF/RO pilot plant (E 3039) supplied by TIA Company, France (Fig. 1). The TMP used ranged from 5 to 70 bar. The pilot plant was equipped with two identical pressure vessels operating in series, each pressure vessel contains one element. The pressure loss was about 2 bars corresponding to 1 bar of each pressure vessel. The two spiral wound modules were equipped with two identical commercial membranes. The temperature was kept at 29°C using the heat exchanger. Permeate samples were collected and analyzed following standard methods previously described [31,32].

Table 1
Feed water characteristics

Parameter	Well 1	Well 2	Well 3	Moroccan Standards
pH	8.1	8.2	8.0	6–9.2
Conductivity, µS/cm	1,926	2,068	4,240	2,700
Magnesium, mg/L	42	45	120	–
Calcium, mg/L	145	142	237	–
Chloride, mg/L	188	259	629	750
Nitrate, mg/L	331	233	470	50
Sulfate, mg/L	158	184	454	200

2.3. Membranes characteristics

The two spiral wound modules are equipped with two identical commercial NF membranes. Table 2 gives the characteristics of the membranes used. After each use, the membranes were cleaned using alkaline and technical acidic solutions according to the manufacturer's recommendations.

2.4. RSM modules optimization

RSM is a statistical technique used for determining and representing the relationship between actual mean responses and input variables. The main idea of RSM is to use a set of experiments designed to obtain an optimal response [33]. Factors can be both numerical and categorical and the type of numerical factors can be changed from continuous to discrete and can estimate linear, interaction, and quadratic effects of parameters [34]. A custom historical design approach applied in the present work which is a subgroup of RSM. For this purpose, the previously performed experimental data (16 experiments) containing two input variables (TMP (X_1), volumetric concentration factor, VCF (X_2)), and two responses PF (Y_1), TR (Y_2) which are imported into the Design–Expert software (version 13) to describe the performance governed for the membrane (RO). The factor levels and corresponding codes for the different independent variables are presented in Table 3, while the design matrix obtained after applying (CD) is mentioned in Table 4. As well as to optimize the relevant conditions of the variables in order to predict the best values of the responses. The predicted response values (Y) are described by a second-order polynomial equation, in general is written as:

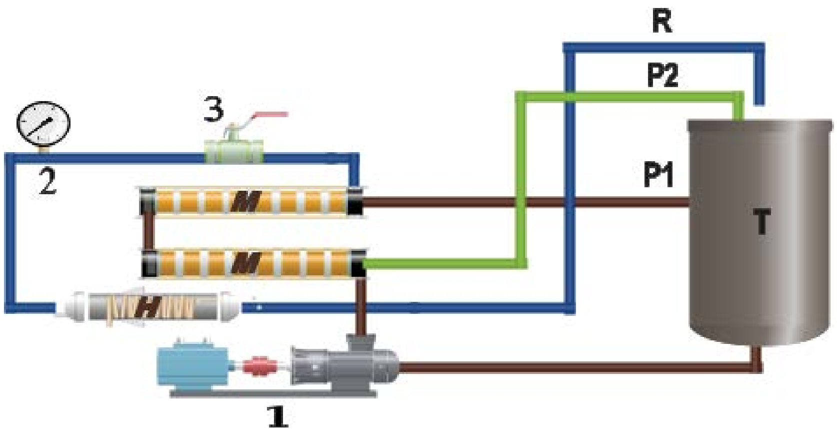

Fig. 1. Schematic diagram of the nanofiltration/reverse osmosis pilot plant [32]. T: tank; M: nanofiltration module; P: permeate recirculation; R: retentate recirculation; H: heat exchanger; 1: high-pressure pump; 2: pressure sensor. 3: pressure regulation valves.

Table 2
Characteristics of the membranes used

Membrane	Manufacture	Technic	Cut-off	Geometry	Area (m²)
NE90	CSM	Nanofiltration	200 D	Spiral	7.6
RE-BN	CSM	Reverse osmosis	–	Spiral	7.6

Table 3
Variables and their levels used in the experiments

Factors	Type	Min.	Max.	Coded low	Coded high	Mean	Std. Dev.
X_1 (TMP), bar	Numeric	5	40	–1–5.00	+1–40.00	23.05	12.42
X_2 (VCF), bar	Numeric	1	4	–1–1.00	+1–4.00	2.45	1.13

