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# Box–Behnken experimental design method application in pretreatment of olive oil mill wastewater by ultrafiltration

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**ABSTRACT**

In this study, the pretreatment of olive oil mill wastewater with a laboratory-scale ultrafiltration membrane was investigated. The Box–Behnken statistical experimental design method was used to investigate the effect of ultrafiltration on permeate flux, chemical oxygen demand (COD) and color removal efficiency. With this method, the effects of three independent variables (pH, pressure, and ultrafiltration time) on the response functions (flux, COD and color removal efficiency) were examined, and the optimum conditions were determined and presented in the study. The Design-Expert 13.0 program was used for statistical analyses. As a result of the experimental studies, it was observed that the ultrafiltration time did not have a significant effect on all three response functions. The highest permeate flux of 30.4 $L/m^2 \cdot h$ was obtained at pH = 10 and 3 bar pressure, while the highest COD removal efficiency (48%) was obtained at pH = 2 and 1 bar pressure. The only effective parameter for color removal efficiency was pH. The highest color removal efficiency was obtained as 77% at pH = 2. It has been proven that the Box–Behnken experimental design method gives statistically reliable results for flux, COD, and color removal efficiency in ultrafiltration of olive mill wastewater. An analysis of variance was also done within the scope of the study. The predicted and observed correlation coefficients ($R^2$) were found to be 0.9875 for permeate flux, 0.9952 for COD removal, and 0.9997 for color removal efficiency. This shows that the estimations made by the response function and the experimental results are in agreement, and the method used is statistically suitable.

*Keywords:* Box–Behnken experimental design; pH; Olive oil wastewater; Ultrafiltration

## 1. Introduction

Olive oil production is one of the most important industrial activities in Mediterranean countries. Approximately 30 million·$m^3$ of wastewater is generated annually during production. This wastewater, called olive oil mill wastewater (OMW), is a mixture of different wastewaters generated during the olive oil production process. It is acidic and dark in color [1]. The composition of olive oil mill wastewater varies according to the method of olive oil extraction (traditional pressing process, three-phase centrifugal continuous process, or two-phase centrifugal continuous process). Although the two-phase centrifuge process is more efficient and produces less wastewater, most olive oil-producing countries use the three-phase centrifuge system [2].

Olive oil wastewater, which is released as a liquid by-product during olive oil production, has a dark color, strong odor, and high turbidity. It contains high levels of organic matter, suspended solids, oil, and persistent pollutants. Since OMW contains phenolic compounds such as polyphenols, polyalcohols, and tannins, it has high toxicity, and low biodegradability. Physical, physicochemical, biological, and advanced treatment methods are used in the treatment of this wastewater. However, complete treatment cannot be achieved by using all these methods alone, and therefore discharge standards cannot be met [3].

The membrane is a semi-permeable barrier. It is used for different purposes, such as separating the two phases, obtaining a purer or concentrated product, limiting the transport of various components. Membrane systems provide high separation performance in wastewater treatment, separation, and purification of recyclable materials. It also provides less energy consumption [4]. It has been observed that microfiltration, ultrafiltration, and nanofiltration membranes are used individually or in combination in studies where membrane technologies are applied in OMW treatment. In a study in which microfiltration and ultrafiltration processes were used sequentially, 91% suspended solids (SS) and 26% total organic carbon (TOC) removal efficiencies were obtained by direct microfiltration of OMW. When OMW was taken into nanofiltration after microfiltration, the TOC removal efficiency increased to 72% [5]. In a nanofiltration study in which three different flowrates and three different membrane pressures were applied, the optimum conditions were found to be 0.5 m/s and 15 bar, and 78% chemical oxygen demand (COD) removal was obtained in this study [6].

Since OMW is a difficult wastewater to treat, there is a need to use a combination of different technologies in its treatment. In a study, the primary objective was to reduce suspended solids, and therefore a pre-centrifugation step was applied. The centrifuged OMW was passed through an ultrafiltration membrane, and 90% COD removal efficiency was obtained by using the two treatment methods applied consecutively [7]. In another study for the treatment of OMW, a combination of microfiltration, nanofiltration, osmotic distillation, and membrane emulsification was applied. Four units were used in this study. The first unit is a pre-treatment unit consisting of acidification, and a microfiltration step. A nanofiltration unit is the second unit, which allows to improve the effluent quality and obtain a concentrated polyphenol solution. The osmotic distillation unit first utilized the nanofiltration residue and then concentrated the polyphenols. Finally, a fourth unit consisting of a membrane emulsification process was used. Thus, 92% TOC and 98% polyphenol removal were obtained [8]. In another study investigating the physicochemical treatability of OMW, flocculation, photolysis, and microfiltration processes were applied consecutively. The COD, TOC, and total phenol removal efficiencies obtained in this study are 96.2%, 80.3%, and 96.6%, respectively. [9]. In a study by El-Abbassi et al. [10], ultrafiltration was applied to OMW at different pH values and the removal of color, COD, and phenolic compounds was investigated. The highest removal efficiency of phenolic compounds was 30% at pH = 12. In the same study, the highest color removal efficiency (83%) was obtained at pH = 4 and the highest COD removal efficiency (60%) was obtained at pH = 2.

