

# Optimisation of the nanofiltration process of residual wastewater from table olives using synthetic solutions for the recovery of phenolic compounds

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## Abstract

Synthetic solution of ultrafiltration permeate from brine wastewater from the elaboration process of table olives was used to investigate the simulation and optimisation of the nanofiltration process with the aim of reducing the contents of salt and organic material, as well as maintaining the major phenolic content in the permeate of nanofiltration as a contribution to their possible recovery. The synthetic solution was elaborated by considering the main characteristics of the ultrafiltration permeate of residual brine from table olive fermentation. A response surface methodology – central composite design (RSM-CCD) was used. The efficiency of conductivity ( $E_c$ ), total polyphenol content (TPC) and chemical oxygen demand rejections ( $R_{TPC}$  and  $R_{COD}$ ) were the response variables selected. Transmembrane pressure (TMP), cross-flow velocity (CFV) and nanomembrane type (NF270 and NF245) were the independent variables. The range for  $R_{TPC}$  was from 0.59 to 3.34%, while the values for  $E_c$  were higher than the NF270 membrane, being between 13.63 and 24.13%. The RSM-CCD results indicate that the optimum that satisfies the objectives of the research were: nanomembrane (NF245), TMP (14.43 bar) and CFV (1.50 m/s). This allowed the permeate to keep 97.39% of polyphenol contents and reduce organic material and salts by 52 and 23%, respectively.

**Key words:** nanofiltration, response surface, synthetic solutions, table olive, wastewater

## Highlights

- The NF245 nanomembrane kept 97.39% of the TPC in the permeate.
- The optimal conditions obtained reduced organic material and salts by 52 and 23%, respectively.
- The cleaning procedure achieved a recovery of the initial hydraulic permeability that was greater than 90%.

## INTRODUCTION

Table olive processing is widespread around the world and plays a key socio-economic role in producing countries (Cappelletti *et al.* 2011). Nonetheless, most table olives are grown in Mediterranean countries, with Spain, Turkey, Egypt, Greece and Italy being the main contributors. Other countries with important productions are the USA, Argentina, Peru and Australia (Arroyo-López *et al.* 2012). According to the International Olive Oil Council (<https://www.internationaloliveoil.org>, accessed: January 20, 2020) (IOOC 2019), in the 2018/2019 period, table olives' world production reached around 2.75 Mt. However, table olive production brings serious environmental challenges due to

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the high amounts of wastewater that are generated in the processing of olives, which have a huge organic load that includes phenols, fatty acids and a high salinity (Deligiorgis *et al.* 2008). The effluent composition can vary according to the degree of maturation, processing method used, type of finished product and country (Rincón-Llorente *et al.* 2018).

The production of table olives (green, naturally black, etc.) generates flows of wastewater from min 0.5 to 6 L/kg per olive produced (Cappelletti *et al.* 2011). Taking into account the world production index in the 2018–2019 period, it can be estimated that 1.38–16.5 Mt of wastewater was generated from the processing of table olives. The main wastewater characteristics of the fermentation brines from table olive processing are: conductivity of 70–90 mS/cm, pH ~4, chemical oxygen demand (COD) of 6,000–21,000 mg O<sub>2</sub>/L and total phenols content (TPC) of 500–1,500 mg Tyrosol eq./L (Ferrer-Polonio *et al.* 2017). This environmental problem can be addressed in various ways, one of which is reducing the environmental impact of the wastewater by introducing improvements to the treatment systems. This approach has the advantage of not having to make modifications to the table olive elaboration process. Each modification to the traditional process can influence the quality parameters of the final product.

In the past, several methods have been investigated for the treatment of table olive wastewater by biological means (Kyriacou *et al.* 2005), the use of advanced oxidation processes (Javier Benitez *et al.* 2001), a combination of ozonation with UV irradiation (Benitez *et al.* 2002) and electrochemical oxidation (Deligiorgis *et al.* 2008). Most of these research projects were analysed by Rincón-Llorente *et al.* (2018) in their review, 'Table olive wastewater: Problem, treatments and future strategy'. These studies have focused on removing most of the TPC, reducing the COD and improving the biodegradability of the table olive wastewater. However, these processes have a high energy consumption, high costs and require equipment and reagents for their development, which makes them economically unviable at present.

However, membrane technologies are a good option for purifying wastewater from the production of table olives. In the last years, there has been a growing amount of interest regarding the use of membranes in wastewater purification processes, as well as in the recovery and concentration of phenolic compounds from wastewater produced by agro-industrial processes (Cassano *et al.* 2016; Ferrer-Polonio *et al.* 2017). An advantage of using membranes is that both the permeate and rejection current can be recovered.

