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Pretreatment of olive mill wastewater by ultrafiltration process using chitosan

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ABSTRACT

This paper presents pretreatment experiments of olive mill wastewater with ultrafiltration process using chitosan. The optimization of major process variables, such as chitosan concentration, transmembrane pressure, and operation time, on permeate flux and chemical oxygen demand (COD) removal efficiency was investigated. To find the most appropriate result for the experiment, the Box–Wilson experimental design was employed. The predicted values of permeate flux and COD removal efficiency obtained using the response function were in good agreement with the experimental data. The optimum set of chitosan concentration and pressure for permeate flux were 100 mg/L and 2 bar, respectively, with 42 L/m^2 h flux value at 80 min operation time. On the other hand, optimum set was 500 mg/L and 1 bar for COD removal with 80.3% COD removal efficiency at the same operation time.

Keywords: Box–Wilson experimental design; Chitosan; COD removal; Olive mill wastewater; Permeate flux; Ultrafiltration

1. Introduction

Olive and olive oil production is one of the most important agricultural activities in the Mediterranean countries. These activities have an important place in economy of these countries [1].The most important pollutant source that is released during the production of olive oil is the olive mill wastewater (OMW) that is turned into a liquid by-product. Olive oil has an exceptional nutritional value. However, OMW, which is produced in high quantities during the production of olive oil, affects the environment negatively. Approximately 30,000,000 m^3 of OMW is produced annually in the Mediterranean region [2], and around 1,000,000 m^3 of this quantity is produced in Turkey [3].Very high pollutant loads also occur due to the high amount of OMW released. Particularly, Mediterranean countries face very serious environmental problems in the management of OMW.

The chemical structure of OMW varies depending on a wide variety of factors. These factors can be listed as tree age, cultivation system, fruit maturity level, olive type, geographical and climatic conditions, type of oil extraction process applied, use of pesticides and fertilizers, etc. [4]. OMW is characterized by dark brown color, characteristic unpleasant odor, low pH, a high suspended solid (SS) content, high turbidity, and high organic load [5]. OMW contains phenolic compounds, polysaccharides, sugars, proteins, lipids, tannins, pectin, and organic acids, which are generally resistant to biodegradation. The abovementioned persistent organic substances can cause adverse effects on the environment. These effects can be listed as bad smells, threats to aquatic life, soil saturation, changes in soil quality, color change in natural waters, eutrophication of surface waters, pollution in superficial and groundwater, and toxicity [6,7].

In previous works, different kinds of wastewater management methods have been used for OMW purification, applied either alone or in combination with other techniques, such as treatment with clay [8] and with lime [9], physicochemical processes including coagulation-flocculation [10,11], electrocoagulation [12], advanced oxidation processes comprising ozonation [6], Fenton's reaction [13], photocatalysis [14], electrochemical treatments [15], lagoons

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or natural evaporation and thermal concentration [16,17], and composting [18].

Membrane processes have also been examined for the purification of OMW. Several authors have proposed different membrane processes for OMW treatment. Paraskeva et al. examined a treatment sequence consisting in screening with 80 μm polypropylene filter followed by ultrafiltration (UF) and nanofiltration (NF) or reverse osmosis (RO) membrane. They obtained 90% lipid and 50% phenol separation with UF process. They stated that effluent from these processes are suitable for irrigation or aquatic receptors [19]. Coskun et al. proposed centrifugation as pretreatment of OMW previously before UF followed by NF. The maximum chemical oxygen demand (COD) removal efficiencies obtained ranged from 59.4% to 79.2% for NF membranes, whereas 96.2% to 96.3% for RO membranes [20]. Zirehpour et al. studied microfiltration-UF-RO system for irrigation purposes of OMW. Obtained permeate fluxes were 34.2 L/m^2 h for UF and 9.4 L/m^2 h for NF with 98.8% COD removal efficiency in whole integrated system [21]. Almeida et al. (2018) investigated the performance of an integrated membrane system for the treatment and valorization of OMW. They first processed a UF pilot unit after pretreatment by screening. Under optimal conditions (TMP = 1.5 bar and T = 20°C), 20.6% and 26.8% for COD and total phenolic content (TPh) removal were achieved, respectively. The permeate from UF was then treated by NF in order to obtain a retentate enriched in phenolic compounds. The best conditions that maximize the COD abatement (83.3%) and TPh removal (93.1%) were found as ΔP = 18 bar, T = 20°C, and a pH of 2.7 [22].