In our previous study, the effects of chitosan concentration, flow rate, and ultrafiltration time on permeate flux and COD removal efficiency in an ultrafiltration process applied to wastewater from the settling tank of an olive oil production plant were investigated [11]. In this study, the ultrafiltration process was again applied to a different wastewater from the same plant, and the effects of pH, pressure, and ultrafiltration time on permeate flux, COD, and color removal efficiencies were investigated. The Box–Behnken statistical experimental design method was used to determine the optimum conditions under which the highest permeate flux, COD, and color removal efficiencies were obtained. There are studies in the literature on the ultrafiltration of olive mill wastewater. However, there is no study investigating the effects of pH, pressure, and ultrafiltration time on permeate flux, COD and color removal efficiencies using the Box–Behnken statistical experimental design method. This shows the novelty of this study.

## 2. Material and method

### 2.1. Analytical methods

Standard methods were used for COD, SS, and oil–grease analyses [12]. An 890 MD pH meter was used for pH measurement. TOC analysis was performed with the Dohrmann DC-190 TOC analyzer. A Hach Lange DR5000 model spectrophotometer was used for color measurements, and measurements were made at a wavelength of 456 nm.

### 2.2. Characterization of raw wastewater

The olive oil mill wastewater used in the experimental studies was taken from the sedimentation tank of an olive oil production plant in Izmir, which produces olive oil according to the 3-phase continuous method. Wastewater taken in December, when the production was made, was stored in the refrigerator at 4°C and homogenized by shaking before each experiment.

The general composition of OMW is given in Table 1.

### 2.3. Ultrafiltration experiments

In experimental studies, an ultraphilic MW-coded membrane obtained from the Osmonics Company was used. The molecular weight cut-off of the membrane is 100 kDa, and the effective membrane surface area is 15.5 $cm^2$. Ultrafiltration experiments were carried out on the Osmonics SEPA CF II membrane system with a plate frame module at room temperature (25°C ± 2°C). The permeate passing through the membrane was collected in the permeate collection vessel and measured continuously to calculate the permeate flux. Detailed information about the experimental setup is given in our previous publication [13]. Filtration was done with distilled water before and after each experiment. The schematic diagram of the experimental system is given in Fig. 1.

Table 1
Characterization of olive mill wastewater

| Parameter | OMW characterization |
|---|---|
| pH | 4.8 |
| Chemical oxygen demand (g/L) | 84.0 |
| Total organic carbon (g/L) | 25.54 |
| Suspended solids (g/L) | 11.2 |
| Oil and grease (g/L) | 2.51 |

To observe the effect of pH on the performance of the ultrafiltration process, 2 M HCl solution or 2 M NaOH solution was added to the raw OMW, thus adjusting the pH of the OMW to various values ranging from pH = 2 to pH = 10. The membranes were washed and cleaned after each use. The treated wastewater caused discoloration of the membrane. To remove the discoloration, the membrane was soaked overnight in an isopropanol/water (1:1 v/v) solution containing sodium hypochlorite.

### 2.4. Experimental design procedure

In this study, the Box–Behnken statistical design of experiments was used to optimize the operating parameters of OMW in the ultrafiltration process. The Box–Behnken statistical design of experiments method is an experimental design model used to investigate the relationship between independent variables and response values and to estimate the optimal conditions. This method requires the least amount of work among all response surface methodology designs. It provides and demonstrates moderate efficiencies that have not been experimentally studied [14]. In this study, a three-factor and three-level Box–Behnken experimental design method was applied. Design-Expert 13.0 (trial version) was used.

The Box–Behnken experimental design method was used to determine the effects of operating parameters on permeate flux, COD, and color removal efficiencies. The independent variables selected for optimization are pH ($X_1$), membrane pressure ($X_2$), and ultrafiltration time ($X_3$).

Preliminary experiments were carried out to determine the conditions of the independent variables. Each variable was coded at three levels between –1, 0, and 1 to represent low, medium, and high levels (Table 2). As a result of the experimental design, a total of 15 experiments were conducted with 12 different combined coding levels and 3 central coding levels.

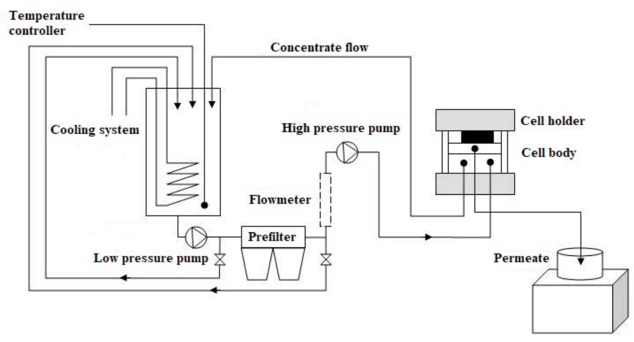


Fig. 1. Schematic diagram of ultrafiltration system.

Table 2
Independent variables and their values for the Box–Behnken experimental design

| Independent variable | Symbol | Coded level | | |
|---|---|---|---|---|
| | | –1 | 0 | +1 |
| pH | $X_1$ | 2 | 6 | 10 |
| Membrane pressure (bar) | $X_2$ | 1 | 2 | 3 |
| Ultrafiltration time (min) | $X_3$ | 10 | 65 | 120 |

The mathematical relationship that is offered by the Box–Behnken design application between the dependent variables ($Y$) and the independent variables ($X$) can be approximated by a (second-order) polynomial equation as follows:

$$Y = b_0 + \underbrace{\sum b_i X_i}_{\text{linear}} + \underbrace{\sum b_{ij} X_j}_{\text{interaction}} + \underbrace{\sum b_{ij} X_i^2}_{\text{squared}} \quad (1)$$

where $Y$ is the predicted response, $b_0$ is the offset term, $b_i$ is the linear effect, while $b_{ii}$ and $b_{ij}$ are the square and interaction effects, respectively.