Table 4
Custom design of the two independent variables

Experiment number	Input variables RE-BN membrane		Output variable	
	X_1 (bar)	X_2 (VCF)	PF (L/m²·h)	TR
1	25.475	2.69475	40.3	0.9523
2	17.25	1	33.6	0.9625
3	10.775	4	14.5	0.8523
4	17.25	1	33.6	0.9625
5	10.775	4	14.5	0.8523
6	5	1.075	9.17	0.9452
7	40	1.375	75	0.9701
8	27.75	1.6	50.2	0.9596
9	13.05	2.95	17	0.921
10	25.4859	3.94	40.3	0.9523
11	40	1.375	75	0.9701
12	25.475	2.69475	40.3	0.9523
13	40	4	60	0.9702
14	5	2.14	5.2	0.9401
15	25.475	2.69475	40.3	0.9533
16	40	2.65	64.2	0.9623

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (1)$$

where Y is the predicted response; b_0 is the constant coefficient; b_i is the linear coefficients; b_{ii} is the quadratic coefficients; b_{ij} is the interaction coefficients; n is the number of design variables and x_i, x_j are the coded levels of design variables. In order to validate the model, an analysis of variance (ANOVA) study of the model is performed.

3. Results and discussion

3.1. Effect of TMP and conversion rate

3.1.1. Effect of TMP

The tests were carried out using nanofiltration (NE90) and reverse osmosis (RE-BN) membranes on three types of groundwater. The permeate samples were taken instantaneously after 5 min of experiment operations in continuous configuration and the establishment of the water-membrane equilibrium.

Fig. 2 gives the variation of the permeate flow, the conductivity retention rate and the nitrate ions concentration in the permeate as a function of the pressure. The results show that, the permeate flux increases with TMP according to Darcy's law and the NF fluxes are greater than in RO. Moreover, the flows are influenced by the salinity, when the salinity increases the flow decreases either in both membranes tested, also, this influence is more noted in the NF case.

The RO conductivity retention rates are higher than in NF. In both processes, a slight increase in the retention rates was observed, with a TMP follow up a stabilization: 8 bars for NF and 10 bar for RO.

For the three types of groundwater, the nitrate content decreases with the increase of the TMP, up to 8 bars for NF and 10 bar for RO with a very slight variation. The influence of the initial nitrate concentration is more marked in NF case than in RO. Moreover, the values obtained in both studied experiments are below the standards for water of wells 1 and 3, except the well 2 permeate in which the values are below the standards especially in NF case.

Concerning the ions variation rejection rate (NO^{3-}, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}), Fig. 3 shows the variation in both membranes. The results show that, the ion rejection rate varies according to TMP, ion nature and ion concentration. This variation is more observed in NF than in RO process. However, for the three treated waters, the selectivity order of the two membranes tested are: $O_4^{2-} > Ca^{2+} > Mg^{2+} > Cl^- > NO_3^-$.

3.1.2. Conversion rate influence

The tests were carried out on the three groundwater types using NF and RO processes. The operating conditions used: semi-batch configuration, the addition of 50 ppm of A-NET RO sequestrate for waters 1 and 2, for water 3 it was 100 ppm, the working pressure was 8 bars for NF and 10 bar for RO. The final volume concentration factor was 4 with a conversion rate of 75%.

Fig. 4 gives the variation of the flux, the electrical conductivity and the concentration of instantaneous nitrate ions as a function of time in the output of NF and RO membranes. The results show that, in the two cases studied, the evolution of the permeation flux for waters 1 and 2 is identical. Also, the permeation flow gradually decreases from pressure 8 bars in NF and 10 bars in RO. Moreover, the VCF range between 1 and 4. The composition of water no. 3 contains more minerals and the permeation flow is lower than in the other waters studied (from wells 1 and 2). The evolution of the conductivity and the instantaneous nitrate content is similar in waters 1 and 2 and it increases during the time, these two parameters are much higher in water 3. However, in NF step, an exceeding of standards was observed in water 3 and it started appearing from 20 min in water 1 and 35 min in water 2. Regarding RO, the exceeding of standards was only observed in water 3 from 30 min.