Previously, certain authors have conducted studies into the recovery of polyphenols from food industry wastewaters. For instance, a membrane system in the treatment of olive mill wastewaters was applied to obtain a fraction enriched in polyphenols (Cassano *et al.* 2013). Moreover, a nanofiltration process was employed to separate and concentrate phenolic compounds from orange peel liquors (Cassano *et al.* 2014; Conidi & Cassano 2015) and ultrafiltration (UF) and nanofiltration separation were utilised to recover and purify organic acids from black liquor from the kraft pulping process (Mänttari *et al.* 2015). Most of the works published about the use of nanofiltration on wastewater from the olive industry have investigated the olive oil process (Cassano *et al.* 2013; Abdel-Shafy *et al.* 2015; Cassano *et al.* 2016). Meanwhile, research papers that address the use of nanofiltration on residual wastewater from the elaboration process of table olives are scarce. In addition, nanomembrane processes are ideal for recovering phenolic compounds given that they do not use solvents or other chemical additives, rendering them highly valued for most food and cosmetic applications (Crespo & Brazinha 2010). Therefore, nanofiltration has great potential as a subsequent step to ultrafiltration and for improving the quality of the permeate for phenolic compound recovery.

On the other hand, optimisation by response surface methodology (RSM) allows for the analysis of the variables using a system where the mathematical relationship of the factors and the independent variable is unknown. This data modelling tool is capable of capturing and representing complex non-linear relationships between dependent and independent variables, while requiring fewer experimental runs than traditional experimental methodology. Model verification can be carried out using an analysis of variance (ANOVA) (Witek-Krowiak *et al.* 2014). Among the most used standard RSM

designs, central composite design (CCD) constitutes a reliable option due to its high efficiency with respect to the number of required experimental runs (Asadollahzadeh *et al.* 2014).

Ochando-Pulido *et al.* (2020) published a recent study on the optimisation of polymeric nanofiltration performance for olive-oil-washing wastewater phenols recovery and reclamation. The authors have applied RSM (Box-Behnken Design) to determinate the optimised parameters of the olive-oil-washing wastewater nanofiltration process. In their study they suggest that it is important to be able to predict the performance of a nanomembrane prior to its an industrial scale implementation.

This study aimed to investigate the simulation for optimising the nanofiltration process in order to reduce the contents of salt and organic material in the ultrafiltration permeate of residual brine from the elaboration process of table olives using a synthetic solution. An additional objective was to provide the optimal operational conditions for maintaining the highest phenolic content possible in the permeate of nanofiltration as a contribution to their possible recovery.

## MATERIALS AND METHODS

### Feed solution

In this paper, a synthetic solution was elaborated by considering the characteristics of the ultrafiltration permeate of residual brine from table olive fermentation, as reported by Carbonell-Alcaina *et al.* (2018). Table 1 shows the real reference values reported in the literature and the values of the model solutions used.

**Table 1** | The real and synthetic values of the solutions of ultrafiltration permeates of residual brine from the elaboration process of table olives

Parameter	Literature <sup>a</sup> Mean ± S.D	Synthetic solutions Mean ± S.D
pH	4.0 ± 0.2	4.02 ± 0.01
Conductivity (mS/cm)	77.5 ± 7.3	80.05 ± 0.07
COD (mg O <sub>2</sub> /L)	6,577.62 ± 803.9	6,362.50 ± 88.39
TPC (mg Tyrosol eq./L)	615.22 ± 156.7	563.43 ± 5.53

<sup>a</sup>Carbonell-Alcaina *et al.* (2018).

The pH was adjusted by adding HCl (ac) (Sigma-Aldrich Co., St. Louis, MO, USA) until the desired value was reached.

Conductivity: NaCl was added to regulate the conductivity value, which is used in the real process of the fermentation step and the high conductivity values are due to its presence.

COD: Lactic acid (Sigma-Aldrich Co.) was used to adjust the organic material, considering that it is the main component of the UF permeate, and 5.5 g/ L of lactic acid concentration was selected. This is a common value in the residual brines of the fermentation process of the table olives.

TPC: Tyrosol (Sigma-Aldrich Co.) was added to regulate the TPC value.

### Analytical methods

#### pH and conductivity

pH and conductivity were measured using a pH-Meter GLP 21+ and EC-Meter GLP 31+ (Crison, Spain), respectively, in the feed solution and permeate. It is very important to measure both pH

and conductivity to check the stability of the feed solution and determine if the membrane has rejected the salts.

### Chemical oxygen demand and total phenolic content

The determination of the COD was determined by means of LCK 114 kits (Hach Lange, Germany). The values were measured in a DR6000 spectrophotometer (Hach Lange) according to a previously described method (Carbonell-Alcaina *et al.* 2018).