## 3. Results and discussions

### 3.1. Box–Behnken experimental design method results

The experimental conditions determined according to the Box–Behnken experimental design method are given in Table 3. The results obtained as a result of the experimental studies carried out under these conditions are also presented in the same table. After the experimental studies are done, the predicted results with the Box–Behnken statistical design are also determined. The correlation coefficient between the observed and predicted results is very important in determining the applicability of the Box–Behnken method. Correlation coefficients are also given in the study.

The actual and predicted values of permeate flux, COD, and color removal efficiencies determined with the Design-Expert 13.0 regression program are presented in Fig. 2. As can be seen from Fig. 2, the match between the predicted values and the experimental data points indicates a good agreement. The correlation coefficients ($R^2$ values) were found to be 0.9875, 0.9952, and 0.9997 for permeate flux, COD, and color removal efficiency, respectively. This indicates the suitability of the experimental design method used.

The correlation between experimental results and response functions was also determined with Design-Expert 13.0. Response functions with determined coefficients for permeate flux ($Y_1$), COD removal efficiency ($Y_2$), and color removal efficiency ($Y_3$) are given in Eqs. (2)–(4).

$$\begin{aligned} Y_1(\text{Permeate flux}) = &+4.32923 + 1.43781X_1 \\ &+ 0.76269X_2 - 0.019691X_3 \\ &- 0.000227X_1X_2 - 0.00005X_1X_3 \\ &- 0.0000227545X_2X_3 + 0.10646X_1^2 \\ &+ 0.88083X_2^2 + 0.0000705X_3^2 \end{aligned} \quad (2)$$

$$\begin{aligned} Y_2(\text{COD removal}) = &+63.08652 - 4.44602X_1 \\ &-5.92045X_2 - 0.012190X_3 \\ &+ 0.12500X_1X_2 - 0.0002272X_1X_3 \\ &+0.000455X_2X_3 + 0.14844X_1^2 \\ &+0.12500X_2^2 + 0.0000413X_3^2 \end{aligned} \quad (3)$$

Table 3
Results of the Box–Behnken experiments at the pre-determined experimental points

| Run | Actual levels of variables | | | Experimental results | | | Predicted results | | |
|---|---|---|---|---|---|---|---|---|---|
| | pH | Pressure (bar) | Ultrafiltration time (min) | Permeate flux (L/m²·h) | COD removal efficiency (%) | Color removal efficiency (%) | Permeate flux (L/m²·h) | COD removal efficiency (%) | Color removal efficiency (%) |
| 1 | 10 | 2 | 120 | 27.0 | 22.9 | 66.3 | 27.0 | 22.7 | 66.3 |
| 2 | 6 | 1 | 120 | 15.8 | 35.1 | 75.4 | 15.1 | 35.1 | 75.4 |
| 3 | 6 | 1 | 10 | 16.9 | 37.2 | 75.1 | 16.6 | 36.7 | 75.2 |
| 4 | 2 | 2 | 120 | 9.6 | 44.8 | 77.3 | 10.1 | 44.5 | 77.4 |
| 5 | 6 | 2 | 65 | 17.4 | 31.3 | 74.1 | 17.4 | 31.3 | 74.1 |
| 6 | 6 | 3 | 10 | 21.2 | 27.9 | 73.1 | 21.9 | 27.9 | 73.1 |
| 7 | 10 | 3 | 65 | 30.4 | 20.1 | 65.0 | 30.1 | 19.8 | 65.1 |
| 8 | 10 | 2 | 10 | 29.2 | 24.3 | 66.1 | 28.8 | 24.7 | 66 |
| 9 | 2 | 1 | 65 | 7.4 | 48.5 | 78.2 | 7.7 | 48.8 | 78.1 |
| 10 | 2 | 3 | 65 | 15.9 | 39.9 | 76.2 | 15.1 | 39.8 | 76.2 |
| 11 | 2 | 2 | 10 | 11.4 | 44.3 | 77.1 | 11.4 | 44.5 | 77.1 |
| 12 | 10 | 1 | 65 | 26.2 | 27.1 | 67.1 | 27.0 | 27.3 | 67.1 |
| 13 | 6 | 3 | 120 | 20.0 | 26.9 | 73.5 | 20.3 | 27.4 | 73.4 |
| 14 | 6 | 2 | 65 | 17.4 | 31.2 | 74.0 | 17.4 | 31.3 | 74.1 |
| 15 | 6 | 2 | 65 | 17.4 | 31.3 | 74.1 | 17.4 | 31.3 | 74.1 |

$$Y_3(\text{Color removal}) = +79.01529 - 0.50937X_1 - 1.25871X_2 - 0.00449X_3 - 0.00625X_1X_2 - 0.000001X_1X_3 + 0.000455X_2X_3 - 0.15667X_1^2 + 0.066667X_2^2 + 0.0000468X_3^2 \quad (4)$$

The magnitudes and signs of the coefficients in the response function show the effect of the independent variables on the response function. According to Eq. (2), the permeate flux increases with increasing pH and pressure and decreases with increasing ultrafiltration time. The effect of a change in pH on permeate flux is greater than pressure and ultrafiltration time. According to Eq. (3), all three independent variables have a negative effect on the COD removal efficiency. The same is true for the color removal efficiency [Eq. (4)]. However, since the coefficients in Eq. (3) are larger, the effects of the independent variables on the COD removal efficiency are greater than on the color removal efficiency.