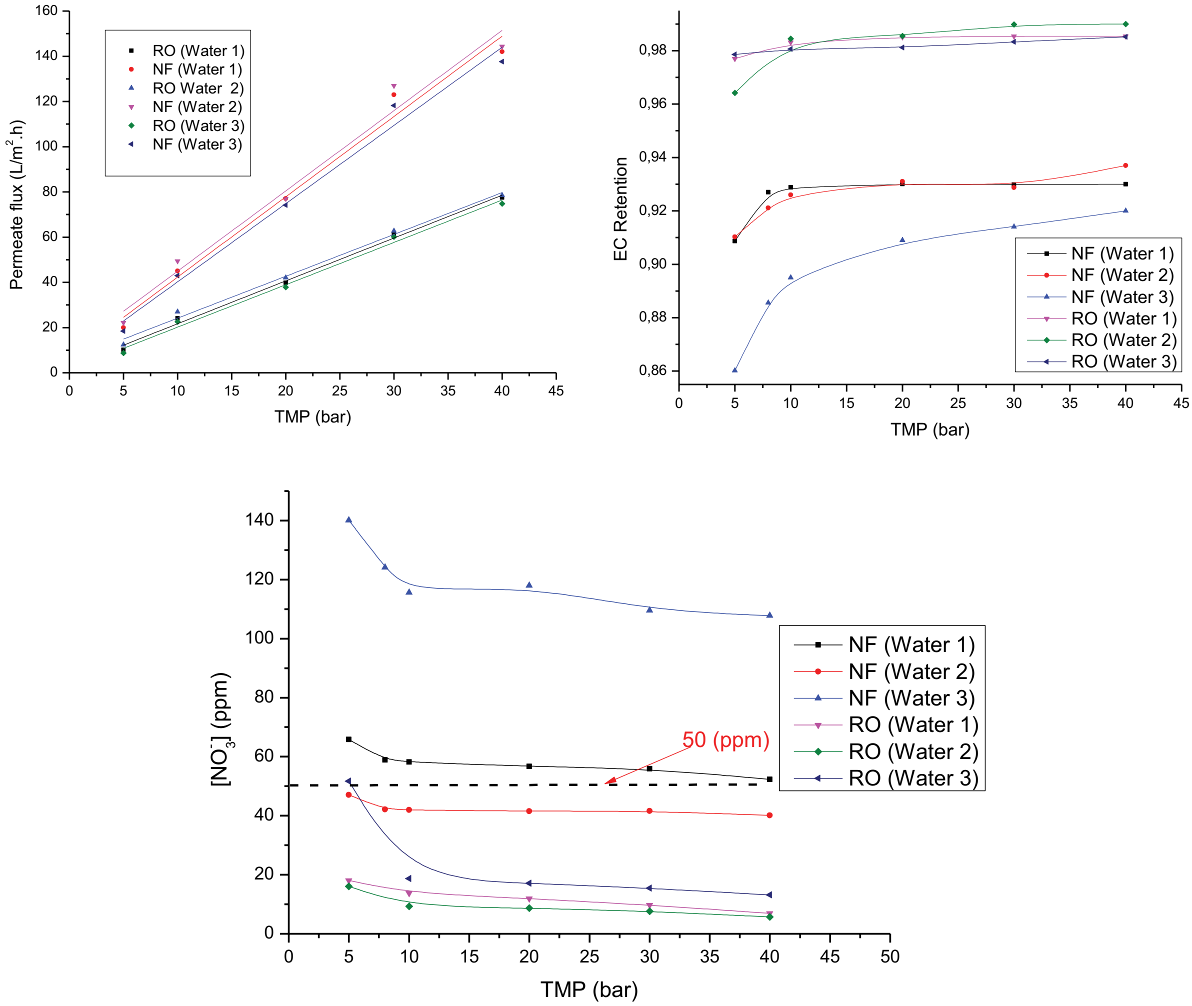

Fig. 2. Variation of the permeate flow, the conductivity retention rate and the nitrate ions concentration in the permeate as a function of the pressure.

3.2. Statistical analysis and modelling by RSM

3.2.1. Optimization of operating parameters using the RSM method

Variance analysis is essential to test the validity significance and fit of the model. It subdivides the total variation in results into two sources of variation, the model and the experimental error, shows whether the model is significant compared to the variation due to the residual error [31]. Table 5 shows the ANOVA results for the two responses (PF and TR) of RO membrane. From the *P*-values of the two models, it is possible to conclude that the developed model is highly significant at the probability level ($p < 0.0001$). In general, a *P*-value less than 0.0001 indicates that the model is significant, while values greater than 0.05 indicate that the model is not significant [35]. The *F*-values of the models imply that the models are significant. In addition, high values of the coefficient of higher correlation ($R = 0.9$) are reported for two models, which explains the good correlation between the experimental and predicted response values [36].

