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Treatment of edible oil processing wastewater using micellar-enhanced ultrafiltration process

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ABSTRACT

In the present study, micellar-enhanced ultrafiltration (UF) has been applied to treat edible oil processing wastewater using linear alkylbenzene sulfonate (LAS) and sodium dodecyl sulfate (SDS) as surfactants. In particular, the effects of different operating conditions on process performance were investigated in terms of product flux and reductions of wastewater turbidity, oil and grease content, chemical oxygen demand (COD), electrical conductivity (EC), and total dissolved solids (TDS). Experimental results showed that transmembrane pressure and temperature of wastewater had direct effect on permeate flux while surfactant concentration influenced it reversely. To achieve the highest pollutants removal, the optimum operating conditions were found and applied. Finally, optimum permeate quality was compared to the permissible limits of environmental standards. As a result, LAS was shown to reduce pollution indicators more effectively in comparison with SDS, since combination of LAS and UF could eliminate turbidity, oil and grease, COD, EC, and TDS by 98, 95.7, 84.7, 90.6, and 90.7%, respectively.

Keywords: Micellar-enhanced ultrafiltration; Linear alkylbenzene sulfonate; Sodium dodecyl sulfate; Wastewater; Edible oil

1. Introduction

Water shortages, deterioration of water quality, and environmental constraints have led to an increased interest of recovering water and wastewater in most of the industries around the world. The recovered water may be used in different ways, according to its quality, such as agricultural irrigations and cooling processes. In this regard, various innovative treatment technologies have been proposed.

Vegetable oil production industry generates considerable amount of wastewater every year. To treat this type of wastewater, various techniques such as electrocoagulation [1,2], electrolysis [3], coagulation-air flotation [4], biological treatment [5], ultrafiltration (UF) [6–10], and nanofiltration [11] have been examined. With respect to the low efficiency of some of these processes, the use of micellar-enhanced ultrafiltration (MEUF) as a surfactant-based separation technique is suggested here. It has been shown that heavy metal ions [12–15] and organic solutes of aqueous

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streams [16–18] could be effectively removed from water and wastewater using MEUF.

When a surfactant is added into a polluted aqueous medium, it aggregates and forms micelles at a concentration above its critical micelle concentration (CMC). These micelles are capable of attracting metal ions or solubilizing organic solutes existing in the solution. In MEUF process, the micellar solution is then treated by UF membrane having membrane pore size small enough to block the passage of micelles [18–24]. The permeate side will consequently contain very low concentrations of unbound ions and organic molecules which are not trapped in micelles and surfactant monomers, resulting in a clean permeate that can be recycled or discarded. In fact, MEUF process combines the high selectivity of reverse osmosis and the high flux of UF [25].

In the present study, MEUF was applied to treat edible oil processing wastewater. The experiments were conducted at varying surfactant type and operating conditions including transmembrane pressure (TMP), temperature, and surfactant concentration. In addition to the pollutants retentions, transient and steady state fluxes were considered as performance characteristics of the process.

2. Materials and methods

2.1. Materials

A PAN-350 membrane was supplied by Sepro Company (USA) and used as the ultrafilter. The membrane characteristics are presented in Table 1. The anionic surfactants, linear alkylbenzene sulfonate (LAS) with molecular weight of 348.48 g/mol and sodium dodecyl sulfate (SDS) with molecular weight of 288.38 g/mol, were obtained from Aldrich and Merck, respectively.

Table 1
PAN-350 membrane characteristics

Parameter	Value
Thickness (mm)	0.165
P_{max} (bar)	83
T_{max} (°C)	100
Process pH limitations	3–10
Normalized water flux at 25°C and 2.068 bar (L/m^{2}min)	27.58
MW of marker (kD)	20 kD polyethylene glycol
Normal marker rejection (%)	80

The wastewater used in this work was the effluent of an edible oil processing factory. This type of wastewater is characterized by a large load of dissolved organic and mineral substances (chemical oxygen demand (COD), oil and grease content) and a high salinity which was determined by measuring total dissolved solids (TDS) and electrical conductivity (EC). The result of the wastewater analysis after sedimentation is shown in Table 2.

2.2. Experimental set up

Prior to the membrane filtration, the surfactant was added to the wastewater and the solution was stirred continuously. It was then used as the feed of the membrane process.

The cross-flow UF pilot plant, shown in Fig. 1, had a 5 L feed tank. During the experiments, the feed solution was pumped toward the disk-shaped module with an effective area of 113 cm^2. The tangential flow rate of the feed in the membrane module was kept constant at 6 L/min. The desired TMP was obtained by re-adjustment of the valves. Permeate was returned to the feed tank to ensure constant feed conditions. Permeate flow rate was recorded at different time intervals till it became constant. After that, the sample was collected to analyze the pollutants rejections.