Analysis of variance (ANOVA) results are presented in Table 4 for permeate flux, COD, and color removal efficiencies. ANOVA is used to determine the statistical significance of all analyses. The statistical significance of the quadratic fit is determined by the lack of fit between the values determined by the model and the experimentally found values, the estimated correlation coefficient ($R^2$), and the calculated correlation coefficient. Another parameter is lack of fit. ANOVA tests the difference in the mean value of a dependent variable between groups of subjects. The significance of the difference is tested by the $F$-ratio. The rule often used in regression analysis is that the null hypothesis can be rejected if $F > 2.5$. This indicates that there is at least one non-zero parameter value. The larger the $F$-ratio in the model, the more significant it is. The model $p$-value being less than 0.05 (<0.05) indicates that the applied model is significant for interpreting the experimental results [15]. The $p$-values for the model terms being greater than 0.1000 (>0.1000) indicate that the model terms are not significant [16]. According to Table 4, the $p$-value (lower than 0.0001) is significant for permeate flux, COD, and color removals. This shows that all the independent variables selected are significant, and the model used can be a suitable model for the estimation of experimental values.

The model $F$-ratio of 123.47 for the permeate flux indicates that the model is statistically significant. For the model terms to be meaningful, the $p$-value must be less than 0.05. Accordingly, a $p$-value of model less than 0.0001 indicates the suitability of the presented model for flux. It can be said that $X_1$, $X_2$, $X_3$, $X_1X_2$, and $X_1^2$ are important model terms for permeate flux. Estimated and calculated correlation coefficient ($R^2$) values of 0.9955 and 0.9875 show that the model is statistically compatible with the experimental results. The model $F$-ratio for the COD removal efficiency was calculated at 323.76, and the $p$-value was <0.0001. This shows that the model is statistically significant. Considering the model $p$-values, it can be said that the terms $X_1$, $X_2$, $X_3$, and $X_1^2$ are important for COD removal. Estimated and calculated correlation coefficient ($R^2$) values (0.9983 and 0.9952) showed that the model was definitely suitable for COD removal. An $F$-ratio of 4509.30 for color removal efficiency indicates that the model is significant. $X_1$, $X_2$, $X_3$, $X_1^2$, $X_2^2$, and $X_3^2$ are important model terms because their $p$-values are less than 0.05. Estimated and calculated $R^2$ values of 0.9999 and 0.9997 show that the model is also suitable for color removal.

In order to display the obtained results in 3D, the Adeq. Precision value (Adeq. Prec.) of the model graph should