There is very little work done on pretreatment of the OMW with chitosan. Rizzo et al. worked the combined pretreatment of OMW by coagulation with chitosan and then the Fenton and photo-Fenton processes. The chitosan used in their study ranged from 100 to 600 mg/L. The optimum removal (81%) of total SSs by chitosan coagulation was achieved for 400 mg/L chitosan dose. They did not research COD removal efficiency by chitosan coagulation [1]. In another study, the pretreatment of both winery wastewater (WW) and OMW by coagulation using chitosan was investigated. The efficiency of the chitosan coagulation was found to be high in terms of total SS (81% and 80% for OMW and WW, respectively) and turbidity (94% and 92% for OMW and WW, respectively) removal for both wastewaters, but a notable difference was observed in terms of organic matter removal (32% and 73% in terms of COD for OMW and WW, respectively) for 400 mg/L chitosan dose [23].

According to the above-discussed OMW characteristics and potential related treatment processes, the aim of the present work was to investigate the treatment of OMW by UF membrane. Chitosan was used to increase the efficiency of the UF process. To the best of our knowledge, this is the first study that is used together with chitosan and membrane in the pretreatment of OMW. Box–Wilson statistical experimental design approach was used by considering the chitosan concentration, transmembrane pressure, and operation time as independent variables while were the objective functions to be optimized. The optimal conditions maximizing permeate flux and COD removal efficiency were determined in the content of this work.

2. Materials and Methods

2.1. OMW sample

Olive oil mill wastewater sample was obtained from a 3-phase continuous olive oil mill plant located in Izmir (Turkey). Sample was collected in December from the effluent of the horizontal decanter. Fresh sample was kept in dark at 4°C.

2.2. Chitosan

Chitosan was taken from Sigma-Aldrich, USA (product number of 419419) with high molecular weight, and the chemical structure of chitosan is depicted in Fig. 1. During membrane experiments, chitosan at the determined doses was weighed and added to the feed vessel.

2.3. Experimental system

The membrane experiments were carried out in a laboratory-scale cross-flow membrane system, which was given in detail in our previous articles [25]. The membrane system was supplied from Osmonics, USA, which was GE SepaTM CF2 membrane cell. The concentrate stream was sent back to feed vessel, whereas permeate stream was being collected separately as shown in Fig. 2. A heat exchanger in the feed vessel was used in all filtration experiments to keep the temperature at 22°C–24°C. A cartridge filter with 20 μm pore size was used as a prefilter to remove coarse particulates from wastewaters before membrane cell. The ultrafilic MW membrane with a molecular weight cutoff of 100,000 Da was used in this study. Membrane area was 0.0155 m^2 for all membrane experiments.

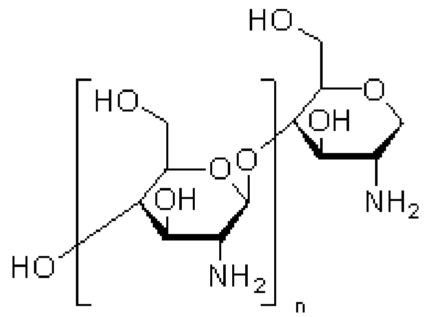

Fig. 1. Chemical structure of chitosan [24].

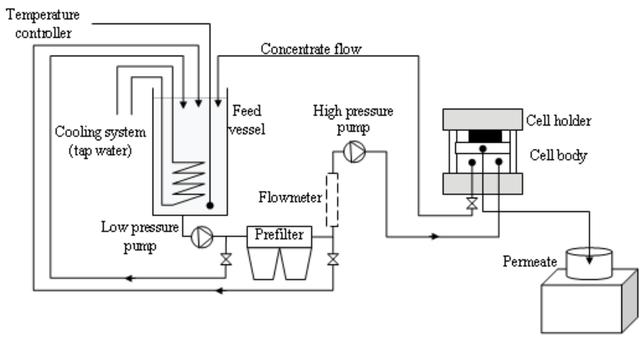

Fig. 2. Schematic flow diagram of the experimental setup.