After each experiment, the membrane had to be washed thoroughly to recover its permeability. At first, the tap water was recycled through the membrane for 10 min to rinse out the residual wastewater. Then, the membrane was washed using 0.1 mol/L NaOH solution. Subsequently, distilled water was recycled several times to reload the membrane performance.

Various parameters such as TMP, temperature, and surfactant concentration influence the MEUF process. To investigate the effect of these parameters, three TMPs in the range of 2–3 bars, three temperatures in the range of 20–50°C, and five concentrations for each surfactant (0–6 mM for LAS and 0–11 mM for SDS) were selected.

2.3. Analytical methods

The collected samples were analyzed to measure turbidity, TDS, COD, oil and grease content, and EC

Table 2
Result of the raw wastewater analysis after sedimentation

TDS (mg/l)	Electrical conductivity (µs/cm)	COD (mg/l)	Turbidity (NTU)	Oil and grease (mg/l)	pH
4,110	6,800	1,180	69	210	9

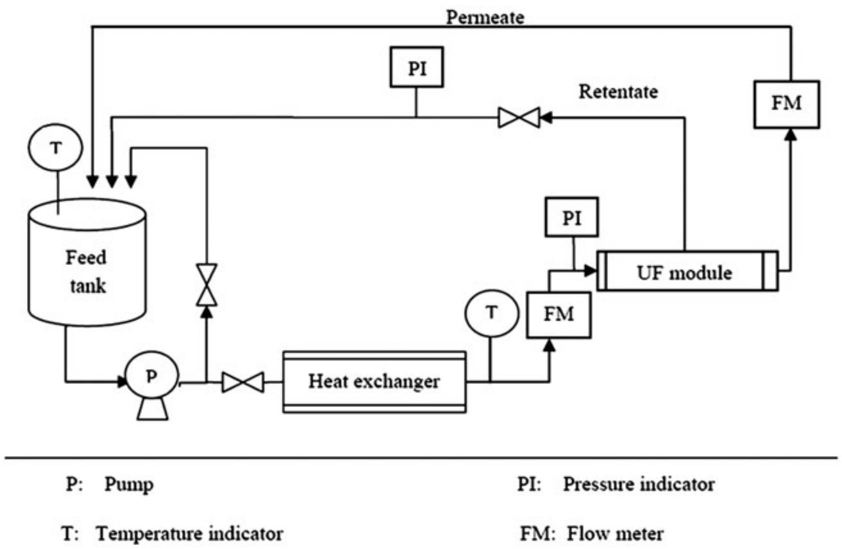

Fig. 1. Membrane pilot plant.

in order to evaluate the process efficiency in reduction of pollutants. Turbidity was measured by a WTW 355IR turbidity meter. The TDS and EC of each sample were determined using JENWAY conductometer. COD measurement was done using AQUALYTIC AL800 spectrophotometer. Oil and grease content of the samples were measured using the Soxhlet extraction method.

3. Results and discussion

3.1. Effect of surfactant concentration on permeate flux and rejection of pollutants

Fig. 2 illustrates permeate flux variations vs. time at different surfactant concentrations. As observed, the fluxes are in the same range and their variations follow similar trends for both of the surfactants. Permeate fluxes reduced with time because of concentration polarization and membrane fouling. The flux decrease continued during the first six minutes of the process until it reached a steady state in which the flux change was negligible.

In addition, permeate flux decreased by increasing surfactant concentration. According to the literature, the CMC of LAS and SDS are 1.2 mM [26] and 8.15 mM [27], respectively. At surfactant concentration below the CMC, most of the surfactant molecules existed in form of free monomers with much smaller size than the membrane pore diameter. Therefore, they could easily pass the membrane leading to higher permeate flux. As the surfactant concentration was increased, the monolayer surfactant coverage of the membrane was completed and the concentration polarization caused the permeate flux to decline [28]. However, at surfactant concentration higher than CMC values, change in permeate flux was almost negligible which is in agreement with Zeng et al. [18] findings.