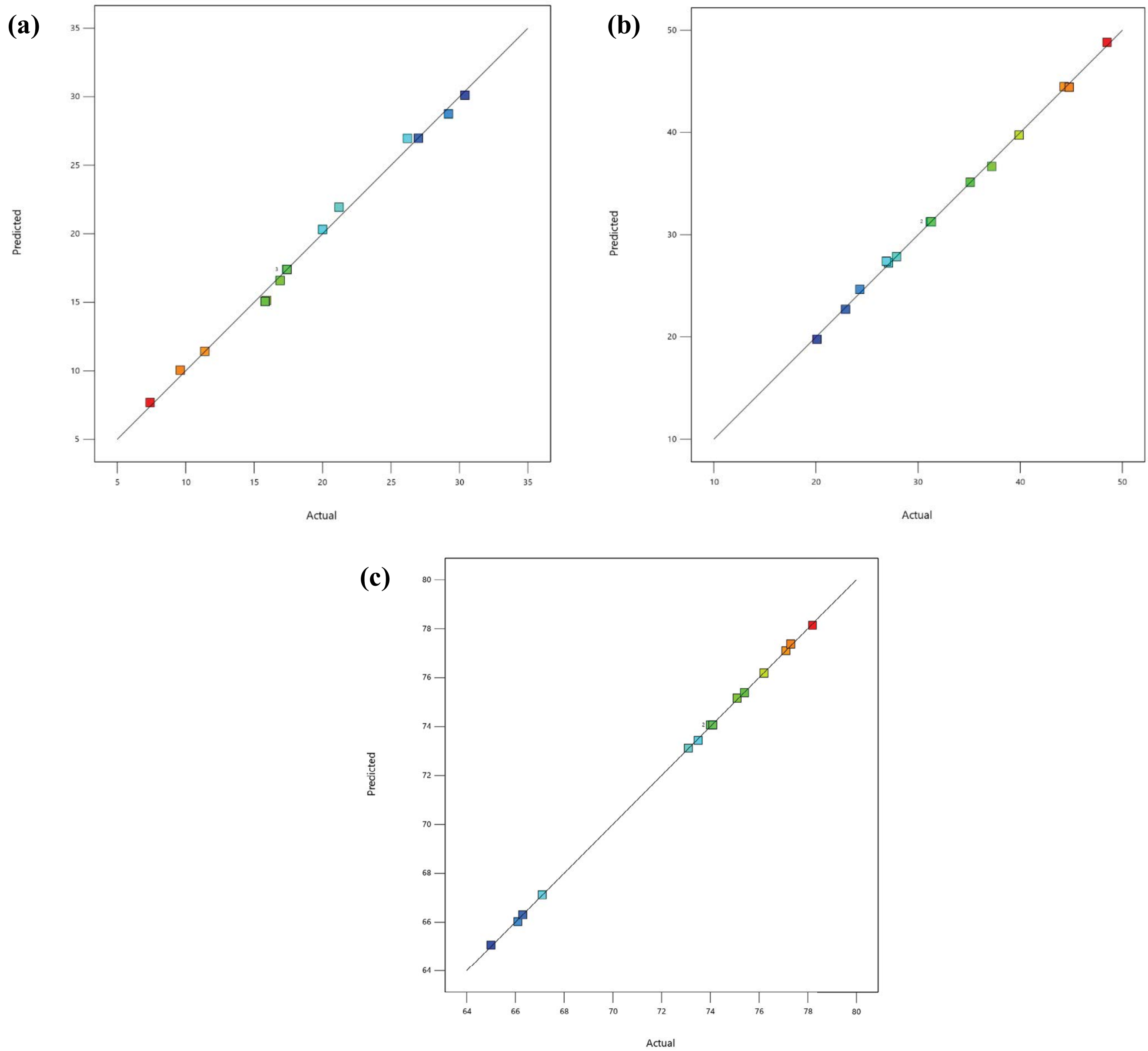


Fig. 2. Relation between predicted and actual results of (a) flux, (b) chemical oxygen demand removal, and (c) color removal.

be greater than 4 [17]. As a result of data analysis with Design-Expert 13.0, this value was determined to be 35.497 for permeate flux, 60.553 for COD removal, and 193.218 for color removal. For this reason, the results obtained within the scope of the study are shown with 3D graphics.

### *3.2. Variation of permeate flux*

The effects of changes in the independent variables on the response functions were evaluated by making 3D surface drawings according to the Design-Expert 13.0 program. While drawing the graphs, one variable was kept at a constant level, while the other two variables were changed at the same time. The effects of the independent variables (pH, pressure, and ultrafiltration time) on the response function (permeate flux) are shown in Fig. 3.

As seen in Fig. 3, the permeate flux increases with increasing pH. This is because fatty acids decompose better in alkaline solutions. Fatty acids are weak acids, and their decomposition takes place according to the equilibrium reaction given in Eq. (5).

$$HA + H_2O \leftrightarrow H_3O^+ + A^- \quad (5)$$

As the pH rises, the reaction equilibrium moves towards the product side. Therefore, fatty acid molecules are converted into ions, thereby reducing their accumulation on the membrane surface. As a result, the permeate flux increases [13,18]. The permeate flux obtained for 1 bar pressure and pH = 2 is 7.4 $L/m^2 \cdot h$. When the pH was increased to 10, the flux increased to 26.2 $L/m^2 \cdot h$. In the study by Saf et al. [19], ultrafiltration of olive mill wastewater was performed at

Table 4
ANOVA test results for the response functions (permeate flux, COD, and color removal)

| Source | Permeate flux | | COD removal | | Color removal | |
|---|---|---|---|---|---|---|
| | *F*-ratio | *p*-value | *F*-ratio | *p*-value | *F*-ratio | *p*-value |
| Model | 123.47 | <0.0001 | 323.76 | <0.0001 | 4,509.30 | <0.0001 |
| $X_1$ (pH) | 980.37 | <0.0001 | 2,401.43 | <0.0001 | 35,899.21 | <0.0001 |
| $X_2$ (pressure) | 93.64 | 0.0002 | 437.50 | <0.0001 | 1,170.73 | <0.0001 |
| $X_3$ (time) | 7.90 | 0.0376 | 8.93 | 0.0305 | 22.13 | 0.0053 |
| $X_1X_2$ | 7.83 | 0.0381 | 2.86 | 0.1518 | 0.37 | 0.5717 |
| $X_1X_3$ | 0.081 | 0.7876 | 2.86 | 0.1518 | 0.0001 | 1.0000 |
| $X_2X_3$ | 0.00104 | 0.9755 | 0.71 | 0.4366 | 0.37 | 0.5717 |
| $X_1^2$ | 17.89 | 0.0083 | 59.51 | 0.0006 | 3,396.66 | <0.0001 |
| $X_2^2$ | 4.78 | 0.0804 | 0.16 | 0.7015 | 2.40 | 0.01819 |
| $X_3^2$ | 0.28 | 0.6190 | 0.16 | 0.0753 | 10.84 | 0.0216 |
| $R^2$ | 0.9955 | | 0.9983 | | 0.9999 | |
| $R^2$ (adjusted) | 0.9875 | | 0.9952 | | 0.9997 | |