2.4. Analytical methods

COD, total organic carbon (TOC), pH, SS, oil, and grease measurements were carried out on the influent and COD measurement was done on the effluent samples for the characterization and treatment studies. COD, SS, oil, and grease analyses were carried out according to Standard Methods [26]. Dohrmann DC-190 High-Temperature TOC Analyzer was used for TOC measurements. pH measurement was done by using 890 MD pH meter.

2.5. Experimental design and statistical analysis

The efficiency of UF process on OMW treatment was determined by the Box–Wilson statistical experimental design. This method was used to investigate the effects of the three independent variables (chitosan concentration, transmembrane pressure, and operation time) on the response functions (permeate flux and COD removal efficiency) and to determine the optimal conditions maximizing the percent COD removal and permeate flux in the UF process.

In the experimental procedure, chitosan concentration (X_1), transmembrane pressure (X_2), and operation time (X_3) were chosen as independent variables. Chitosan concentration (X_1) was changed between 100 and 500 mg/L, transmembrane pressure (X_2) varied between 1 and 2 bar, and operation time (X_3) was changed between 30 and 120 min. For all experiments, flow rate was taken as 200 l/h. Permeate flux and COD removal efficiency were considered as dependent variables in the Box–Wilson statistical design method.

The design principle includes three types of combinations: the axial (*A*), factorial (*F*), and center (*C*) points. The axial points include each variable at its extreme levels coded as $-k$ and $+k$ with the others at their center point levels. The factorial points, with two levels of each of the factors coded as −1 and +1, include all combinations of intermediate levels. The center point, coded as 0, is a single test at the average level of each variable. The coded values for the operating levels of the variables are used for convenience. Table 1 shows the coded values for the operating levels of the variables in Box–Wilson statistical experimental design in UF process, where k is defined as minimum ($-k$) and maximum ($+k$) values for each variable, central (0) = range/2 is defined for each variable, and intermediate values are defined as central ± range/2t, where t is equal to $\sqrt{p}$ (p = number of variables). The experimental conditions determined by the Box–Wilson statistical design method for the UF of OMW are presented in Table 2. The experiments consisted of six axial (*A*), eight factorial (*F*), and three center points (*C*) totaling 17 experiments. Computation was carried out by using the multiple regression analysis with the least squares method.

The predicted permeate flux and COD removal efficiency were correlated with the other independent parameters: chitosan concentration (X_1), transmembrane pressure (X_2), and operation time (X_3) using Eq. (1).

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

The Statistica 5.0 computer program was employed for the determination of the coefficients of Eq. (1) by regression analysis of the experimental data, where Y is predicted yield; b_0 is constant; b_1, b_2, and b_3 are linear coefficients; b_{12}, b_{13}, and b_{23} are cross-product coefficients; and b_{11}, b_{22}, and b_{33} are quadratic coefficients.

3. Results and Discussion

3.1. Characterization of OMW

OMW sample was taken from 3-phase olive oil production plant. The main physicochemical characteristics of the used OMW were given in Table 3. OMW has dark brown color and characteristic smell.

3.2. Box–Wilson experimental design method results

Experimental results found in this study were used to determine the coefficients of the response function [Eq. (1)] using a statistical regression analysis program "Statistica". The calculated coefficients are listed in Table 4, and they were used to calculate the predicted values of permeate flux and COD removal efficiency.

The factors in front of the model terms indicate the intensity and direction of the influence of the independent variable. A positive effect of a factor means that the response is improved when the factor level increases, and a negative effect of the factor reveal that the response is inhibited when the factor level increases. On the basis of the coefficients given in Table 4, the variable of pressure (X_2) exhibited the positive influence on permeate flux. The negative effect of chitosan concentration (X_1) and operation time (X_3) is also shown in this table. If COD removal efficiency is to be investigated, the COD removal efficiency increase with decreasing pressure and increasing chitosan concentration and operation time.