Fig. 3 shows removal percentages of turbidity, oil and grease, COD, EC, and TDS at different surfactant concentrations. It is obvious that the pollutants

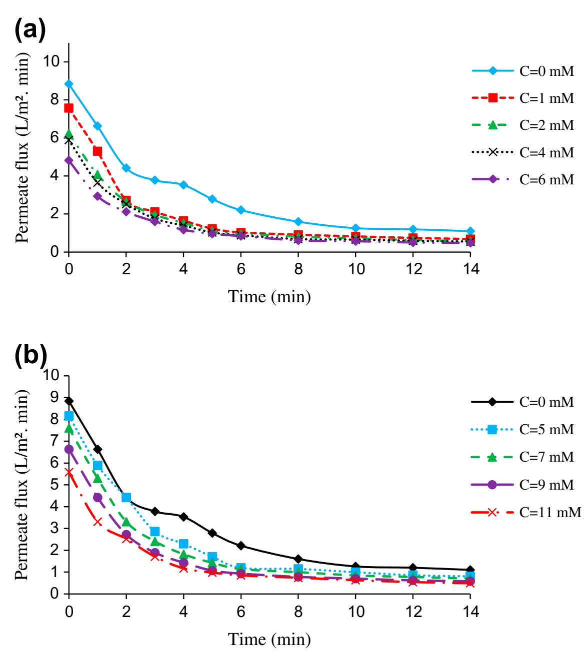

Fig. 2. Effect of surfactant concentration on permeate flux at $T = 20^\circ C$ and TMP = 2.5 bar: (a) LAS, (b) SDS.

rejections increased sharply after adding each of the surfactants. Moreover, the rejections improved by increasing surfactants concentrations, especially at lower concentrations of surfactants. Rejections enhancement below the CMC was mostly caused by the concentration polarization phenomenon. As the surfactant molecules were rejected by the membrane, they gradually deposited and accumulated near the membrane surface, forming a layer in which the surfactant concentration reached the CMC and micelles developed [12]. However, the rejection enhancement was slowed down after reaching the CMC because at surfactant concentrations higher than CMC, the shape and aggregation number of micelles would change but not the number of effective binding sites. The same observation was reported by some other researchers [12,29]. Comparing LAS and SDS, it is concluded that the reduction of EC, TDS, and COD was much higher using LAS, but the two other pollutants were removed equally by both of the surfactants.

With respect to Figs. 2 and 3, applying each of the surfactants led to flux decline and rejection increase. In the real-life filtration process, the flux could be enhanced by minimizing the fouling problem using solutions such as modification of the filter surface and increasing the tangential speed of the feed on the membrane surface in order to decrease concentration polarization. In this way, adding surfactants would be more advantageous.

According to the results, in the next sections, fixed concentrations of 2 mM and 9 mM were chosen for LAS and SDS, respectively.

3.2. Effect of TMP on permeate flux and rejection of pollutants

Effect of TMP on permeate flux is shown in Fig. 4. Generally, TMP increase led to an increase in driving force and thereupon flux values.

Fig. 5 illustrates the effect of TMP on pollution reduction. For both of the surfactants, increasing TMP from 2 bars to 2.5 bars facilitates the passage of water and other components through the membrane. But the amount of passed water is more than other components which leads to rejection increase. At higher TMPs, micelles became compact and deformed; thereby, solubilization capability of micelle decreased and hence, lower quantity of pollutants would be solubilized within the micelles [16,30]. As a result, rejections of COD and oil and grease decreased significantly.

3.3. Effect of temperature on permeate flux and rejection of pollutants

Fig. 6 indicates flux variations over time at different feed temperatures. Temperature increase results in reduction of feed viscosity and thus accretion of

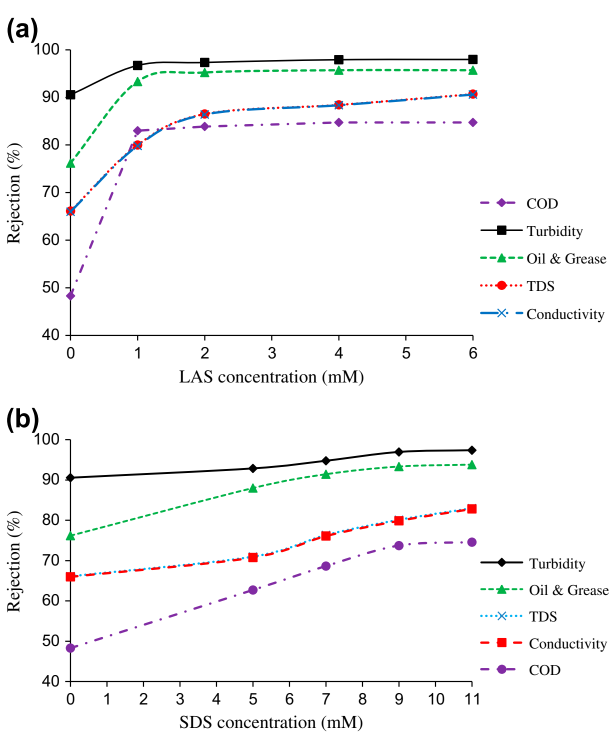

Fig. 3. Effect of surfactant concentration on pollutants removal at $T = 20^\circ C$ and TMP = 2.5 bar: (a) LAS, (b) SDS.