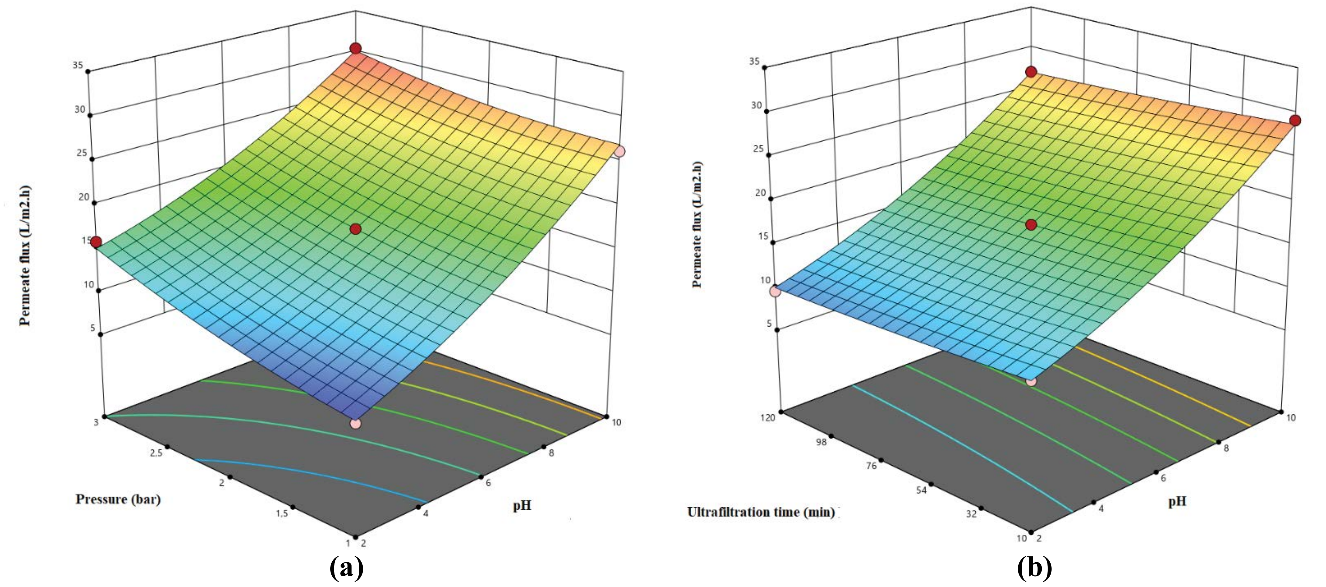


Fig. 3. Variation of permeate flux with (a) pH and pressure at 65 min ultrafiltration time and (b) pH and ultrafiltration time at 2 bar pressure.

pH = 2, 6 and 9 and permeate fluxes of 15, 120, and 130 L/m²·h were measured, and it was observed that the permeate flux increased as pH increased. The results obtained in our study also support this result.

The variation of the permeate flux with pressure at different pH values can also be seen from Fig. 3a. The increased pressure causes more liquid to pass through the membrane surface, thus increasing the permeate flux. While the permeate flux obtained at 1 bar pressure for pH = 10 was 26.2 L/m²·h, the flux value increased to 30.4 L/m²·h when the pressure increased to 3 bar.

The change of permeate flux with ultrafiltration time was also investigated, and the results are given in Fig. 3b. For all pH values studied, the permeate flux does not change much with time. At pH = 10, the flux was 29.2 L/m²·h at 30 min filtration time and 27.3 L/m²·h at 120 min filtration time. The permeate flux values obtained at pH = 2 for the same periods are 11.3 and 9.6 L/m²·h, respectively.

As a result of ultrafiltration experiments to observe the change in permeate flux, the maximum flux was reached at pH = 10 and 3 bar pressure.

### *3.3. Variation of COD removal efficiency*

In the second part of the study, the effects of pH, pressure, and ultrafiltration time on COD removal efficiency were investigated. The variation of COD removal efficiency with pressure and pH is given in Fig. 4a, and its variation with ultrafiltration time and pH is given in Fig. 4b. As seen in Fig. 4a, the COD removal efficiency of the permeate