Based on the experimental results of the CD (Table 5), a quadratic polynomial is established to identify the relationship between the response Y_i and the different factors. The regression equations for Y_1, Y_2 in terms of current values:

$$Y_1 = +5{,}679 + 2.236X_1 - 8{,}505X_2 - 0.133X_1X_2 - 0{,}002X_1^2 + 1.577X_2^2$$

$$Y_2 = +0{,}969 + 0{,}001X_1 - 0{,}015X_2 + 0{,}001X_1X_2 - 0{,}003X_1^2 - 0{,}006X_2^2$$

where variable X_1 is found to have a positive effect on Y_1, while variable X_2 has a negative effect. As for the X_1 X_2 interaction, its effects are not significant, as evidenced by the near-nullity of their coefficients. A positive value suggests a beneficial impact on optimization, while a negative value indicates an inverse relationship between the factor and the response. Quadratic effects have negligible coefficients, close to zero. For the Y_2 response, all coefficients are also of near-zero order.

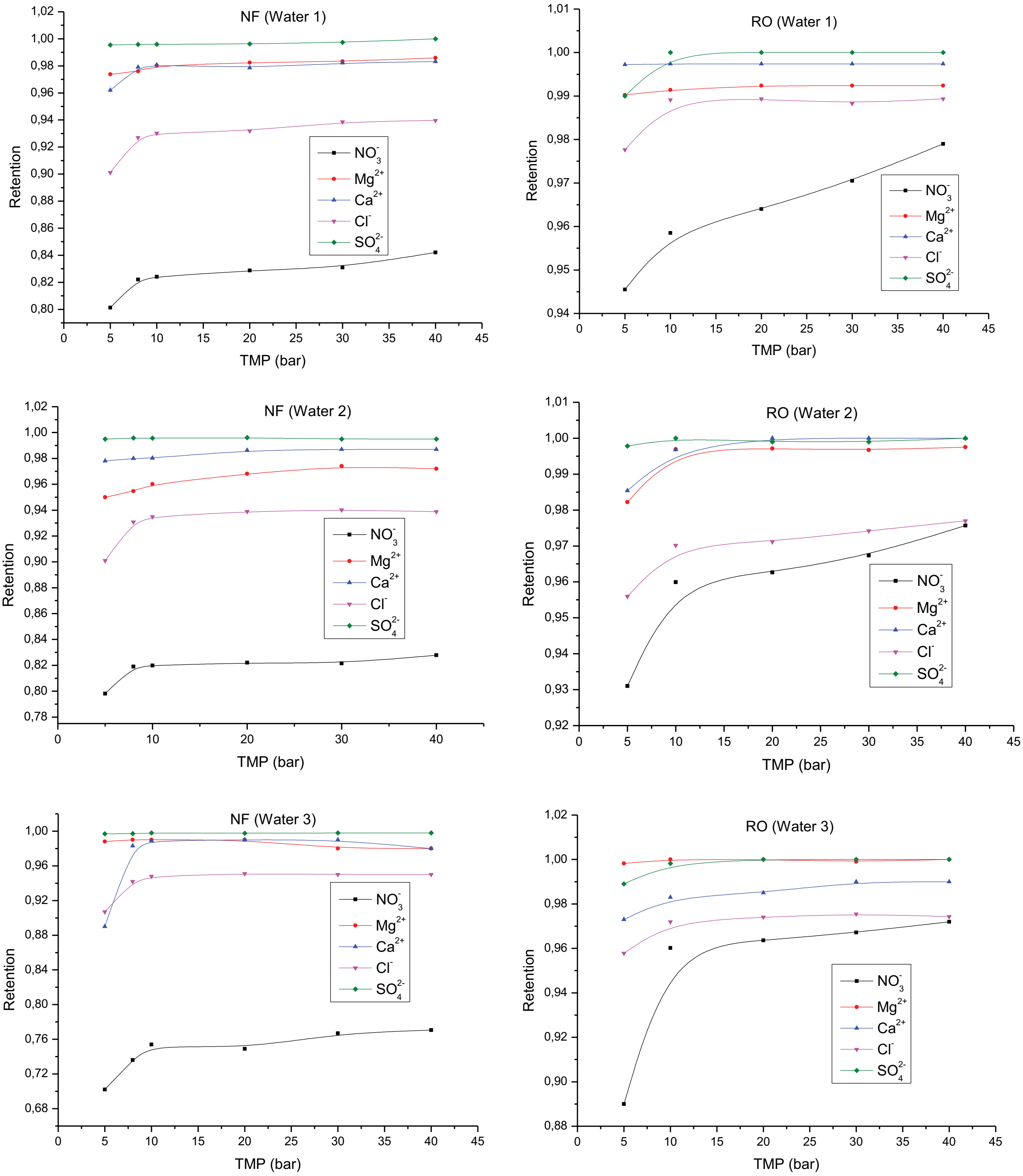

Fig. 3. Variation of ions rejection rate, for the two membranes nanofiltration and reverse osmosis.

