



Statistical optimization of process parameters for ultrafiltration of olive oil mill wastewaters

Ezgi Oktav Akdemir*, Adem Ozer

Engineering Faculty, Department of Environmental Engineering, Dokuz Eylul University, Tinaztepe Campus, Buca, Izmir 35160, Turkey

Tel. +90-232-3017129; Fax: +90-232-4531143; email: ezgi.oktav@deu.edu.tr

Received 12 October 2012; Accepted 5 January 2013

ABSTRACT

Ultrafiltration of olive oil mill wastewaters was investigated in this study. The Box–Behnken statistical experiment design and response surface methodology were used to investigate the effects of major operating variables. Flow rate, transmembrane pressure, and operation time were selected as independent variables in Box–Behnken design while chemical oxygen demand (COD) removal and permeate flux were considered as the response function. The predicted values of COD removal and permeate flux obtained using the response function were in good agreement with the experimental data. For the highest COD removal efficiency, the optimum set of flow rate, pressure, and operation time were 100 L/h, 1 bar, and 30 min, respectively, with 86.8% removal efficiency. On the other hand, for the maximum permeate flux, the optimum set was 200 L/h, 3 bar, and 30 min with 32.9 L/m²h flux value.

Keywords: Box–Behnken design; Olive oil mill wastewater; Operating conditions; Pretreatment; Ultrafiltration

1. Introduction

There are more than 800 million productive olive trees worldwide and Mediterranean countries account for around 97% of the world's olive oil cultivation, estimated at about 10,000,000 hectares (ha). The main olive oil producers are Spain (36%), Italy (27%), Greece (15%), Tunisia and Syria (6%), and Turkey (4%) [1].

Olive mill wastewaters (OMWW) are by-products of the olive oil extraction whose production is estimated to be 1.1–1.5 times the weight of milled olives for the three-phase centrifugal olive oil extraction [2]. The composition of OMWW is affected by different parameters such as the oil extraction technology, the kind of olives, and ripeness. The pH of OMWW is in

the range 4.9–5.3 due to the presence of organic acids such as acetic, malic, fumaric, lactic, malonic, citric, tartaric, ossalic, and succinic. Organic substances determine the high polluting load of these wastewaters. Biochemical oxygen demand (BOD₅) and chemical oxygen demand (COD) may be as high as 100 and 200 g/L, respectively. The organic fraction contains sugars, tannins, polyphenols, polyalcohols, pectins, lipids, proteins, and organic acids [3].

In previous works, different kinds of wastewater management methods have been used for OMWW purification, applied either alone or in combination with other techniques. OMWW disposal to uncultivated and agricultural soils, lagooning or natural evaporation, thermal concentration, treatment with lime and clay, physical–chemical treatment, electrocoagulation

*Corresponding author.

process, and Fenton and electro Fenton processes have been reported and in several cases practiced. Membrane processes including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) have been previously used for OMWW purification [4]. Membrane processes have recently become a great topic of research due to their applicability in wastewater treatment. Decreasing costs of installation and operation of membranes favored the use of membrane processes. MF and UF processes are used mainly for primary treatment purposes while NF and RO are used for final treatment. MF and UF are typically applied for the removal of particulate contaminants due to larger pore diameter than NF and RO. In order to prevent the clogging of NF and RO membranes, MF and UF pretreatment will be necessary. Specifically, RO membranes offer so high treatment efficiencies that they are used in a wide range of applications including recovery of materials from industrial wastewaters and treatment of seawater for drinking purposes [5].

In a study, the OMWW was treated efficiently by using UF, NF, and/or RO membranes to obtain a permeate fraction which can be discharged in aquatic systems or to be used for irrigation purpose [6]. In another study, applied membrane processes were preliminary treatment of OMWW by MF, followed by two UF steps realized by using 6 and 1kDa membranes, respectively, and a final RO treatment. The retentate of RO, containing enriched and purified low-molecular weight polyphenols, was proposed for food, pharmaceutical, or cosmetic industries, while MF and UF retentates can be used as fertilizers or in the production of biogas in anaerobic reactors. [7]. In another study, integrated membrane processes were applied to OMWW. First of all, OMWW was pretreated by MF without preliminary centrifugation; this step allowed to achieve a 91 and 26% reduction of suspended solids (SS) and total organic carbon (TOC), respectively. The MF permeate was submitted to an NF treatment. In this step almost all polyphenols were recovered in the permeate stream. A concentrated solution containing 0.5g/L of free low-molecular weight polyphenols was obtained by treating the NF permeate by osmotic distillation [8].

Statistical design of experiments reduces the number of experiments to be performed, considers interactions among the variables, and can be used for optimization of the operating parameters in multivariable systems. Response surface methodology (RSM) is used when only several significant factors are involved in optimization. The main idea of RSM which is an efficient statistical technique for optimization of multiple variables with minimum number of experiments is to use a set of designed experiments to

obtain an optimal response [9–11]. Different types of RSM designs include three-level factorial design, central composite design (CCD), Box–Behnken and D-optimal designs.