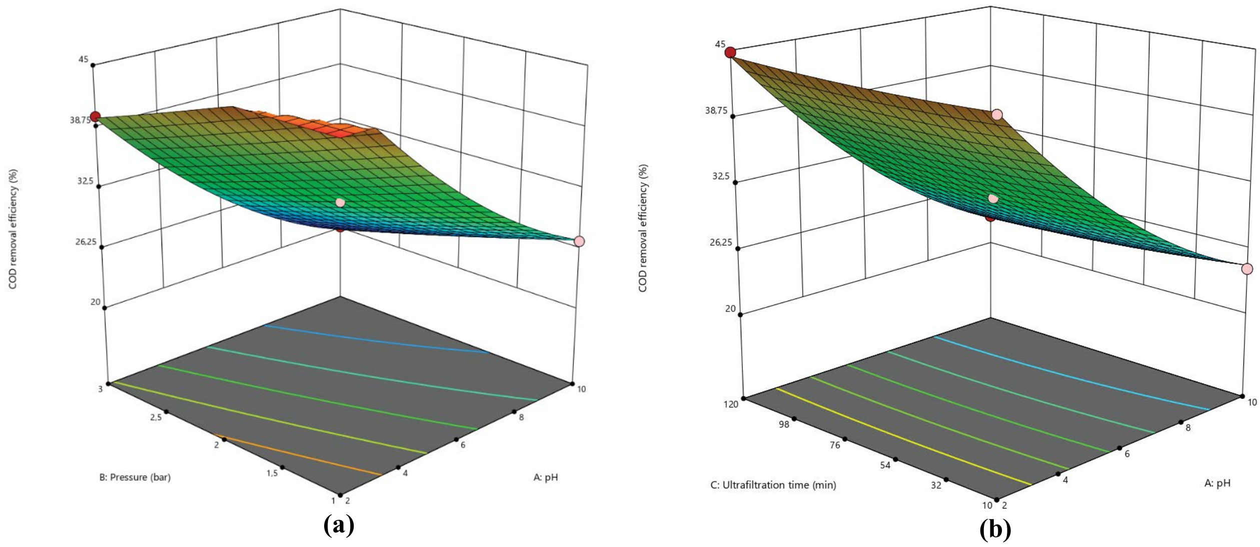


Fig. 4. Variation of chemical oxygen demand removal efficiency with (a) pressure and pH at 65 min ultrafiltration time and (b) ultrafiltration time and pH at 2 bar pressure.

decreases with increasing pH. While the COD removal efficiency obtained at pH = 2 at 65 min ultrafiltration time and 2 bar pressure was 48%, the efficiency obtained at pH = 10 decreased to 39%. El-Abbassi et al. [10] investigated the treatment of olive oil mill wastewater with an ultrafiltration membrane, and it was observed that the COD removal efficiency decreased with increasing pH. The results found in this study also confirm the results of El-Abbassi's study.

In order to evaluate the performance of the membrane, the COD removal efficiencies in the permeate at different pressure values were also examined, and the results are given in Fig. 4a. As can be seen from the figure, the increase in pressure decreases the COD removal efficiency in treated water. This is because at higher pressures, the pressure effect is more dominant than the pore size effect. As a result, more organic compounds pass through the membrane [18]. As the COD concentration in the permeate increases, the COD removal efficiency decreases. Similar results were obtained in this study as well. While the COD removal efficiency obtained at 1 bar pressure was 48% in the experiments performed at pH = 2 and 65 min ultrafiltration time, the efficiency decreased to 39% at 3 bar pressure.

The variation of the COD removal efficiency with ultrafiltration time as a function of pH is given in Fig. 4b. No significant difference in COD removal efficiency was observed during the whole ultrafiltration period. At 2 bar pressure and pH = 2, while the COD removal efficiency obtained at 10 min filtration time was 45%, the efficiency decreased to 44% at 120 min filtration time.

As a result of the experimental studies, the highest COD removal efficiencies are obtained at lower pH and pressure. The maximum COD removal efficiency obtained in this study was found to be 48% at pH = 2 and 1 bar pressure.

### *3.4. Variation of color removal efficiency*

In the last part of the study, the variation of color removal efficiency with pH, pressure, and ultrafiltration time was investigated, and the results are shown in Fig. 5. No significant effect of variations in pressure and ultrafiltration time on color removal efficiency was observed. In Fig. 5a, the color removal efficiency obtained at 1 bar pressure for pH = 2 is 77%, while the efficiency is calculated as 76% at 3 bar pressure. In Fig. 5b, the color removal efficiency remained constant at all ultrafiltration times.

The most important parameter in color removal is pH. The variation of color removal efficiency with pH can be observed from both figures. As the pH increased, the efficiency decreased. While the color removal efficiency was 77% at pH = 2 at 1 bar pressure and 65 min ultrafiltration time, the efficiency decreased to 67% at pH = 10.

In our preliminary experiments with OMW, it was observed that the color of OMW darkened with increasing pH, and OMW turned red at acidic pHs. In the study by El-Abbassi et al. [10], the dark color of OMW increases significantly at pH > 8 and reaches a value twice higher than the initial color. The color increases more than six times when the pH is increased from 4 to 12. Among other natural pigments, tannins and anthocyanins are responsible for OMW color. These pigments are pH-sensitive and change color with varying levels of acidity. At an acidic pH, the pigments show a red color, while in basic conditions, the color becomes black-purple and darker [10].

Ateş et.al. [3] investigated the relationship between pH and color removal efficiency in the oxidation of olive oil mill wastewater and found that high color removal efficiency was achieved in acidic conditions. In this study, the highest color removal efficiency was obtained in the ultrafiltration of olive oil mill wastewater under acidic conditions.

### *3.5. Optimization*

The independent variables for maximum permeate flux, COD, and color removal efficiencies were optimized by Box–Behnken design, which is a response surface method performed with the Design-Expert 13 program used to