This is confirmed by all ANOVA results which is to define the descriptive quality of the model.

The actual and predicted plots for the two responses are shown in Fig. 5. These plots reveal that the model-predicted values are in agreement with the experimental values for the range studied. In addition, the points are located closer to the diagonal line, which means that the errors are normally distributed and the regression models fit the actual values quite well.

3.2.2. Permeate flux

The ANOVA results indicate a significant effect of TMP on permeate flux, while the effect of VCF is more subtle,

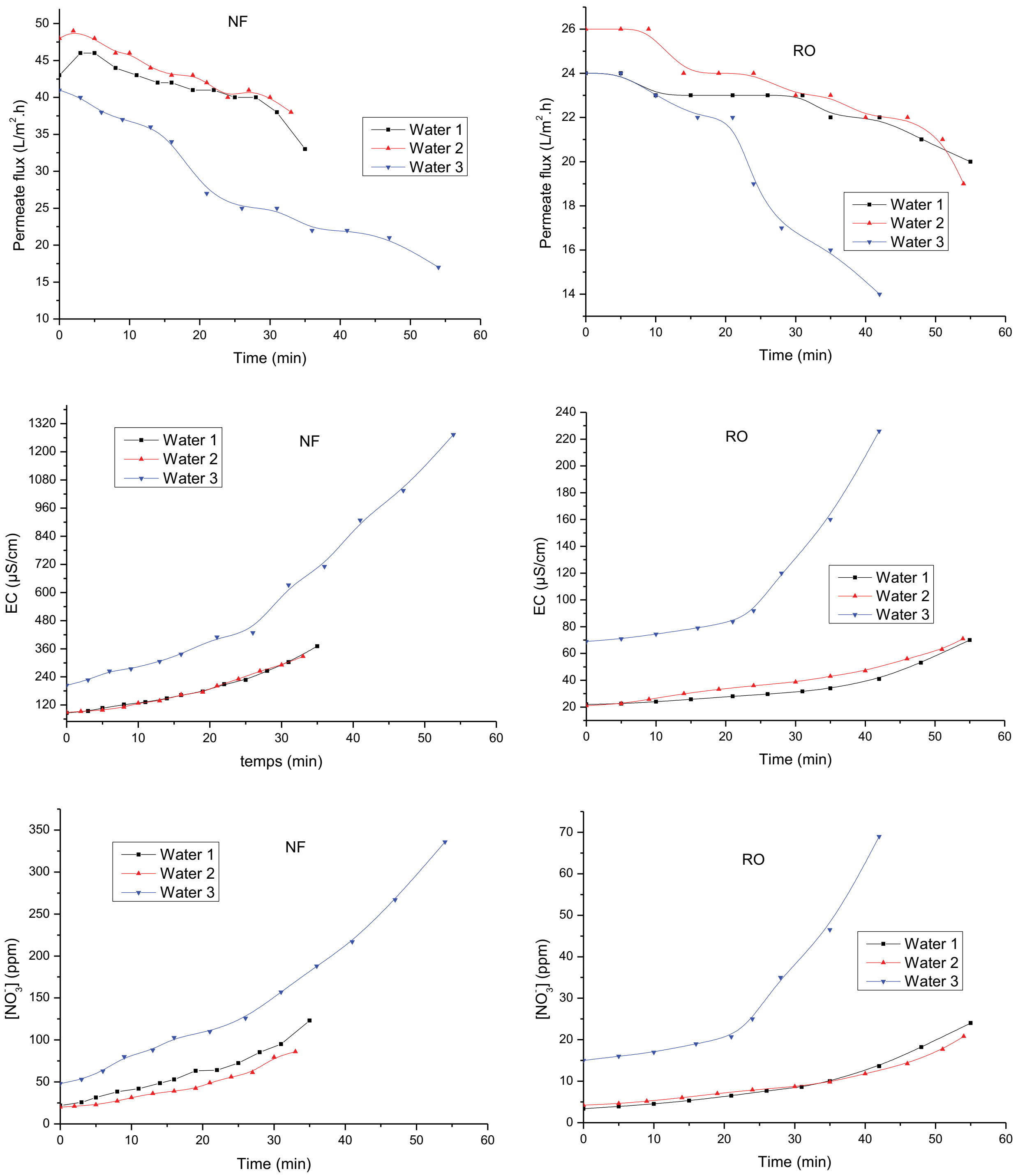

Fig. 4. Variation of the flux, the electrical conductivity and the concentration of instantaneous nitrate ions as a function of time in the permeate.