The permeate fluxes and COD removal efficiencies obtained from the experiments are summarized in Table 5. The observed permeate fluxes varied between 5.42 and 14.26 L/m^2 h,

Table 1
The coded values for the operating levels of the variables in Box–Wilson statistical experimental design

Variable	Symbol	Coded variable level				
		Maximum (+*k*)	Minimum (−*k*)	Central (0)	Intermediate-a (+1)	Intermediate-b (−1)
Chitosan	X_1	500	100	300	416	184
Pressure	X_2	2	1	1.5	1.8	1.2
Time	X_3	120	30	75	101	49

Table 2
Experimental conditions according to Box–Wilson statistical design

	Coded values			Real values		
	X_1	X_2	X_3	Chitosan concentration (mg/L)	Pressure (bar)	Time (min)
Axial point						
*A*1	*k*	0	0	500	1.5	75
*A*2	–*k*	0	0	100	1.5	75
*A*3	0	*k*	0	300	1.5	75
*A*4	0	–*k*	0	300	1.5	75
*A*5	0	0	*k*	300	2	120
*A*6	0	0	–*k*	300	1	30
Factorial points						
*F*1	–1	1	1	184	1.8	120
*F*2	1	–1	1	416	1.2	120
*F*3	1	1	–1	416	1.8	30
*F*4	1	–1	–1	416	1.2	30
*F*5	–1	–1	1	184	1.2	120
*F*6	–1	1	–1	184	1.8	30
*F*7	1	1	1	416	1.8	120
*F*8	–1	–1	–1	184	1.2	30
Center point						
C	0	0	0	300	1.5	75

Table 3
Characterization of raw olive oil mill wastewaters

Parameter	Value
pH	5.1
COD, mg/L	100,000
TOC, mg/L	21,870
SS, mg/L	17,600
Oil and grease, mg/L	3,070

Table 4
Coefficients of the response functions for permeate flux and COD removal

Coefficients	Permeate flux	COD removal
b_0	52.4465	58.73215
b_1	–0.1186	0.01073
b_2	4.45291	–1.58430
b_3	–0.22542	0.33559
b_{12}	0.000158	0.00000001
b_{13}	0.000152	0.00010
b_{23}	0.000169	0.000000001
b_{11}	0.000109	0.00005
b_{22}	0.000748	–0.58763
b_{33}	0.000866	–0.00217
R^2	0.962	0.936

and COD removal efficiencies changed between 68.9% and 83.0%. The observed permeate fluxes and COD removal efficiencies were compared with the predicted ones obtained from the response function.

The coefficients were used in calculating predicted values of permeate flux and COD removal efficiencies. The correlation coefficients (R^2) between the observed and predicted values were 0.962 and 0.936 for permeate flux and COD removals, respectively. These results indicated excellent agreement between the observed and the predicted values. The effects of the operating variables on the permeate flux and COD removal performance of the system were determined by obtaining the projections of the response functions on certain planes of the known parameter values.

3.3. *Effect of chitosan concentration*

In order to determine the effect of chitosan concentration on permeate flux and COD removal efficiencies at pressure of 1 bar, some results are predicted by using response equation with calculated coefficients. Fig. 3 depicts the variation of permeate flux with the chitosan concentration at different operation time. The increase in the concentration of chitosan causes a decrease in permeate flux. In a 30-min operation time, the flux obtained at a 100 mg/L of chitosan concentration was 40.6 L/m^2 h while at 500 mg/L chitosan this value dropped to 21.4 L/m^2 h. As the concentration of chitosan added to the OMW increases, the membrane surface is covered with chitosan, in which case the flux value is reduced.