Among all the RSM designs, Box–Behnken design requires fewer runs than the others (e.g. 15 runs for a three-parameter experimental design). A three-factor, three-level design would require a total of 30 runs with three repetitions for the central point. In statistical experiment designs, the ratio of the number of experiments to the number of coefficients in the quadratic model should be reasonable. In most of the experimental designs this ratio is within the range of 1.5–2.6 and is 1.67 for the Box–Behnken experiment design (BBD) with three variables. A comparison between the BBD and other response surface designs (central composite, Doehlert matrix, and three-level full factorial design) has demonstrated that the BBD and Doehlert matrix are slightly more efficient than the CCD, but much more efficient than the three-level full factorial designs [12]. By careful design and analysis of experiments, Box–Behnken design allows calculations of the response function at intermediate levels and enables estimation of the system performance at any experimental point within the range studied [13].

In recent years, Box–Behnken design has been successfully tested in the treatment of the industrial wastewaters by electrocoagulation. This study was focused on coupled electrochemical and sedimentation processes by studying the removal of COD, total solid, and turbidity using aluminum as electrode material in batch system. The relationship between the sludge settling velocity and three quantitative variables, i.e. pH, electric current density, and electrolysis time was investigated in the study. They were optimized by Box–Behnken design of surface response analysis to determine the optimum operational conditions for the coupled electrochemical and sedimentation processes, and determine a domain that satisfies the expected specifications [14]. In another study, decolorization of an azo dye, Reactive Yellow 15 (RY 15), by coagulation with chitosan was investigated using Box–Behnken design. Dyestuff concentration (RY 15), chitosan concentration, and settling time were selected as independent variables in Box–Behnken design, while color and TOC removals were considered as the response functions [15].

This study focuses on the investigation of the performance of UF process in the treatment of OMWW. Box–Behnken statistical experiment design approach was used by considering the recycling flow rate, transmembrane pressure, and operation time as independent variables while COD removal efficiency and permeate flux were the objective functions to be

optimized. The optimal conditions maximizing COD removal efficiency and permeate flux were determined.

2. Materials and methods

2.1. Sample collection

Olive oil mill wastewater was taken from a three-phase continuous olive oil mill plant located in Izmir-Turkey. Samples were collected in December from the effluent of the horizontal decanter. Fresh sample was kept in dark at 4 °C.

2.2. Experimental system

The membrane experiments were carried out in a laboratory-scale cross flow membrane system, which was given in detail in our previous article [16]. The membrane system was supplied from Osmonics, which was GE Sepa™ CF2 membrane cell. The concentrate stream was flowed back to feed vessel while permeate stream was being collected separately as shown in Fig. 1. A cartridge filter with 20 µm pore size was used as a prefilter to remove coarse particulates from wastewaters before membrane cell. The ultrafiltration membrane with a molecular weight cutoff of 100 kDa were used in this study. Membrane area was 0.0155 m² for all membrane experiments.

2.3. Analytical methods

COD, TOC, pH, SS, oil and grease measurements were carried out on the influent and effluent samples for the characterization and treatment studies. The raw OMWW is specified as influent and the treated OMWW by UF membrane is specified as effluent sample. COD, SS, oil and grease analyses were carried out according to Standard Methods [17]. DOHRMANN DC-190 High Temperature TOC Analyzer was used

for TOC measurements. The pH measurement was done by using 890 MD pH meter.

3. Results and discussion

3.1. Characterization of olive oil mill wastewater

OMWW sample was taken from three-phase olive oil production plant. The main physicochemical characteristics of the used OMWW were as follows: COD: 92 ± 1.8 g/L; TOC: 37.8 ± 0.7 g/L; SS: 12.21 ± 0.8 g/L; oil and grease: 2.74 ± 0.5 g/L; pH: 4.5 ± 0.2. OMWW has dark brown color and characteristic smell.

3.2. Experimental design and statistical analysis

In this study, Box–Behnken statistical experiment design and the RSM [18] was used to investigate the effects of the three independent variables on the response function and to determine the optimal conditions, maximizing the percent removal of COD and the permeate flux. The optimization procedure involves studying the response of the statistically designed combinations, estimating the coefficients by fitting the experimental data to the response functions, predicting the response of the fitted model, and checking the adequacy of the model [19].

For UF process, three important operating parameters such as flow rate, transmembrane pressure, and operation time were chosen as the independent variables and designated as X_1 , X_2 , and X_3 , respectively. Flow rate (X_1) was changed between 100 and 200 L/h, transmembrane pressure (X_2) varied between 1 and 3 bar, and operation time (X_3) ranged from 30 to 120 min. As presented in Table 1, the experimental design involved three parameters (X_1 , X_2 , and X_3), each at three levels, coded -1, 0, and +1 for low, middle, and high concentrations, respectively.