Table 5
Analysis of variance for the two models, permeate flux, nitrate rejection of RE-BN membrane

Response	Sum of squares	Degree of freedom	Mean square	*F*-value	*P*-value	R^2	Meaning
Y_1 (PF)	7,560.490	5	1,512.10	2,015.17	<0.0001	0.999	Significant
Y_2 (TR)	0.019	5	0.0038	22.48	<0.0001	0.918	Significant

resulting in slight modulation. In Fig. 6, the response surface and contour plot indicate an increase in TMP which leads to an increase in permeate flux. Moreover, the permeate flux increases gradually in the lower ranges and increases rapidly in the upper ranges for this membrane. The same observations and results were also founded by Srivastava et al. [28].

3.2.3. Nitrate rejection

ANOVA results reveal a significant impact of VCF on the (TR), with a moderate effect of TMP. An increase in TMP results in an increase in TR, while an increase in VCF results in a decrease in TR. In the upper ranges, the TR evolved from a VCF of 1.5. Thus, a maximum TR (97%) was achieved using this membrane (Fig. 7).

3.3. Optimization and prediction of modeling using RSM

RSM is used to fit a quadratic model to optimize the dependent parameters based on the values of the independent variables obtained from the experimental data [37]. Fig. 8 show the RSM optimization results for the membrane RE-BN maximizing both responses (PF and TR), under the optimal conditions for each independent variable. Each graph includes the predictions X_1 and X_2, the values

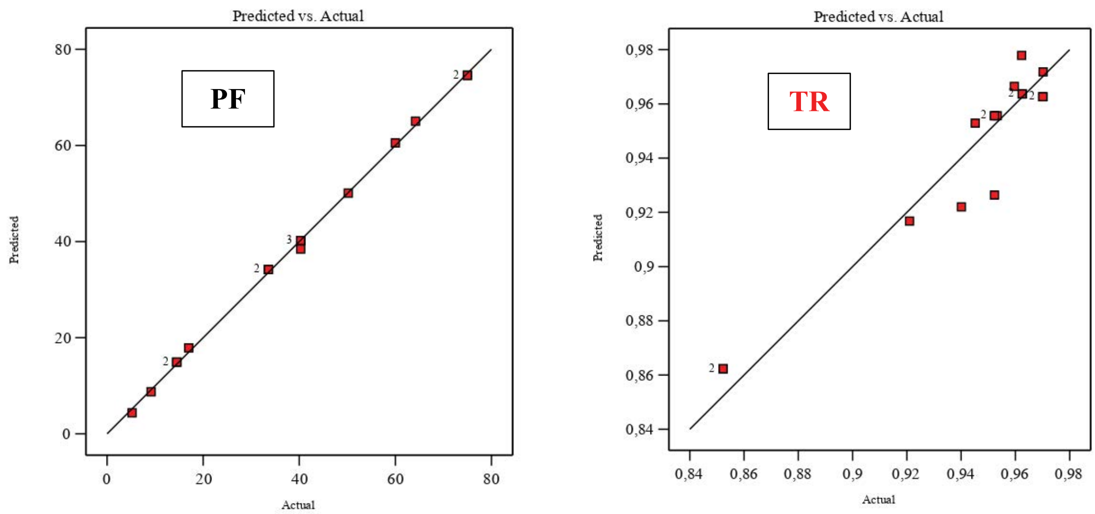

Fig. 5. Experimental permeate flux and nitrate rejection values vs. predicted data for RE-BN membrane.