TPC was determined using the Folin-Ciocalteu method according to that which was outlined by Singleton *et al.* (1999). In short, 0.2 mL of the sample was placed in a 25 mL volumetric flask. Subsequently, 6.8 mL of distilled water and 0.5 mL of the Folin reagent were added. The blank was prepared in the same manner but without adding the sample. Then, each was stirred for three minutes. Next, 1 mL of 20% w/v by weight sodium carbonate was added. Finally, it was stored for an hour in the dark at room temperature. The absorbance was measured at a wavelength of 765 nm in the Hach Lange model DR6000 spectrophotometer. The results were expressed as milligrams of tyrosol equivalents per litre (mg Tyrosol eq/L). All the measurements were conducted in triplicate.

The removal efficiency of the membranes referring to the conductivity was determined according to the equation (Equation (1)), and TPC and COD rejections ( $R_{\text{TPC}}$  and  $R_{\text{COD}}$ ) using the equation (Equation (2)).

$$E_c(\%) = \left(1 - \frac{C_P}{C_F}\right) * 100 \quad (1)$$

$$R_i(\%) = \left(1 - \frac{C_{pi}}{C_{fi}}\right) * 100 \quad (2)$$

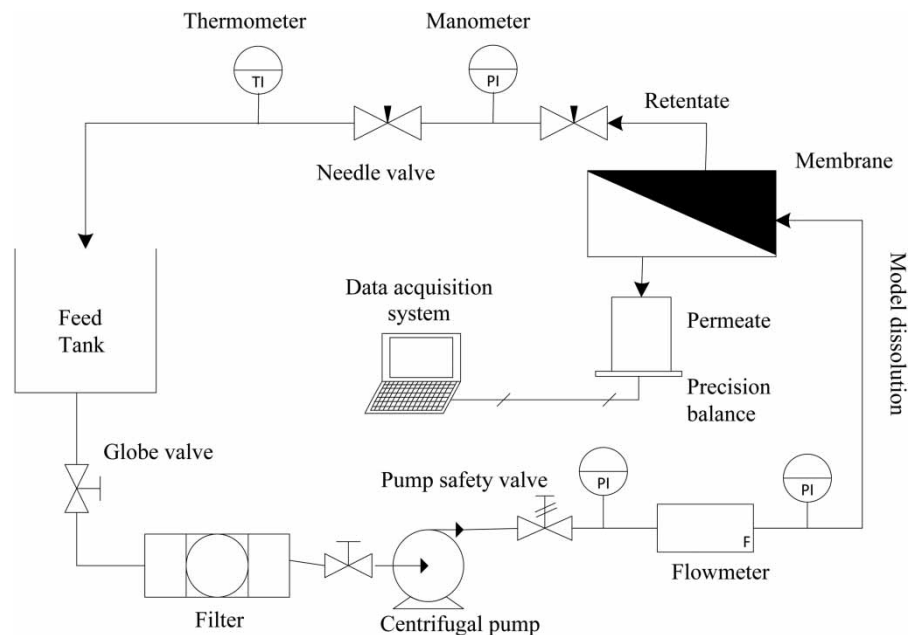
where  $E_c$  is the elimination efficiency of conductivity,  $C_P$  is the value of conductivity in the permeate,  $C_F$  is the value of conductivity in the feed solution.  $R_i$  is the rejection ( $i = \text{COD}$  or  $\text{TPC}$ ),  $C_{Pi}$  and  $C_{Fi}$  are the concentration of parameter  $i$  in the permeate and in the feed, respectively. All measurements were performed in triplicate and expressed as Mean  $\pm$  S.D.

### Nanofiltration pilot plant

The experimental procedure was carried out at the Environment Laboratory of the Department of Chemical and Nuclear Engineering in the Polytechnic University of Valencia (Spain). Figure 1 shows a schematic diagram of the nanofiltration plant.

Two nanofiltration membranes, NF 270 and NF 245 (Polyamide, Dow Chemical, USA) were tested. The main characteristics are shown in Table 2.

The nanofiltration pilot plant consists of a feed tank with a capacity of about 9 L, operating at a constant volume. The flat membrane module consists of two metal plates, between which is a nanofiltration membrane. The system operates at constant recirculation during the experimental run, both for the permeate and the rejection stream. The operation pressure required by the system was provided through a pump and was measured at the inlet and the outlet of the nanofiltration module using two manometers. The transmembrane pressure (TMP) was determined by the mean pressure value of the two manometers. Also, an analytical balance (Kern, Germany) connected to the data acquisition system was used to record the change of mass every 15 s. The pressure, temperature and flow values were regulated by means of an automatic system and displayed in a computer, where they were also recorded. Each experiment was performed at a temperature of 25 °C and time of 1 h.