The dependent variables (or objective functions) were COD removal efficiency (Y_1) and the permeate flux (Y_2). The dependent and independent variable values and the observed results are presented in Table 2. The center point (0, 0, 0) was repeated three

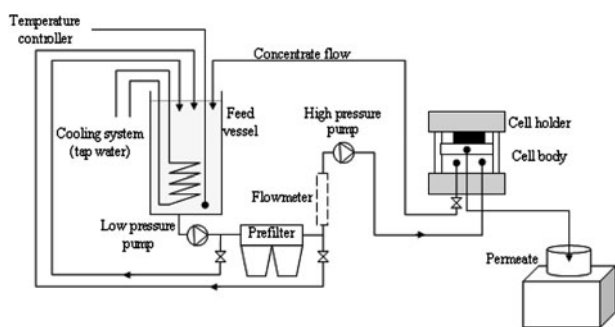


Fig. 1. Schematic flow diagram of the experimental set-up.

Table 1
Levels of each factor for Box–Behnken experimental design

Independent factors	Units	Symbol	Coded levels		
			-1	0	+1
Flow rate	L/h	X_1	100	150	200
Pressure	bar	X_2	1	2	3
Operation time	minute	X_3	30	75	120

Table 2
Results of the Box-Behnken experiments at the predetermined experimental points

Run no.	Actual and coded levels of variables			Experimental results	
	X ₁ flow rate (L/h)	X ₂ pressure (bar)	X ₃ time (minute)	Y ₁ COD removal (%)	Y ₂ flux (L/m ² h)
1	100 (−1)	1 (−1)	75 (0)	83.5	5.5
2	200 (+1)	1 (−1)	75 (0)	63.2	23.1
3	100 (−1)	3 (+1)	75 (0)	61.8	21.9
4	200 (+1)	3 (+1)	75 (0)	74.0	27.6
5	100 (−1)	2 (0)	30 (−1)	74.5	13.8
6	200 (+1)	2 (0)	30 (−1)	45.0	28.8
7	100 (−1)	2 (0)	120 (+1)	77.4	17.3
8	200 (+1)	2 (0)	120 (+1)	79.4	22.7
9	150 (0)	1 (−1)	30 (−1)	64.9	11.1
10	150 (0)	3 (+1)	30 (−1)	58.0	25.8
11	150 (0)	1 (−1)	120 (+1)	82.6	12.1
12	150 (0)	3 (+1)	120 (+1)	78.0	18.7
13	150 (0)	2 (0)	75 (0)	70.0	15.5
14	150 (0)	2 (0)	75 (0)	70.0	15.4
15	150 (0)	2 (0)	75 (0)	69.9	15.5

times and the same results were obtained indicating the reproducibility of the data. Observed and predicted permeate fluxes, and COD removals are given in Table 3 and Fig. 2. The plot of the comparison of observed and predicted values for COD removal efficiency (Y₁) and permeate flux (Y₂) indicated an adequate agreement between real data and the ones obtained from the model.

Table 3
Observed and predicted values for the response functions

Run no.	COD removal efficiency (%)		Permeate flux (L/m ² h)	
	Predicted	Observed	Predicted	Observed
1	81.45	83.50	5.81	5.50
2	62.91	63.20	22.68	23.10
3	62.09	61.80	22.32	21.90
4	76.05	74.00	27.29	27.60
5	74.22	74.50	13.88	13.80
6	42.96	45.00	29.61	28.80
7	79.44	77.40	16.49	17.30
8	79.68	79.40	22.62	22.70
9	67.23	64.90	10.71	11.10
10	57.99	58.00	25.30	25.80
11	82.61	82.60	12.55	12.05
12	75.67	78.00	19.09	18.70
13	69.90	70.00	15.47	15.50
14	70.10	70.00	15.47	15.40
15	69.90	69.90	15.47	15.50

The mathematical relationship between the response function (Y) and the independent variables (X) can be approximated by a quadratic polynomial equation as follows:

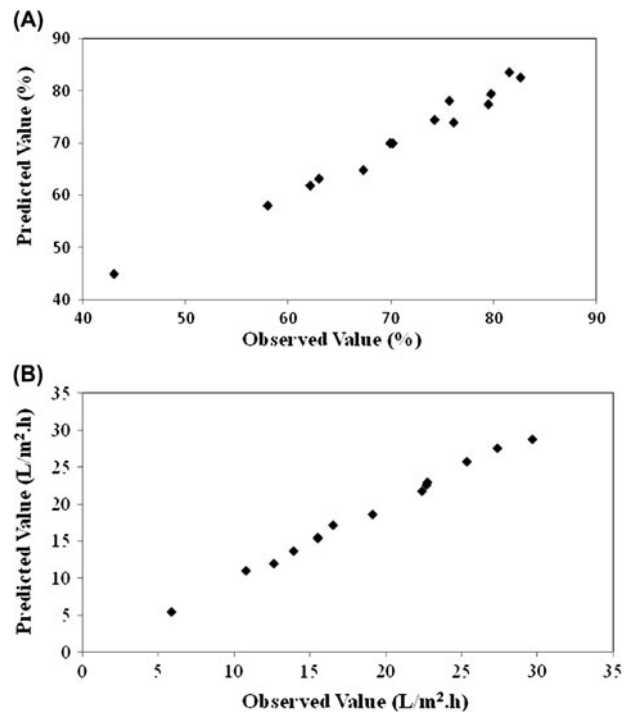


Fig. 2. Observed and predicted values for the response functions (a) COD removal efficiency and (b) permeate flux.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \tag{1}$$

where Y is the predicted response surface function (percent COD removal or permeate flux), b_0 is the model constant, b_1 – b_3 are linear coefficients, b_{12} , b_{13} , and b_{23} are the cross product coefficients, and b_{11} , b_{22} , and b_{33} are the quadratic coefficients.

The coefficients of the response functions for different dependent variables were determined correlating the experimental data with the response functions by using a Stat-Ease Design Expert 7.0 regression program. The response functions for percent COD removal (Y_1) and permeate flux (Y_2) have the following forms:

$$Y_1 = 170.84667 - 0.73483X_1 - 28.13333X_2 - 0.48111X_3 + 0.16250X_1X_2 + 0.004611X_1X_3 + 0.012778X_2X_3 - 7.083 \times 10^{-5}X_1^2 + 1.667 \times 10^{-5}X_2^2 - 2.480 \times 10^{-3}X_3^2 \tag{2}$$

$$Y_2 = -6.92523 - 0.15950X_1 + 16.91875X_2 + 0.12992X_3 - 0.059500X_1X_2 - 0.00106667X_1X_3 - 0.044722X_2X_3 + 0.00155917X_1^2 + 0.16042X_2^2 + 0.0006348X_3^2 \tag{3}$$

The results of analysis of variance (ANOVA) for percent COD removal and permeate flux are presented in Tables 4 and 5 indicating the fact that the

predictability of the model is at 95% confidence interval. Response function predictions are in good agreement with the experimental data with a coefficient of determination (R^2) of larger than 0.98. The model F value and very low probability value (0.0001) indicated that the model was statistically significant and model equation can adequately be used to describe the COD removal and permeate flux under a wide range of operating conditions. The p -values are used to estimate whether F is large enough to indicate statistical significance and used to check the significance of each coefficient. p -values less than 0.05 indicate the model terms are significant. Flow rate, transmembrane pressure, and operation time had significant effects on COD removal and permeate flux. The parameters X_1 , X_2 , X_3 , X_{12} , X_{13} , and X_3^2 were determined to be significant model terms with p -values less than 0.05 for COD removal. The ANOVA test results for permeate flux indicated that the variables X_1 , X_2 , X_3 , X_{12} , X_{13} , X_{23} , X_1^2 , and X_3^2 were significant model terms with p -values less than 0.05.

3.3. Variation of COD removal

Response functions with determined coefficients were used to estimate variations of response functions with the independent variables under different conditions. Fig. 3 shows the effect of feed flow rate on percent COD removal at different operation time at 1.5bar pressure. Experimental data for different pressures (1, 2, 2.5, 3 bar) were obtained and plotted in the similar way. COD removal efficiency increased with decreasing feed flow rate. It is because of the

Table 4
ANOVA test for the response function Y_1 (% COD removal)

Source	Sum of squares	d.f.	Mean square	F ratio	P value
Model	1743.713	9	290.6188	85.33545	<0.0001
X_1 (flow rate)	81.92	1	81.92	24.05447	0.0012
X_2 (pressure)	62.72	1	62.72	18.4167	0.0026
X_3 (time)	903.125	1	903.125	265.1879	<0.0001
X_1X_2	264.0625	1	264.0625	77.53764	<0.0001
X_1X_3	430.5625	1	430.5625	126.4276	<0.0001
X_2X_3	1.3225	1	1.3225	0.388331	0.5505
X_1^2	1.08	1	1.08	5.91	0.0593
X_2^2	0.01	1	0.01	0.00	0.9562
X_3^2	2.31	1	2.31	12.62	0.0163
Residual	27.24483	5	3.405604		
Lack of fit	27.23817	3	4.539694	1361.908	0.0007
Pure error	0.006667	2	0.003333		
Total (corr)	1774.357	14			

Note: R -squared = 0.9846, R -squared (adjusted for d.f.) = 0.9731.