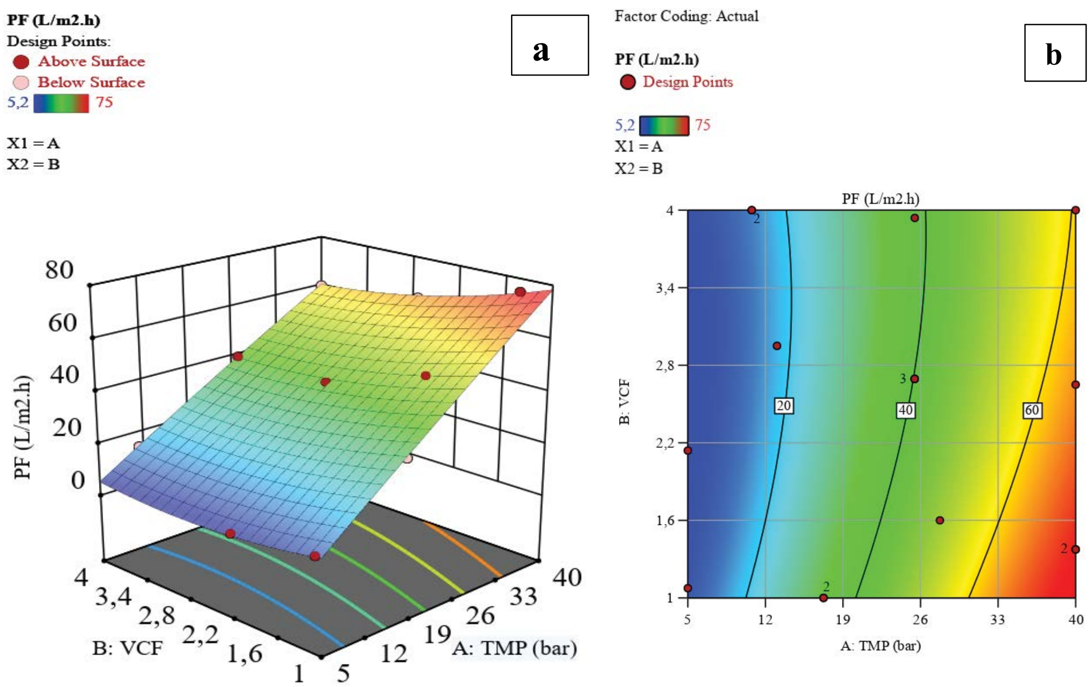

Fig. 6. 3D response surface (a) and 2D contour plot (b) for two parameters on the response (nitrate rejection) for the RE-BN membrane.

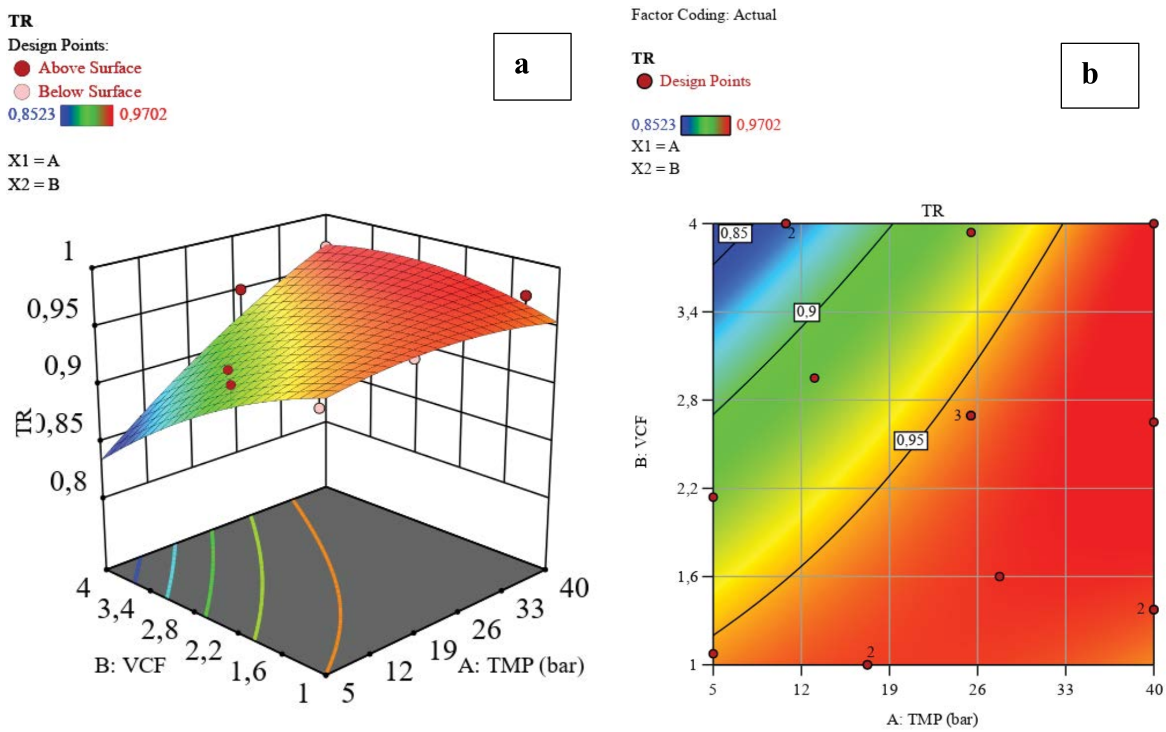

Fig. 7. 3D response surface (a) and 2D contour plot (b) for two parameters on the response (nitrate rejection) for the RE-BN membrane.