**Figure 1** | Schematic diagram of the nanofiltration plant.

**Table 2** | Characteristics of the nanomembrane used in the process

Membrane	Total active surface (m <sup>2</sup> )	Permeate flow density <sup>a</sup> (L/hm <sup>2</sup> )	Max. Pressure (bar)	Max. Temperature (°C)	pH operating range	Chlorine tolerance (ppm)
NF245	0.0072	39,351.4	54.8	50	2–11	Not detectable
NF270		18,518.1	41	45		<0.1

<sup>a</sup>Operation conditions: Feed solution 2000 ppm MgSO<sub>4</sub>, 9 bar and 25 °C and recovery 15%.

In addition, before the experimental stage, NF membranes were subjected to the tests of compaction and permeability with osmotised water to guarantee its proper functioning. The results of conditioning the NF membranes have been published previously (Cazares Carrión *et al.* 2019). These authors determined that the osmotic water permeances for the NF270 and NF245 membranes were 9.93 and 3.47 L/hmbar, respectively. At the end of each experimental run, the membranes were cleaned.

### NF nanomembrane cleaning protocol

In the membrane reconditioning, the following protocol was used. (1) Running water throughout the pilot plant system was circulated for a period of 10 min, without recirculation. The purpose of this first step was to eliminate the remnants of model solution that may remain in the system, as well as to remove the dirt that is weakly deposited on the surface of the membrane (reversible fouling). (2) Subsequently, the highly alkaline P3 Ultrasil 115 detergent (25–30% NaOH and 5–10% ethylenediaminetetraacetate, Ecolab, Hispano-Portuguesa S.A.) was used to remove dirt embedded in the pores of the membrane. P3 Ultrasil 115 was added into the feed tank until a pH of ~12 was obtained. The solution was heated to 38 °C to facilitate the cleaning process and it was circulated for 1 h. The retentate stream was continuously recirculated to the feed tank. (3) We repeated step 1 to eliminate the remnants of P3 Ultrasil 115 in the system. (4) Finally, the solution was washed in de-ionised water without pressure and without recirculation for 5 minutes, and then the system pressure was changed to 1 bar for a period of 30 min with recirculation of the rejection.

### Determination of final permeance after cleaning

After the membrane reconditioning and with the purpose of checking its recovery, the water permeability test was done. The water permeability of the membrane assay was carried out for 1 h, at 10 bar pressure, CFV 1.0 m/s and at 25 °C. The water permeability determined should be equal to the initial or have a difference of <10%. If this criterion is not met, the cleaning protocol should be repeated or changed.

### Experimental design and statistical analysis

A response surface methodology – central composite design (RSM-CCD) framework was applied to optimise the nanofiltration process and obtain a predictive model that adequately represented the changes in the response variables selected. The TMP, CFV and nanomembrane type were considered as the independent variables, whilst the efficiency of conductivity ( $E_c$ ), rejection of COD ( $R_{COD}$ ) and phenolic compounds ( $R_{TPC}$ ) were measured as the response variables.

The level of the three factors taken into account in the experimental design in coded and uncoded terms are shown in Table 3.

**Table 3** | The level and range of the factors chosen for the RSM-CCD

Factor	Units	Type	Level	
			Low (-1)	High (+1)
A-TMP	Bar	Numeric	5	15
B-CFV	m/s	Numeric	0.5	1.5
C-NM Type	–	Categoric	NF270	NF245

The ANOVA was utilised as a statistical tool to study the influence of factors (TPM, CFV and NM type) on response variables ( $R_{TPC}$ ,  $R_{COD}$  and  $E_c$ ).

The experimental runs were performed according to the sequence and conditions provided by the Design-Expert software, version 10.0.3 (Stat-Ease, USA) for this type of design, as seen in Table 4. In total, 26 experimental runs were carried out, 18 non-central points and 8 central points.

### Statistical validation of the RSM model

The statistical validation of the model fit with the experimental data using the coefficient of determination ( $R^2$ ), lack of fit and adequate precision (Wang *et al.* 2008; Abreu-Naranjo *et al.* 2018). In this kind of study, it is important to ensure that the selected model is providing an adequate approach to the real system. The diagnostic plots, such as predicted vs. experimental values, allow the model adequacy to be judged (Li *et al.* 2013). This statistical parameter has been previously considered by several researchers to evaluate the accuracy of the model (Pompeu *et al.* 2009; Nazir *et al.* 2017; Abreu-Naranjo *et al.* 2018).