Table 5
ANOVA test for the response function Y_2 (Permeate flux)

Source	Sum of squares	d.f.	Mean square	F ratio	P value
Model	605.9298	9	67.32553	126.6212	<0.0001
X_1 (flow rate)	238.7113	1	238.7113	448.9515	<0.0001
X_2 (pressure)	223.1328	1	223.1328	419.6527	<0.0001
X_3 (time)	9.570313	1	9.570313	17.99918	0.0081
X_1X_2	35.4025	1	35.4025	66.58256	0.0004
X_1X_3	23.04	1	23.04	43.33203	0.0012
X_2X_3	16.20063	1	16.20063	30.46901	0.0027
X_1^2	56.10,002	1	56.10002	105.509	0.0002
X_2^2	0.095016	1	0.095016	0.1787	0.6901
X_3^2	6.100785	1	6.100785	11.47393	0.0195
Residual	2.658542	5	0.531708		
Lack of fit	2.651875	3	0.883958	265.1875	0.0038
Pure error	0.006667	2	0.003333		
Total (corr)	608.5883	14			

Note: R -squared = 0.9956, R -squared (adjusted for d.f.) = 0.9878.

turbulence due to increasing cross flow velocity or feed flow rate. Increasing turbulence reduces the membrane fouling. Lower fouling increases the permeate flux through the membrane and decreases the retention coefficients [16,20]. However, operation time is not effective operating parameter for percent COD removal. Maximum COD removal efficiency was obtained as 78.8% at 100 L/h flow rate for all operation time. Minimum efficiency was 41.4% at 200 L/h flow rate and 30 min operation time.

Variations of COD removal efficiency with time as a function of pressure at 125 L/h flow rate are given in Fig. 4. As expected, COD removal efficiency decreased with increasing pressure. Because, deposited organic matter in the fouling layer is scoured and carried at higher pressures, the captured material is carried into permeate and therefore, COD concentration of permeate increases [21]. COD removal efficiencies for 1 bar pressure are 73.3 and 83.0% for 30 and

120 min; for 3 bar pressure, 58.4 and 70.4% for 30 and 120 min operation time, respectively.

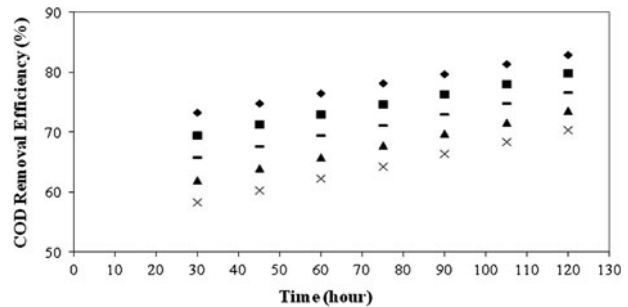


Fig. 4. Variation of COD removal efficiency with time as a function of pressure at 125 L/h flow rate, \blacklozenge = 1 bar, \blacksquare = 1.5 bar, $-$ = 2 bar, \blacktriangle = 2.5 bar, \times = 3 bar.

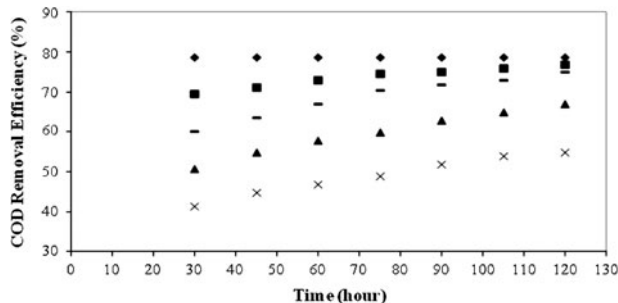


Fig. 3. Variation of COD removal efficiency with time as a function of feed flow rate at 1.5 bar pressure, \blacklozenge = 100 L/h, \blacksquare = 125 L/h, $-$ = 150 L/h, \blacktriangle = 175 L/h, \times = 200 L/h.

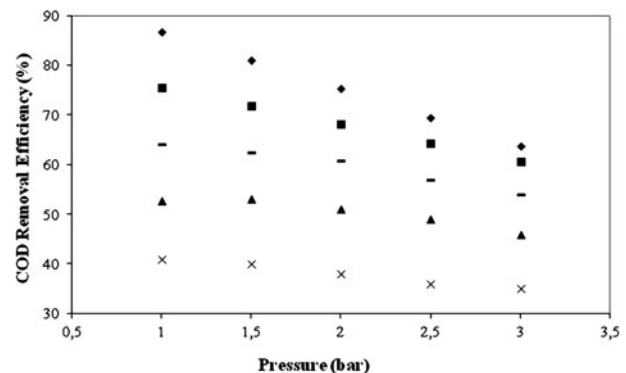


Fig. 5. Variation of COD removal efficiency with pressure as a function of flow rate at 30 min operation time, \blacklozenge = 100 L/h, \blacksquare = 125 L/h, $-$ = 150 L/h, \blacktriangle = 175 L/h, \times = 200 L/h.