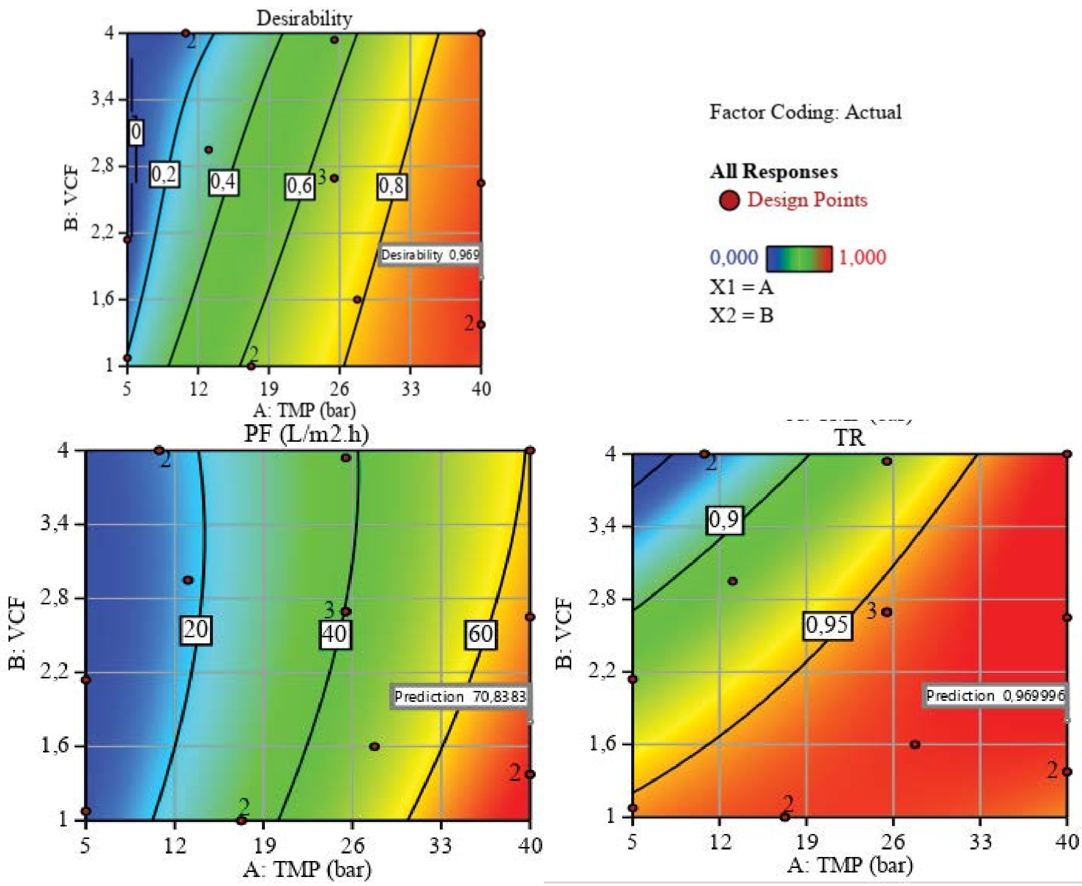

Fig. 8. Optimum conditions for the permeate flux and nitrate rejection maximization for RE-BN membrane.

are optimized with respect to the two responses, where X_1 refers to the horizontal axis (TMP) and X_2 to the vertical axis (VCF). The optimal value obtained for X_1 was 40 bars, and for X_2 it was 1.80 bars. These results are confirmed by the desirability values. If the value is close to zero, the response is totally unacceptable, and if the value is close to or equal to 1, the response is accepted [37].

4. Conclusion

This research work deals with nitrate ion removal by nanofiltration (NE90) and reverse osmosis (RE-BN) performed on groundwater from the Mnasra region. The experimental results show that, the nitrate content obtained in RE-BN membrane was compliant with the recommendation, it was in the range of the initial concentration and the pressure studied. For the NE90 membrane, the nitrate content is lower than the recommendations for initial nitrate concentrations (400 ppm) and above these nitrate concentrations, the permeate obtained exceeds the standards with all pressures tested. no exceedance of the standards was observed for RE-BN.

In addition, the RSM method shown in the CD, is one of the appropriate methods to optimize the operating conditions by maximizing both permeate flux (PF) and nitrate rejection (TR) in the membrane (RE-BN). The ANOVA shows a high value of the determination coefficient ($R^2 > 0.9$), thus ensuring an adequate fit of the second-order regression model with the experimental data.

The optimization of the three models leads to the following conclusions:

- The TMP factor has a significant impact on PF, while VCF has a more moderate effect. As for the TR, it is more influenced by VCF than by TMP.
- In the optimized conditions, the TR and PF were (97%, 70 L/m^2·h) for RE-BN.

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