## RESULTS AND DISCUSSION

### Model fitting

A summary of the ANOVA results from RSM-CCD is shown in Table 5 for the response variables considered. These were fitted to a Response Surface Reduced Cubic Model. Design-Expert software

**Table 4** | RSM-CCD setting in the original values of the independent variables and experimental results of dependent variables

Run <sup>a</sup>	TMP (bar)	CFV (m/s)	NM Type	R <sub>TPC</sub> (%)	R <sub>COB</sub> (%)	E <sub>c</sub> (%)
1	5.0	1.00	NF270	1.46	24.6	6.00
2	10.0	0.50	NF245	2.00	44.8	16.8
3	10.0	1.00	NF245	1.87	34.1	18.7
4	10.0	1.00	NF270	2.13	37.5	9.13
5	10.0	0.50	NF270	2.67	35.1	10.9
6	15.0	1.00	NF270	3.93	47.6	16.4
7	10.0	1.00	NF245	1.85	34.4	19.0
8	10.0	1.00	NF245	1.87	34.2	19.2
9	10.0	1.50	NF270	3.58	41.6	16.9
10	10.0	1.00	NF270	2.13	37.5	9.13
11	10.0	1.50	NF245	1.92	30.7	16.8
12	10.0	1.00	NF245	1.89	34.1	19.0
13	15.0	1.00	NF245	3.17	53.8	20.9
14	15.0	1.50	NF245	2.54	55.2	24.1
15	15.0	0.50	NF245	3.34	50.8	19.0
16	5.0	1.00	NF245	0.73	33.5	10.3
17	15.0	1.50	NF270	4.63	56.9	19.6
18	10.0	1.00	NF270	2.13	37.7	9.13
19	10.0	1.00	NF270	2.10	37.5	9.14
20	5.00	1.50	NF270	2.76	40.7	14.0
21	5.00	1.50	NF245	1.55	24.5	13.6
22	10.0	1.00	NF270	2.15	36.4	9.12
23	10.0	1.00	NF245	1.87	34.1	19.0
24	5.00	0.50	NF270	2.14	25.1	8.13
25	15.0	0.50	NF270	5.01	35.7	16.7
26	5.00	0.50	NF245	0.59	37.7	13.0

<sup>a</sup>Non-randomised.**Table 5** | Summary of the ANOVA results for the three response variables for the response surface reduced cubic model

Source	R <sub>TPC</sub> p-value	R <sub>COB</sub> p-value	EC p-value
Model	<0.0001	<0.0001	<0.0001
A-TMP	<0.0001	<0.0001	<0.0001
B-CFV	0.0312	0.0549	0.0003
C-NM Type	0.0104	0.1966	<0.0001
AB	<0.0001	0.0151	0.5807
AC	0.0636	0.1851	0.484
BC	0.0553	<0.0001	0.0468
A <sup>2</sup>	0.0004	0.0201	0.9187
B <sup>2</sup>	<0.0001	0.1776	0.003
ABC	0.1114	0.165	0.0694
A <sup>2</sup> C	0.0026	0.011	0.0212
B <sup>2</sup> C	<0.0001	0.615	0.0012
Lack of Fit	5.42	20.3	3.69
R <sup>2</sup>	0.988	0.936	0.963
Adeq. Precision	42.43	16.1	19.54

recommended this model out of the five models evaluated: Design model, Linear, 2FI, Quadratic and Cubic. Thus, on the basis of ANOVA and after developing a cubic polynomial model, we studied the parameters' influence on the response variables and the optimisation of conditions within the nano-filtration process.

From the ANOVA results (probability value) shown in Table 5, one can determine the variables and their interactions that have a significant impact ( $p < 0.05$ ) on the polyphenol content,  $R_{\text{COD}}$  and conductivity value of the nanofiltration permeate. A  $p$  of  $<0.05$  indicates that there exists a less than 5% risk of something happening because it was influenced by a factor when in reality it occurred due to pure chance. Similarly, it can be assumed that the results are significant at a 95% confidence level. The TMP factor proved to be highly significant for the three independent variables analysed with  $p$ -values of  $<0.0001$ . However, the NM type and CFV showed significant effects on  $R_{\text{TPC}}$  and  $E_c$  variables, whilst for the  $R_{\text{COD}}$ , the  $p$ -value was superior and slightly superior to the former variables, respectively. From these results, it can be determined that the  $R_{\text{COD}}$  was not significantly influenced by the membrane change, yet this was not the case for the other two variables. It is worth noting that for  $R_{\text{TPC}}$ , all the interactions that involved the TMP factor had a significant effect. For the other two response variables, the impact of the factor interactions was varied.

A  $p$ -value of  $<0.0001$  for the reduced cubic model was obtained in the modelling of the independent variables. The coefficients of determination, in all cases, were greater than 0.930, whereby 0.988 for  $R_{\text{TPC}}$  was the best value. This indicates that 98.8% of the variation in the  $R_{\text{TPC}}$  concentration may be attributed to the factors considered in this study. The three adjusted models satisfactorily explain the variation in the response variables. Also, lack of fit was non-significant with  $p > 0.05$ , which suggests that the model is adequate for representing the experimental data at a 95% confidence level (Whitcomb & Anderson 2004). The parameter 'Adequate Precision' is the signal to noise ratio, which gives a measurement of whether the model can be used to navigate the design space analysed. In this type of study, the literature recommends that this ratio should be greater than 4. For all cases, the values obtained were superior, indicating an adequate signal.