Fig. 5 depicts the variation of COD removal efficiency with pressure as a function of flow rate at 30 min operation time. The same pattern was observed for 60, 75, 90, 105, and 120 min operation time. Increasing flow rate and pressure resulted in the decrease of COD removal efficiency. So, maximum COD removal efficiency was achieved at 100 L/h flow rate and 1 bar pressure as 86.8%.

3.4. Variation of permeate flux

In order to determine the effect of flow rate, transmembrane pressure, and operation time on permeate flux, some experiments were carried out. Variation of permeate flux with operation time at different flow rates and at constant pressure of 1.5 bar is shown in Fig. 6. Permeate flux increased with increasing feed flow rate and cross-flow velocity. Increase in cross-flow velocity results in an increase in the forced convection of the solutes enhancing the solute transport from the membrane surface to the bulk feed. This reduces the concentration polarization and increases the permeate flux [22]. Maximum permeate values were obtained at flow rate of 200 L/h as 26.8 L/m²h for 1.5 bar pressure.

Changes in permeate flux of OMWW with operation time reflect the dynamics of development of flux resistances, including membrane fouling and concentration polarization [23]. Maximum flux decline was observed for 200 L/h flow rate. In this case, initial permeate flux was 27 L/m²h and it reached a steady-state value of about 18 L/m²h after 105 min operation time. The same condition was observed for 150 and 175 L/h flow rates. The permeate flux did not reduce drastically for lower flow rates (e.g. 100 and 125 L/h). For 100 L/h flow rate, initial and final permeate flux values were 8 and 7 L/m²h, respectively.

The effect of pressure on the permeate flux as a function of time at 125 L/h flow rate is given in Fig. 7.

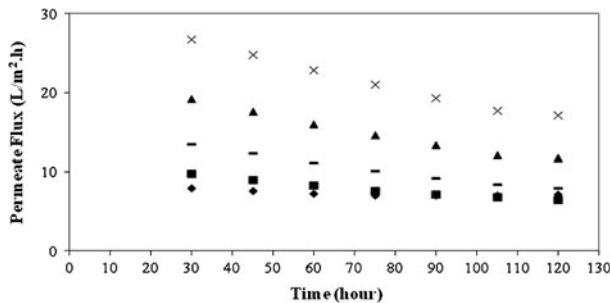


Fig. 6. Variation of permeate flux with time as a function of feed flow rate at 1.5 bar pressure, ◆ = 100 L/h, ■ = 125 L/h, – = 150 L/h, ▲ = 175 L/h, x = 200 L/h.

In general, increasing the applied pressures leads to an increase in the permeate flux values. This effect could be explained by Darcy’s law. So, increasing pressure gradient increases permeate flux. An increase in applied pressure could also be attributed to membrane fouling [21,24]. However, the permeate flux did not reduce drastically with the operation period in our study. Therefore, it can be thought that, membrane fouling is not too important for this flow rate and OMWW used in the experiments.

Fig. 8 depicts the variations of permeate flux with pressure at different flow rates and constant operation time of 60 min. As it can be seen from the figure, the permeate flux increases with the increasing transmembrane pressure up to 2 bar. At the pressure of 2.5 and 3 bar, almost a constant value of flux is reached. This is because of the formation of cake layer on the membrane surface, which accelerates the membrane fouling [25]. This cake layer is one of the main causes that promote the fouling of membranes. At optimum pressure, permeation flux must be high and tendency to cake layer formation should be low. Therefore, pressures less than 2 bars can be selected.

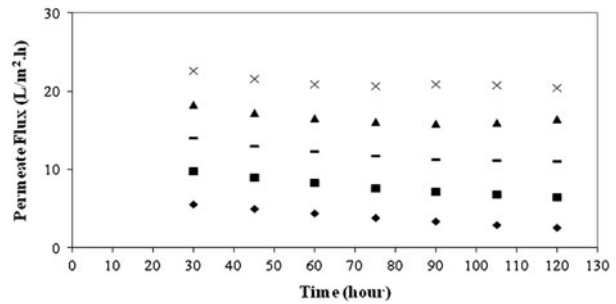


Fig. 7. Variation of permeate flux with time as a function of pressure at 125 L/h flow rate, ◆ = 1 bar, ■ = 1.5 bar, – = 2 bar, ▲ = 2.5 bar, x = 3 bar.

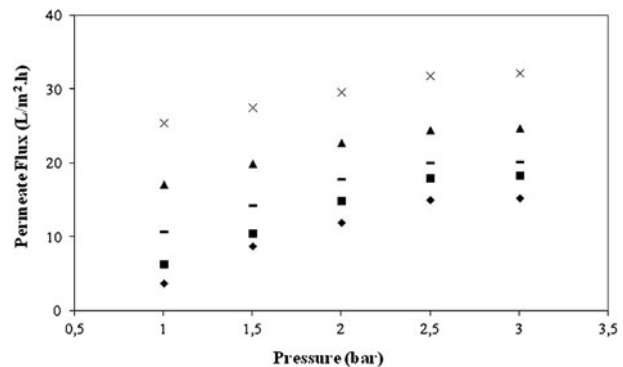


Fig. 8. Variation of permeate flux with pressure as a function of flow rate at 60 min operation time, ◆ = 100 L/h, ■ = 125 L/h, – = 150 L/h, ▲ = 175 L/h, x = 200 L/h.