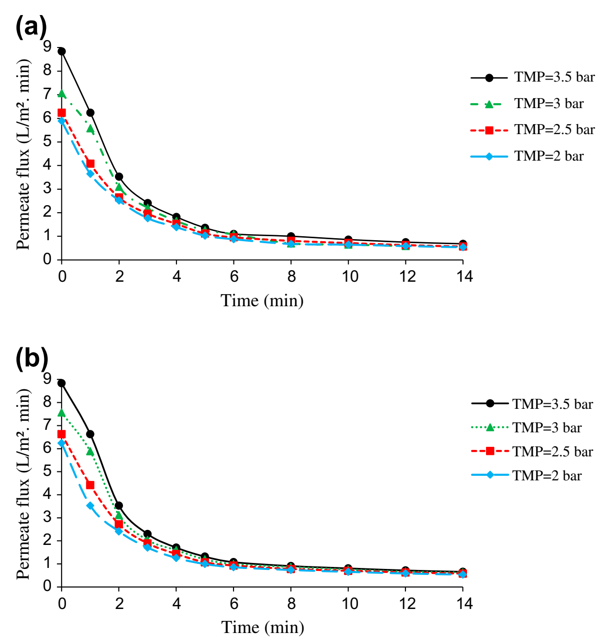

Fig. 4. Effect of TMP on Permeate flux at $T = 20^\circ C$ and (a) [LAS]=2 mM, (b) [SDS]=9 mM.

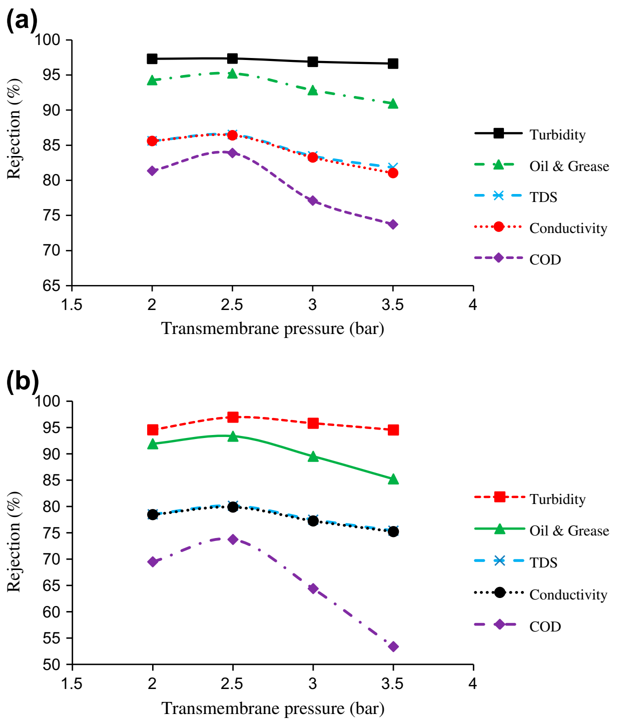

Fig. 5. Effect of TMP on pollutants removal at T = 20˚C and (a) [LAS]=2 mM, (b) [SDS]=9 mM.

permeability through the membrane; therefore, flux had an increasing trend vs. this parameter. Moreover, increasing temperature expands the membrane pores which leads to flux improvement [31].

Variation of pollutants reduction as a function of temperature is presented in Fig. 7. According to the figure, retentions were reduced noticeably by increasing temperature. The result of this observation is the CMC increase which is caused by temperature rise. Therefore, rejection of pollutants decreased because of de-micellization process. Moreover, thermal expansion of membrane pores and enhanced permeability are other factors that cause rejection decrease [17,18].

3.4. Performance of MEUF process at optimum conditions

In Sections 3.1–3.3, effects of different parameters on pollutants reductions were evaluated. Table 3 presents the values of the pollution indicators in permeates of MEUF at optimum conditions, i.e. 2.5 bars and 20˚C. It is obvious that these values are comparable to the corresponding values of indicators in crude wastewater. Moreover, it can be seen that the treated effluent has met the prescribed limits of effluent discharge on land for irrigation.

With respect to Table 3, both of the surfactants were able to eliminate wastewater pollutants considerably. However, LAS provided better performance for the MEUF process than the other anionic surfactant since it helped to decrease all of the pollutants indicators below the environmental standard.