Meanwhile, Figure 2(a)–(c) present the diagnostic plots that show the difference between the calculated data based on the model and the experimental values. In these plots, it can be seen how the calculated points were scattered along the trend line for the three variables considered ( $R_{\text{TPC}}$ ,  $E_c$  and  $R_{\text{COD}}$ ) The best adequacy was obtained for the  $R_{\text{TPC}}$  variable (A), where one can appreciate a distribution of points that is very close to the trend line. The adequacy was lower in the other variables:  $E_c$  (B) and  $R_{\text{COD}}$  (C). These results are in correspondence with the coefficient of determination values presented above. Therefore, it can be concluded that the actual and predicted values are in good agreement and that the models are highly adequate, as suggested by Abdulredha *et al.* (2020) and Li *et al.* (2013).

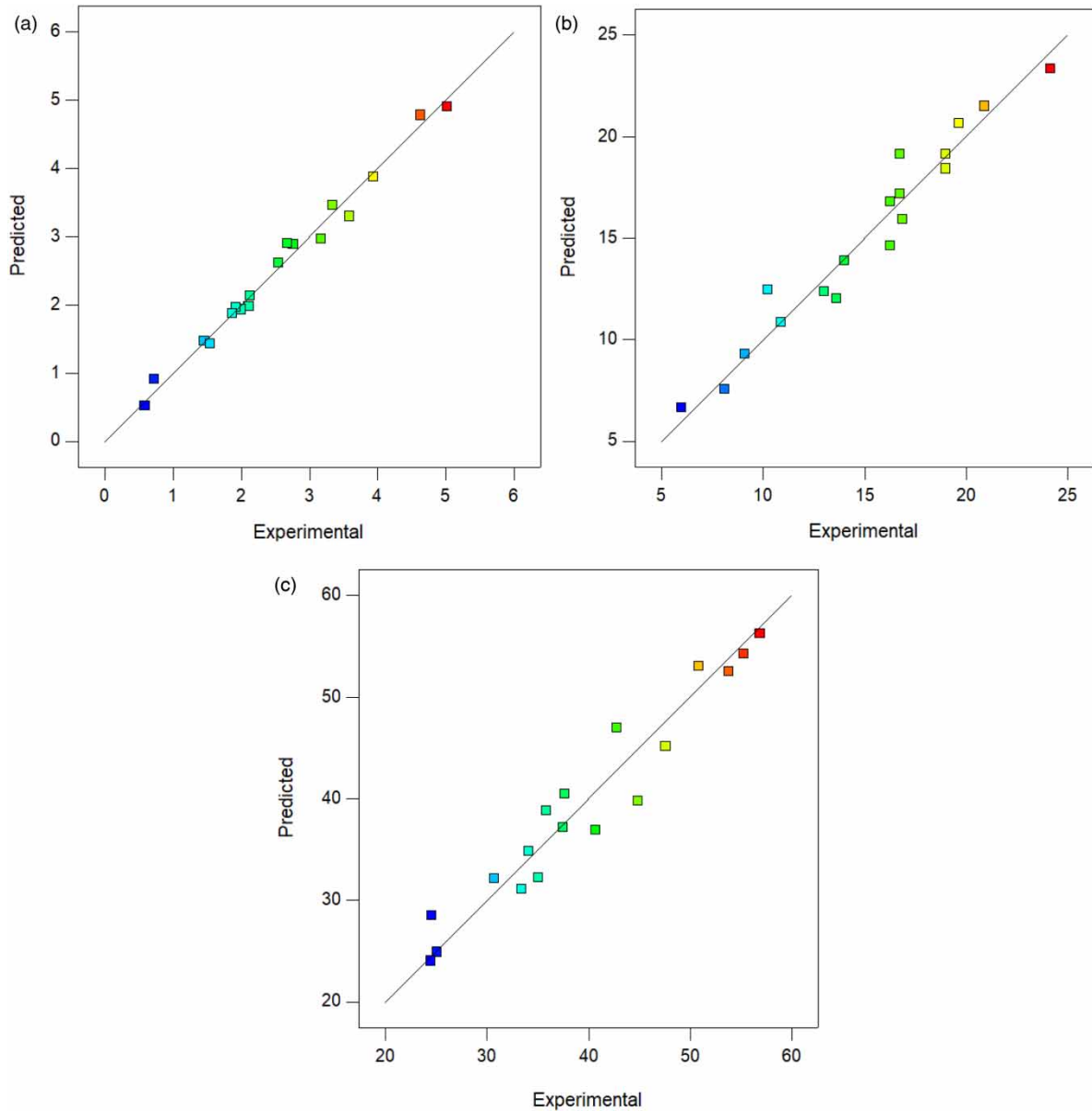
The equation in terms of coded factors (Equation (3)) can be used to make predictions about the response in the range analysed for each factor. This equation is useful for identifying the relative impact of the factors by means of their coefficients.