Table 6

Optimum flow rate, transmembrane pressure, and operation time for the highest COD removal and permeate flux

Response	Flow rate, X_1 (L/h)	Pressure, X_2 (bar)	Time, X_3 (min)	Value
COD removal (%)	100	1	30	86.8
Permeate flux (L/m ² h)	200	3	30	32.9

Table 7

Treatment results of UF process for optimal conditions

Parameter	Raw OMWW	After treatment	Removal efficiency (%)
COD (g/L)	92.0	12.14	86.8
TOC (g/L)	37.8	5.44	85.6
SS (g/L)	12.21	0.26	97.9
Oil and grease (g/L)	2.74	0.36	87.0

Optimal flow rate, transmembrane pressure, and operation time resulting in the highest COD removal and permeate flux were determined by using an optimization program and the results are presented in Table 6. COD removal required lower flow rate and pressure when compared to maximizing permeate flux. The optimum flow rate and pressure were found to be 100 L/h and 1 bar for percent COD removal and 200 L/h and 3 bar and for permeate flux, respectively. In all cases, operation time should be 30 min. For safer operations, avoiding membrane fouling and obtaining higher COD removal efficiency, 100 L/h flow rate, and 1 bar pressure are optimum values for UF of OMWW.

Treatment results of UF process for optimal conditions are given in Table 7. Maximum removal efficiency was achieved for SS removal. However, the major pollutant for OMWW is COD and within the scope of many studies, COD removal efficiency was given to show treatability. So, optimal condition for COD removal was investigated in this study.

A 86.8% COD removal efficiency was achieved by UF process. In a study using electrocoagulation, 52% COD removal was observed as maximal efficiency under pH 6 and 30 min retention time for OMWW [26]. The effective performance of electrocoagulation technique in the treatment of OMWW was investigated in another study using sacrificial aluminum electrodes. The optimum working pH was found to be 4–6 and maximum COD removal efficiency was 76% [27]. In another study using Fenton oxidation with zero-valent iron and hydrogen peroxide, 78% COD removal was observed under initial pH 4.8, 5% H₂O₂ solution, 20 g/L Fe⁰ concentration, and 24 h reaction time [28]. These results show that, UF gives more satisfactory results than electrocoagulation and Fenton oxidation.

4. Conclusions

Box–Behnken statistical experiment design and the RSM were proven to yield statistically reliable results for UF of OMWW. Predictions obtained from the response functions were in good agreement with the experimental results indicating the reliability of the methodology used. The RSM also provided a better understanding for the roles of flow rate, transmembrane pressure, and operation time on UF of OMWW for the highest COD removal and permeate flux.

The optimum flow rate, pressure, and operation time were found to be 100 L/h, 1 bar, and 30 min, respectively, for percent COD removal. In this case, 86.8% removal was obtained. As a contrast, the optimum flow rate, pressure, and operation time were 200 L/h, 3 bar, and 30 min for permeate flux, respectively. However, for safer operations, avoiding membrane fouling and obtaining higher COD removal efficiency, 100 L/h flow rate, 1 bar pressure, and 30 min operation time are optimum values for UF of OMWW.

References

- [1] S.E. Yay, H.V. Oral, T.T. Onay, O. Yenigün, A study on olive oil mill wastewater management in Turkey: A questionnaire and experimental approach, *Resour. Conserv. Recy.* 60 (2012) 64–71.
- [2] C.S. Parinos, C.D. Stalikas, T.S. Giannopoulos, G.A. Pilidis, Chemical and physicochemical profile of wastewaters produced from the different stages of Spanish-style green olives processing, *J. Hazard. Mater.* 145 (2007) 339–343.
- [3] A. Cassano, C. Conidi, E. Drioli, Comparison of the performance of UF membranes in olive mill wastewaters treatment, *Water Res.* 45 (2011) 3197–3204.
- [4] A. Zirehpour, M. Jahanshahi, A. Rahimpour, Unique membrane process integration for olive oil mill wastewater purification, *Sep. Purif. Technol.* 96 (2012) 124–131.