Fig. 4 depicts the variation of COD removal efficiency at the same experimental conditions. Since there was no significant change in the COD removal efficiencies after 80 min,

Table 5
Observed and predicted permeate flux and COD removal efficiencies

Experiment number	Observed permeate flux (L/m² h)	Predicted permeate flux (L/m² h)	Observed COD removal (%)	Predicted COD removal (%)
*A*1	5.77	6.83	83.0	83.1
*A*2	14.26	13.96	73.1	72.9
*A*3	8.36	9.47	76.2	76.5
*A*4	6.6	6.3	77.0	76.5
*A*5	5.42	6.66	73.1	73.0
*A*6	7.87	8.88	70.0	70.0
*F*1	11.45	10.71	72.0	70.5
*F*2	6.55	5.8	78.9	77.5
*F*3	10.71	9.44	72.8	73.0
*F*4	6.71	6.89	74.0	73.0
*F*5	8.74	9.45	69.9	70.5
*F*6	13.87	14.05	68.9	68.0
*F*7	9.72	9.26	76.5	77.5
*F*8	13.81	13.71	67.5	68.0
C	6.97	6.01	76.0	75.7

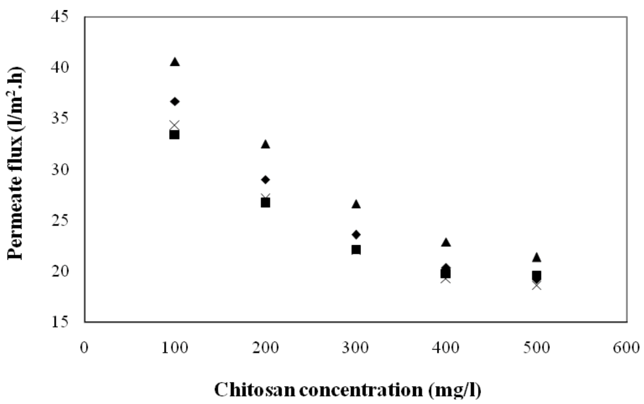

Fig. 3. Variation of permeate flux with chitosan concentration as a function of time at 1 bar pressure. Operation time: (▲) 30 min (◆) 60 min, (x) 90 min, and (■) 120 min.

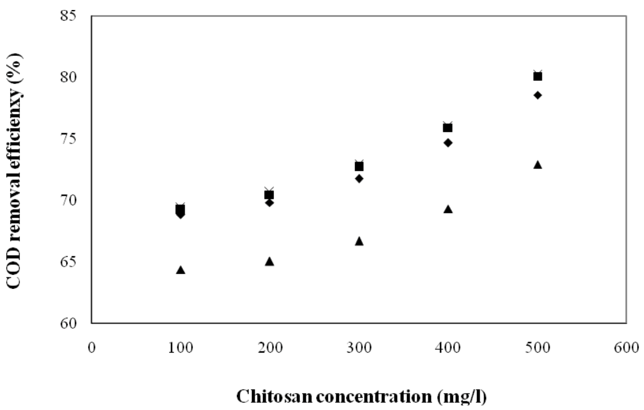

Fig. 4. Variation of COD removal efficiency with chitosan concentration as a function of time at 1 bar pressure. Operation time: (▲) 30 min (◆) 60 min, (x) 90 min, and (■) 120 min.

the curves representing 90 min and 120 min coincided with the overhead. So, maximum COD removal efficiency was obtained as 80% at a chitosan concentration of 500 mg/L at 80 min operation time. In the same operation time, the removal efficiency obtained at a concentration of 100 mg of chitosan is 69%. The increase in chitosan concentration also increases the COD removal efficiency. Rizzo et al. worked on the pretreatment of OMW by coagulation with chitosan, and they found (32%) COD removal efficiency as the optimum efficiency for 400 mg/L chitosan dose [23]. In our study, 76% COD removal efficiency was obtained for 400 mg/L chitosan dose.

3.4. Effect of transmembrane pressure

In the second part of experimental studies, effects of transmembrane pressure on the permeate flux and COD removal efficiency were investigated. Fig. 5 depicts the variation of permeate flux with transmembrane pressure for different chitosan concentrations at constant operation time of 90 min. When the results are examined, it is seen that the flux values increase with the increase in applied pressure. Based on Darcy's law, the increasing pressure gradient increases permeate flux. These data are consistent with the findings of other authors [25,27]. When the flux values for the 100 mg/L chitosan concentration were examined, the flux value at 1 bar pressure was 37 L/m² h. While the pressure increased 2 bar, the permeate flux increased to 42 L/m² h.