Equation in terms of coded factors:

$$R_{\text{TPC}} = 2.01 + 1.12A + 0.11B - 0.13C - 0.35AB - 0.088AC - 0.092BC + 0.30A^2 + 0.52B^2 - 0.091ABC - 0.24A^2C - 0.45B^2C \quad (3)$$

However, the equation in terms of actual factors (Equations (4) and (5)) can be used to make predictions about the response for the levels of each factor that was studied. Unlike Equation (3), these equations should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the centre of the design space.





**Figure 2** | Diagnostic plots of predicted vs. experimental values for the three response variables fitted: TPC (a), Ec (b) and COD (c).

Equation in terms of actual factors for the two membranes studied:

NF270

$$R_{TPC} = 4.30 - 0.0836 (TMP) - 6.29 (CFV) - 0.103 (TMP)(CFV) + 0.021(TMP)^2 + 3.859 (CFV)^2 \quad (4)$$

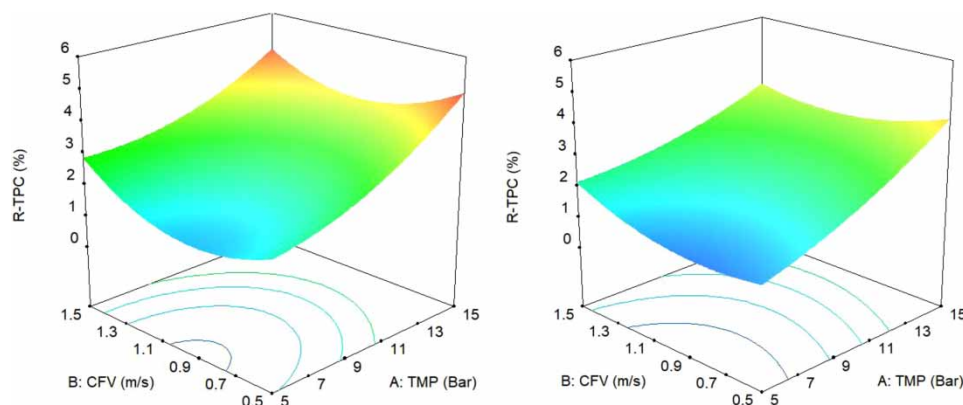
NF245

$$R_{TPC} = -1.423 + 0.33(TMP) + 1.20 (CFV) - 0.176(TMP)(CFV) + 2.52 * 10^3(TMP)^2 + 0.292(CFV)^2 \quad (5)$$

### Response surface methodology analysis

From the adjusted model, we generated a 3D graphics surface, which allowed us to visually inspect the influence of the factors and assess their sensitivity on the response variable. Figure 3 shows the influence of the factors CFV and TMP on  $R_{\text{TPC}}$  for the two nanomembranes studied.

The NF270 membrane managed to retain between 1.46 and 5.01% of the polyphenol content ( $R_{\text{TPC}}$ ). Meanwhile, for the organic material rejection ( $R_{\text{COD}}$ ) and conductivity removal efficiency (Ec), the ranges obtained were from 24.60 to 56.85% and 6.00 to 19.63% respectively (see Table 4). With regard to NF245, the range of polyphenol content retention was lower (0.59–3.34%). However, the conductivity removal efficiency was higher than the NF270 membrane, being between 13.63 and 24.13%. The  $R_{\text{COD}}$  in both nanomembranes had a similar behaviour (from 24.51 to 55.25%).



**Figure 3** | 3D plots regarding the influence of the factors on  $R_{\text{TPC}}$  for the nanomembranes: NF270 (left) and NF245 (right).