- [5] T. Coskun, E. Debik, N.M. Demir, Treatment of olive mill wastewaters by nanofiltration and reverse osmosis membranes, *Desalination* 259 (2010) 65–70.
- [6] C.A. Paraskeva, V.G. Papadakis, E. Tsarouchi, D.G. Kanellopoulou, P.G. Koutsoukos, Membrane processing for olive mill wastewater fractionation, *Desalination* 213 (2007) 218–229.
- [7] C. Russo, A new membrane process for the selective fractionation and total recovery of polyphenols, water and organic substances from vegetation waters (VW), *J. Membrane Sci.* 288 (2007) 239–246.
- [8] E. Garcia-Castello, A. Cassano, A. Criscuoli, C. Conidi, E. Drioli, Recovery and concentration of polyphenols from olive mill wastewaters by integrated membrane system, *Water Res.* 44 (2010) 3883–3892.
- [9] F. Francis, A. Sabu, K.M. Nampoothiri, S. Ramachandran, S. Ghosh, G. Szakacs, A. Pandey, Use of response surface methodology for optimizing process parameters for the production of α -amylase by *Aspergillus oryzae*, *Biochem. Eng. J.* 15 (2003) 107–115.
- [10] S.H. Krishna, B. Manohar, S. Divakar, S.G. Prapulla, N.G. Karanth, Optimization of isoamyl acetate production by using immobilized lipase from *Mucor miehei* by response surface methodology, *Enzyme Microb. Technol.* 26 (2000) 131–136.
- [11] A. Vohra, T. Satyanarayana, Statistical optimization of medium components by response surface methodology to enhance phytase production by *Pichia anomala*, *Process Biochem.* 37 (2002) 999–1004.
- [12] S.L.C. Ferreira, R.E. Bruns, H.S. Ferreira, G.D. Matos, J.M. David, G.C. Brando, E.G.P. da Silva, L.A. Portugal, P.S. dos Reis, A.S. Souza, W.N.L. dos Santos, Box–Behnken design: An alternative for the optimization of analytical methods, *Anal. Chim. Acta* 597(2) (2007) 179–186.
- [13] E. Hamed, A. Sakr, Application of multiple response optimization technique to extended release formulations design, *J. Control Release* 73 (2001) 329–338.
- [14] S. Zodi, O. Potier, F. Lapique, J.P. Leclerc, Treatment of the industrial wastewaters by electrocoagulation: Optimization of coupled electrochemical and sedimentation processes, *Desalination* 261 (2010) 186–190.
- [15] E.O. Akdemir, A statistical experiment design approach for decolorization of textile dyestuff by coagulation with chitosan, *Fresen. Environ. Bull.* 21 (2012) 1461–1467.
- [16] E.O. Akdemir, A. Ozer, Investigation of two ultrafiltration membranes for treatment of olive mill wastewaters, *Desalination* 49 (2009) 660–666.
- [17] A.E. Greenberg, L.S. Clesceri, A.D. Eaton, Standard methods for the examination of water and wastewater, 16th ed., APHA/AWWA/WEF, Washington, DC, 1992.
- [18] R.H. Charles, V.T. Kenneth, *Fundamental concepts in the design of experiments*, University Press, Oxford, 1999.
- [19] E.C. Catalkaya, F. Kargi, Effects of operating parameters on advanced oxidation of diuron by the Fenton's reagent: A statistical design approach, *Chemosphere* 69 (2007) 485–492.
- [20] F.J. Benitez, J.L. Acero, A.I. Leal, Application of microfiltration and ultrafiltration processes on cork processing wastewaters and assessment of the membrane fouling, *Sep. Purif. Technol.* 50 (2006) 354–364.
- [21] E.O. Akdemir, A. Ozer, Application of a statistical technique for olive oil mill wastewater treatment using ultrafiltration process, *Sep. Purif. Technol.* 62 (2008) 222–227.
- [22] K. Auddy, S. De, S. DasGupta, Flux enhancement in nanofiltration of dye solution using turbulent promoters, *Sep. Purif. Technol.* 40 (2004) 31–39.
- [23] E.V. Tsagaraki, H.N. Lazarides, Fouling analysis and performance of tubular ultrafiltration on pretreated olive mill wastewater, *Food Bioprocess Technol.* 5 (2012) 584–592.
- [24] T. Mohammadi, A. Esmaelifar, Wastewater treatment using ultrafiltration at a vegetable oil factory, *Desalination* 166 (2004) 329–337.
- [25] B. Koltuniewicz, W. Field, Process factor during removal of oil-in-water emulsion with cross-flow microfiltration, *Desalination* 105 (1996) 79–89.
- [26] H. Inan, A. Dimoglo, H. Simsek, M. Karpuzcu, Olive oil mill wastewater treatment by means of electro-coagulation, *Sep. Purif. Technol.* 36 (2004) 23–31.
- [27] N. Adhoum, L. Monser, Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation, *Chem. Eng. Process.* 43(10) (2004) 1281–1287.
- [28] M. Kallel, C. Belaid, R. Boussahel, M. Ksibi, A. Montiel, B. Elleuch, Olive mill wastewater degradation by Fenton oxidation with zero-valent iron and hydrogen peroxide, *J. Hazard. Mater.* 163 (2009) 550–554.