The influence of pressure on the COD removal efficiency at different transmembrane pressures is depicted in Fig. 6. The use of lower pressures gives better removal efficiencies. For 500 mg/L chitosan concentration, when 80.3% COD removal efficiency was obtained at 1 bar pressure, the obtained efficiency decreased to 76.9% as the pressure increased to 2 bar. These results are in agreement with the results of UF works done with similar wastewater [25,28,29]. They have obtained decreasing retention coefficient for increasing pressure.

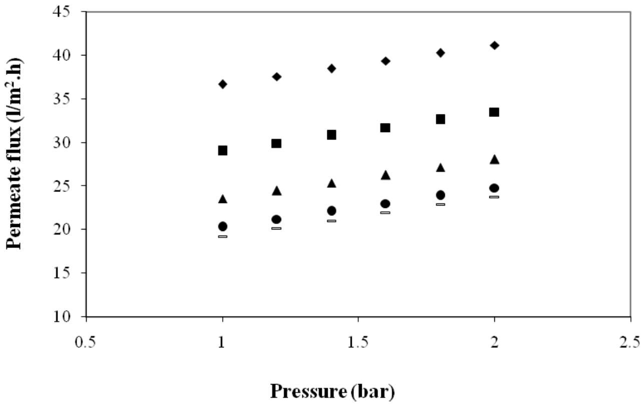

Fig. 5. Variation of permeate flux with pressure as a function of chitosan concentration at 80 min operation time. Chitosan concentration: (◆) 100 mg/L, (■) 200 mg/L, (▲)300 mg/L, (●) 400 mg/L, and (−)500 mg/L.

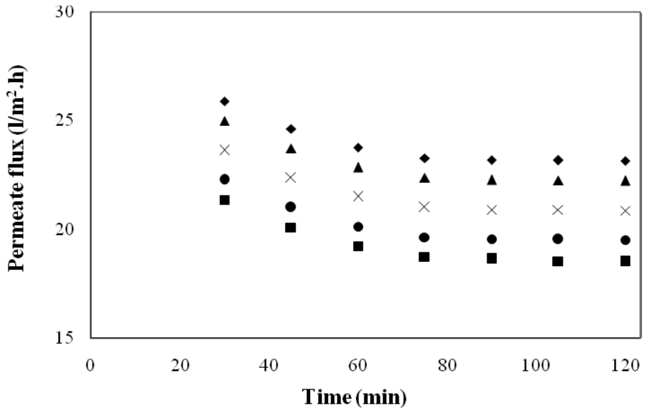

Fig. 7. Variation of permeate flux with time as a function of pressure at chitosan concentration of 500 mg/L. Pressure: (■) 1 bar, (●) 1.2 bar, (x) 1.5 bar, (▲) 1.8 bar, and (◆) 2 bar.

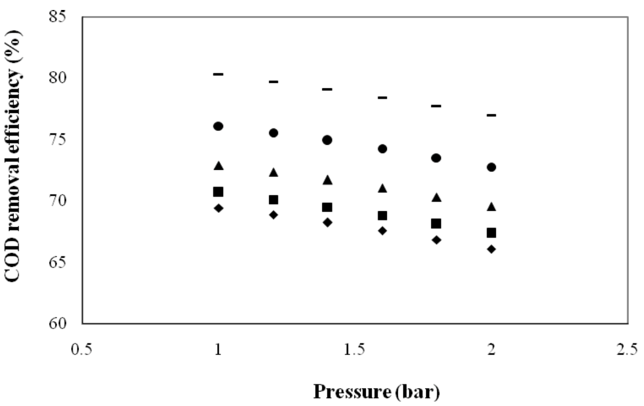

Fig. 6. Variation of COD removal efficiency with pressure as a function of chitosan concentration at 90 min operation time. Chitosan concentration: (◆) 100 mg/L, (■) 200 mg/L, (▲) 300 mg/L, (●) 400 mg/L, and (−) 500 mg/L.