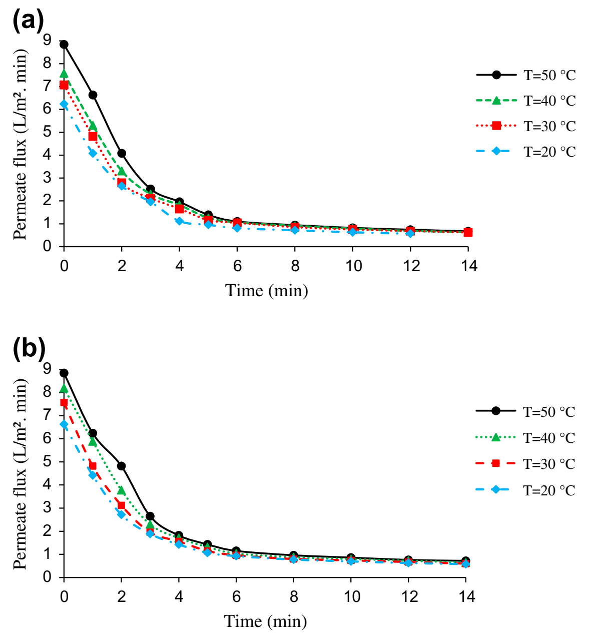

Fig. 6. Effect of temperature on Permeate flux at TMP = 2.5 bar and (a) [LAS]=2 mM, (b) [SDS]=9 mM.

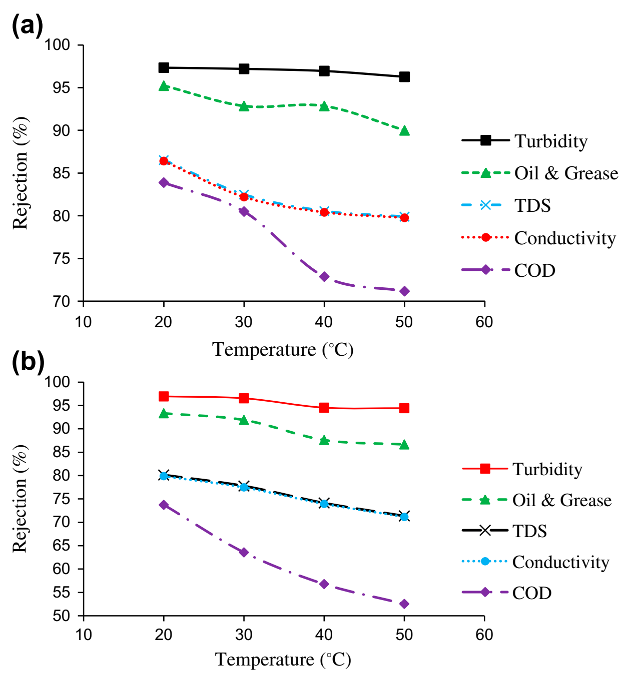

Fig. 7. Effect of temperature on pollutants removal at TMP = 2.5 bar and (a) [LAS]=2 mM, (b) [SDS]=9 mM.

Table 3
Characteristics of the edible oil processing plant effluent before and after MEUF treatment

Parameter	Crude wastewater	Permeate of MEUF using 2 mM LAS	Permeate of MEUF using 9 mM SDS	Standard limits of industrial effluent discharge on land for irrigation (IDOE)*
Turbidity (NTU)	69	1.83	2.11	50
Oil & Grease (mg/l)	210	10	15	10
COD (mg/l)	1,180	190	310	200
EC (μs/cm)	6,800	924	1,368	–
TDS (mg/l)	4,110	554	817	–

*Iran Department of Environment.

4. Conclusion

In this paper, treatment of edible oil processing wastewater by MEUF has been investigated whereas LAS and SDS were used as anionic surfactants. Comparing the surfactants performance, LAS was able to reduce the pollutants more successfully although the permeate fluxes were in the same range for both of them. Another advantage of LAS was its less required concentration according to its lower CMC in comparison with that of SDS.

Evaluating different operating conditions, selecting surfactants concentrations as much as the CMC values were found to be adequately efficient in pollutants removal. Furthermore, for both of the surfactants, the optimum TMP and temperature were found to be 2.5 bars and 20˚C, respectively. Applying these optimum conditions, the maximum reduction in pollutants was obtained. Although both surfactants significantly increased the membrane removal efficiency, LAS performance was remarkable as it could reduce pollutants amounts to lower than permissible limits for wastewater discharge.

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