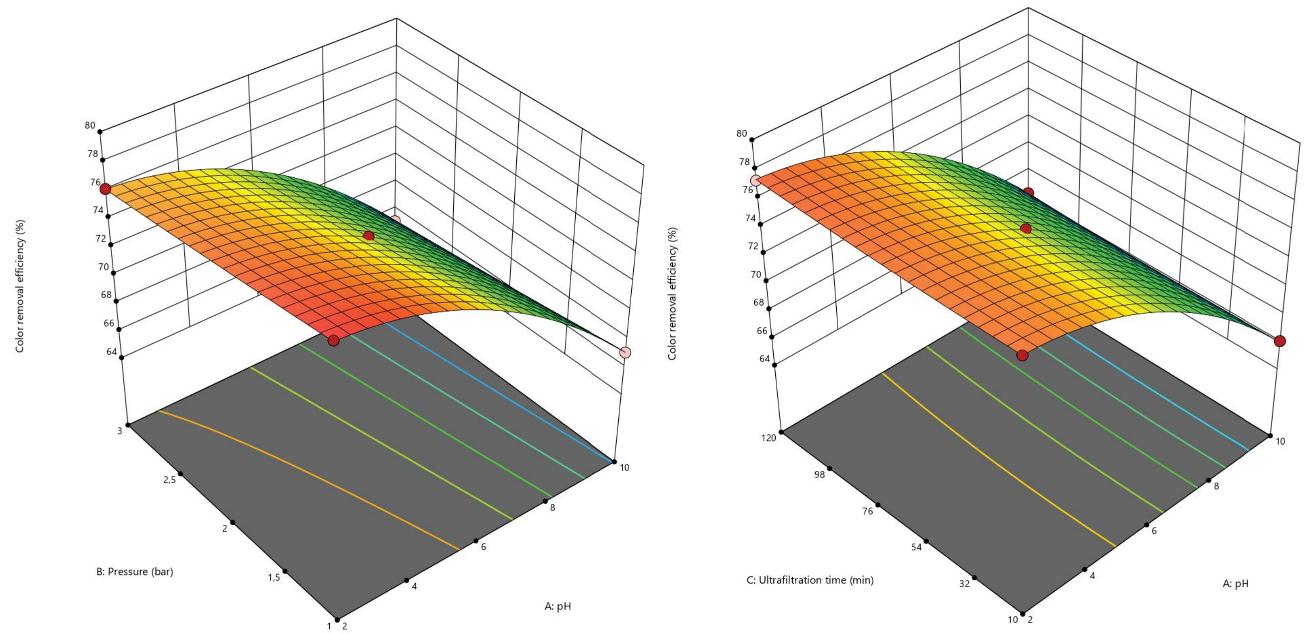


Fig. 5. Variation of color removal efficiency with (a) pressure and pH at 65 min ultrafiltration time and (b) ultrafiltration time and pH at 2 bar pressure.

Table 5
Optimum standards and optimization values for filtrate flux and COD removal

| Optimum standards | | | |
|---|---|---|---|
| | Goal | Lower limit | Upper limit |
| *A*: pH | in range | 2 | 10 |
| *B*: Pressure | in range | 1 | 3 |
| *C*: Time | in range | 10 | 120 |
| Permeate flux | maximum | 7.4 | 30.4 |
| % COD removal efficiency | maximum | 20.1 | 48.5 |
| % Color removal efficiency | maximum | 65.0 | 78.2 |

| Optimum values | | | | | | | |
|---|---|---|---|---|---|---|---|
| Number | pH | Pressure (bar) | Time (min) | Permeate flux (L/m²·h) | COD removal (%) | Color removal (%) | Desirability |
| 1 | 2 | 3 | 10 | 16.1 | 39.8 | 76.2 | 0.905 |

further investigate the ultrafiltration of OMW, and the results are given in Table 5. According to Table 5, the optimum process variables were determined as 2, 3 bar, and 10 min for pH, pressure, and ultrafiltration time, respectively. Under these process conditions, permeate flux was 16.1 L/m$^2$·h and COD removal efficiency was 39.8%, and color removal efficiency was 76.2%. The desirability value calculated by Design-Expert 13 for the Box–Behnken design was 0.905.

Ultrafiltration experiments were carried out considering the optimum parameter values obtained. As a result of three repeated experiments, the average flux was 16.5 L/m$^2$·h, COD removal efficiency was 40%, and color removal efficiency was 75%. According to these results, the results obtained from the Box–Behnken design and experimental study were very close to each other. Therefore, it can be said that they are compatible with one another.

## 4. Conclusions

In this study, the treatability of olive oil mill wastewater with an ultrafiltration membrane was investigated. The effects of operating parameters such as pH, membrane pressure, and ultrafiltration time on permeate flux, COD, and color removal efficiencies were investigated. It has been proven that the Box–Behnken experimental design method gives statistically reliable results for flux, COD, and color removal in the ultrafiltration of OMW. At the end of the analysis of variance, the estimated and calculated $R^2$ values are 0.9955 and 0.9875 for permeate flux, 0.9983 and 0.9952 for COD removal efficiency, and 0.9999 and 0.9997 for color removal efficiency, respectively. The estimates obtained from the response function and the experimental results are in good agreement. This shows that the methodology used is reliable and statistically appropriate.

As a result of the studies, it was seen that the permeate flux increased with increasing pH and pressure, and the ultrafiltration time did not have a significant effect on the permeate flux. The conditions in which the highest permeate flux (30.4 L/m²·h) is obtained are pH = 10 and 3 bar pressure. On the contrary, COD removal efficiency decreases with increasing pH and pressure. The COD removal efficiency obtained at pH = 2 and 1 bar pressure was 48%. The only effective parameter for color removal efficiency was pH. The highest color removal efficiency was obtained at pH = 2 as 77%.

The optimum pH, pressure, and ultrafiltration time determined by the Design-Expert 13 program were 2, 3 bar and 10 min, respectively. Under these conditions, permeate flux was 16.1 L/m²·h, COD removal efficiency was 39.8%, and color removal efficiency was 76.2%.

The COD removal efficiency obtained at the end of the study is 48%, and the effluent COD concentration is as high as 44 g/L. Pretreatment prior to ultrafiltration, followed by further treatment by the ultrafiltration process with ultrafiltration membranes that can be determined by experimental or pilot plant studies, should be considered.

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