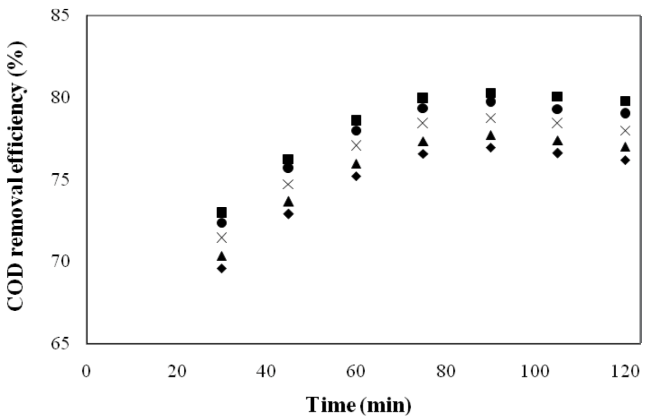

Fig. 8. Variation of COD removal efficiency with time as a function of pressure at chitosan concentration of 500 mg/L. Pressure: (■) 1 bar, (●) 1.2 bar, (x) 1.5 bar, (▲) 1.8 bar, and (◆) 2 bar.

The same result was obtained for OMW UF in this study for the repeated experiments.

3.5. Effect of UF time

In order to determine the effect of UF time, permeate flux, and COD removal efficiency at a constant chitosan concentration of 500 mg/L, the results were predicted for different pressures by using response equation with calculated coefficients. Fig. 7 depicts the variation of permeate flux as a function of time at different pressures at constant chitosan concentration. As it can be seen from figure, permeate flux showed the same trend for all pressures. Declining rate of flux is not significant during the whole filtration period. At each pressure after about 80 min, flux reaches to more or less constant value because the cake layer reaches to equilibrium and its growth ceases after this time. So, the cake layer resistance and subsequently permeate flux remain constant [28,30].

In the last part of the study, the effect of UF time on COD removal efficiency was investigated. The variation of COD removal efficiency with time as a function of pressure at constant chitosan concentration of 500 mg/L is given in Fig. 8. For all pressures, in the first 80 min of the operation, an important increase in the COD removal efficiencies took place and after 80 min more or less steady-state conditions were reached. Efficiencies were not changed considerably after this time. This result is similar to our previous work with same wastewater [29]. As it can be seen from Fig. 8, COD removal efficiency was 80.2% after 80 min and 79.8% after 120 min operation time at 1 bar transmembrane pressure.

Table 6
Treatment results of UF process for optimal conditions

Parameter	Raw OMW	UF effluent	Removal efficiency (%)
COD (mg/L)	100,000	20,000	80
TOC (mg/L)	21,870	4,810	78
SS (mg/L)	17,600	2,640	85
Oil and grease (mg/L)	3,070	700	77

As a result of all experimental studies, maximum COD removal efficiency as 80% was achieved at 500 mg/L chitosan concentration and 1 bar pressure. This condition was chosen as optimal condition, and treatment results of UF process for optimal condition are given in Table 6. Maximum removal efficiency was achieved for SS removal. However, the major pollutant for OMW 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.

4. Conclusions

A Box–Wilson statistical experimental design was used to determine the optimization of operating parameters such as chitosan concentration, transmembrane pressure, and operation time on the permeate flux and COD removal efficiency for UF of OMW. In a Box–Wilson statistical experimental design, response function coefficients were determined by regression analysis of the experimental data and predicted results obtained from the response functions were in good agreement with the experimental results. The correlation coefficients (R^2) between the observed and predicted values were 0.962 and 0.936 for permeate flux and COD removal, respectively. These results indicated excellent agreement between the observed and the predicted values indicating the reliability of the methodology used.

The experimental results indicated that chitosan concentration and transmembrane pressure are significant important parameters for permeate flux and COD removal efficiency. The optimum chitosan dosage and transmembrane pressure were found to be 100 mg/L and 2 bar for permeate flux, respectively. In this case, 42 L/m^2 h permeate flux was obtained. In contrast, maximum COD removal efficiency as 80.3% was achieved at 500 mg/L chitosan concentration and 1 bar pressure. Therefore, objective parameter (COD removal or permeate flux) should be selected at the beginning of the UF process.

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