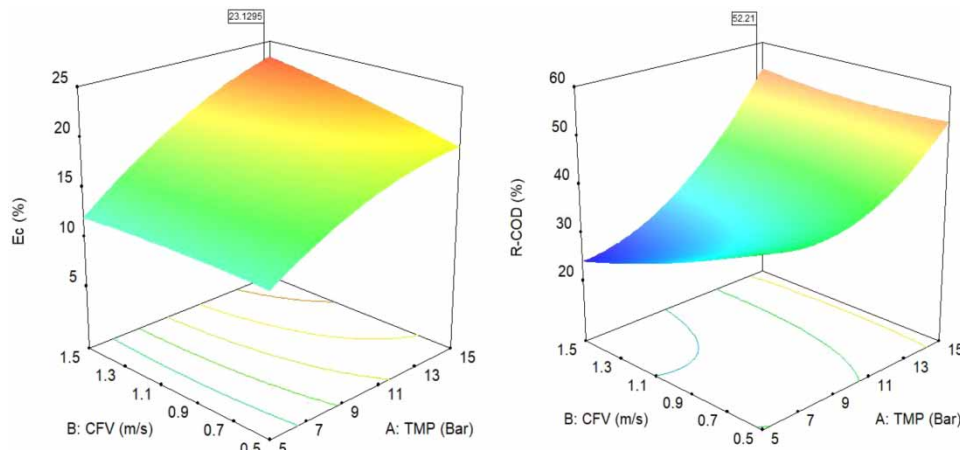
In the two graphs, the greatest influence of the TMP on the output variable can be observed compared with the CFV variable. With the increase in transmembrane pressure, higher values in the polyphenols retention were obtained. The percentage of polyphenol retention was less affected by changes in CFV values in the range selected for both nanomembranes. However, the behaviour on the response variable was slightly different. NF245 showed a linear tendency, yet this was not the case in NF270.

The results obtained for the NF245 nanomembrane were more favourable for obtaining a permeate that conserves the highest polyphenol content and decreases the organic matter and salt concentration to facilitate the subsequent recovery and treatment of the polyphenols. In this context, the NF245 nanomembrane was selected to perform the process optimisation to determine the combination of levels of factors that provide optimal operating conditions for the response variables studied in the experimental space.

### Optimisation of the NF245 membrane

Figure 4 depicts the response surface plots of the optimisation of Ec and  $R_{\text{COD}}$  using the numeric method for the NF245 nanomembrane.

In both graphs, the positive influence in the response variables that produce the changes in TMP values can be appreciated. Meanwhile, when the CFV values varied, the percentages of Ec and  $R_{\text{COD}}$  remain almost constant. However, the variations in CFV showed a greater effect on  $R_{\text{COD}}$  at the lower pressure values studied.



**Figure 4** | Response surface plots of the optimisation of  $E_c$  and  $R_{COD}$  for the NF245 nanomembrane using RSM.

The NF245 nanomembrane was found to retain more than 52 and 23% of the organic material and salts, respectively, while allowing the permeate to conserve 97.39% of the polyphenol contents at a value of TMP (14.43 bar) and CFV (1.50 m/s). These optimal conditions allowed for a decrease in organic matter and salt concentration, while most of the polyphenol content in the residual brine stayed preferentially in the permeate.

### Nanomembrane cleaning

The cleaning procedure is a very important process for membrane recovery and for good long-term operation. Nanomembrane fouling is a serious drawback for these separation processes, since it brings about a decrease in flow through the nanomembrane (Mattaraj *et al.* 2011). The aforementioned cleaning protocol and water permeability method were applied to determine the synthetic solution's recovery when faced with fouling. In both membranes (NF245 and NF270), water permeability values greater than 90% were obtained after the reconditioning was applied. This demonstrated the effectiveness of the cleaning protocol and the recovery of the initial hydraulic permeability of the nanomembrane. These values are higher than the 73% recovery of initial permeance reported by Avram *et al.* (2017) using 0.2% HCl and 0.1% NaOH as a cleaning method in the NF245 nanomembrane. The cleaning protocol used in this paper can be recommended for this type of process for its high percentage of recovery of the nanomembrane permeance.

### CONCLUSIONS

The Response Surface Reduced Cubic Model satisfactorily represented the variation in the dependent variables ( $R_{TPC}$ ,  $R_{COD}$  and  $E_c$ ) for the factors (TMP, CFV and NM type) in the range of values selected. A high fit, with coefficients of determination greater than 0.93 for all the cases, was obtained. The factor of highest influence on the three response variables was TMP, while the NM type was not significant on  $R_{COD}$ . The results showed that the NF245 nanomembrane is more suitable for obtaining a permeate that keeps the highest content of polyphenols with a lower organic matter and salts concentration to facilitate the possible recovery and treatment of polyphenols. The RSM indicates that the optimum for the variables studied that satisfies the aforementioned characteristics for the permeate were: nanomembrane (NF245), TMP (14.43 bar) and CFV (1.50 m/s). This allowed the permeate to keep 97.39% of polyphenol contents and reduce organic material and salts by 52 and 23%, respectively. The cleaning procedure applied to the nanomembranes demonstrated its effectiveness in the

recovery of the initial hydraulic permeability of the membrane, with water permeability values greater than 90%.

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## AUTHOR CONTRIBUTION STATEMENT

**Karem Y. Cazares Carrión:** Investigation, Writing – Original Draft, Conceptualisation, Funding acquisition. **Reinier Abreu-Naranjo:** Visualisation, Methodology, Formal analysis, Writing – Review & Editing.

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## CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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