Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1057868

57 (2016) 12956–12962
June

Micellar-enhanced ultrafiltration of dairy wastewater with anionic and nonionic surfactants

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Received 13 August 2014; Accepted 19 May 2015

ABSTRACT

In this study, the potential of MEUF process has been analyzed to treat a real dairy wastewater. For this purpose, linear alkylbenzene sulfonate (LAS) and Triton X-100 (TX-100) have been used as anionic and nonionic surfactants, respectively. The ranges of 23.5 bars and 0–4 mM are selected for transmembrane pressure (TMP) and surfactants concentration, respectively, to investigate their effects on the permeate flux as a function of operating time. Moreover, it is revealed experimentally that rejection of pollution indices including chemical oxygen demand (COD) and total dissolved solid (TDS) is affected by TMP and feed surfactant concentration, while turbidity is remained relatively unchanged. According to the experimental results analysis, the increase of feed surfactant concentration has negative and positive effects on the permeate flux and rejection efficiency, respectively. TMP enhancement also leads to the higher flux values but it does not necessarily improve the rejection. Furthermore, the effectiveness of anionic surfactant in pollution indices elimination is more than the nonionic one. In the treatment combination assessed for the factors, the best rejection values of COD, TDS, and turbidity using LAS surfactant with polyacrylonitrile (PAN-350) 20-kDa poly(ethylene glycol) membrane are almost 93, 52, and 99.9%, respectively.

Keywords: MEUF; Surfactant; Dairy wastewater; Permeate flux; Rejection

1. Introduction

Development of technology and new industries caused many problems and consequences. One of the most important of these consequences is polluting the environment which has irreparable effects on human life. Food industries, especially dairy industries, have a major share in environmental pollutions. Wastewater of dairy industries includes huge amounts of fat, phosphate, COD, and TDS, thus polluting the environment and requiring a treatment process. Many kinds of techniques have been used to treat the dairy wastewater, such as aerobic and anaerobic [1,2], electrical coagulation and electroFenton [3], and electrochemical [4] processes. To overcome the intrinsic limitations of some of these methods, such as long retention time, high energy consumption, and low efficiency, new approaches are needed.

Pressure-driven membrane processes including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) have been increasingly applied for the treatment of organic and inorganic effluents, concentration and purification in food industry, biotechnology and petrochemical operations due to their convenience and high efficiencies. In this regard, some studies have been done to investigate the performance of UF and NF processes in treatment of dairy wastewater. Nevertheless, NF process is limited in wastewater treatment applications because of high pressure requirements and low water permeability [5–7]. In order to overcome these problems, an alternative approach over the past few decades, i.e. MEUF has been developed which combines high flux of ultrafiltration and high rejection percentage of nanofiltration and RO, simultaneously. This method has already been used to remove heavy metals [8–17], organic materials [14,18–21], and treat industrial wastewaters like soft drink [22], raisin [23], olive oil [24] and edible oil [25].

In this method, surfactants are added to the wastewater, and their concentrations are increased to reach the critical micelle concentration (CMC). In this specific concentration, surfactant monomers join together and create aggregations which are called micelles. It is worth to note that the size of these micelles is greater than ultrafiltration membrane pores, so they are rejected by the membrane. Consequently, pollutants that were absorbed by them are rejected [13,14].

High CMC value of surfactants results in high surfactant amounts to form micelles which attribute to the increase in material cost. High CMC value also leads to large numbers of free surfactant monomers which can penetrate to permeate side through ultrafiltration process and need to further treatment on permeate stream. This raises the environmental impact, capital, and operating costs of the MEUF process. Therefore, the reduction of the CMC value would be a vital task [12–14] which can be made through choosing surfactants with low CMC value. It should be noted that there are many methods to recover surfactants from both permeate and retentate streams.

The aim of this study is to evaluate the potential of MEUF process for dairy wastewater treatment and compare its performance with stand-alone UF. For this purpose, an anionic surfactant LAS which has a low CMC is selected. Moreover, a nonionic surfactant named TX-100 is chosen due to its low environmental impact, capital, and operating costs because of its lower CMC. Effects of TMP and feed surfactant concentration on the permeate flux as a function of operating time are studied. Furthermore, the TMP and feed surfactant concentration effects were investigated on the rejection of pollution indices including turbidity, TDS, and COD.

2. Materials and methods

2.1. Dairy wastewater

The wastewater was provided from a local dairy factory (Iran). The concentration of pollution indices of this wastewater is presented in Table 1.

2.2. Chemicals

All chemicals were of analytical pure grade and used as received. HCl and NaOH were supplied from Merck Co. (Germany) to remove membrane fouling. The anionic (LAS) and nonionic (TX-100) surfactants were purchased from Sigma–Aldrich (France) and Merck (Germany), respectively. Table 2 shows the properties of surfactants.

2.3. Membrane and experimental setup

The ultrafiltration experimental runs were conducted in a cross-flow ultrafiltration laboratory-scale membrane setup using a disk module with an effective area of 0.00708 m^2. In order to control the temperature at 20˚C, a double-pipe heat exchanger was applied in all experiments. The details of the experimental setup are shown in Fig. 1. TMP was controlled by adjusting the inlet and the retentate flow valves. Accordingly, TMP can be calculated using Eq. (1).

$$\mathrm{TMP} = \frac{P_{\mathrm{in}} + P_{\mathrm{out}}}{2} \quad (1)$$

where P_{in} and P_{out} refer to the pressure before and after the membrane cell, respectively. Polyacrylonitrile flat membrane (PAN-350) was used in the experiments. As reported by the supplier, this membrane has provided 80% rejection for 20-kDa poly(ethylene glycol). Other specifications of the membrane have been shown in Table 3.

2.4. Procedure

Prior to the membrane filtration, a homogenous surfactant solution was prepared by stirring a

Table 1
Dairy wastewater characteristics

Pollution indices	TDS (ppm)	COD (ppm)	Turbidity (NTU)
Value	1,700	1,800	700

Table 2
Surfactants properties

Surfactant	Formula	Molecular weight (g/mol)	Type	CMC (mM)
LAS	$C_{12}H_{25}C_6H_4SO_3Na$	348.48	Anionic	1.2
TX-100	$C_{34}H_{62}O_{11}$	347	Nonionic	0.2–0.8

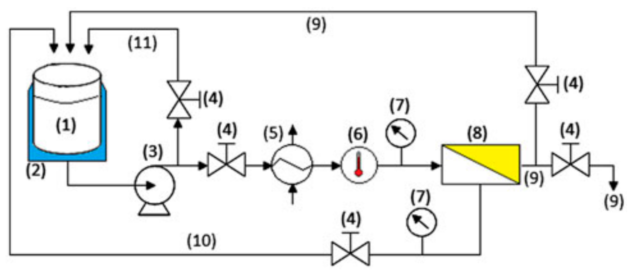

Fig. 1. Schematic diagram of laboratory-scale membrane setup: (1) feed reservoir, (2) water bath, (3) pump, (4) valve, (5) heat exchanger, (6) thermometer, (7) pressure indicator, (8) membrane module, (9) permeate stream, (10) retentate stream, and (11) bypass line.

predetermined weight of the surfactant and 0.1 l distilled water for 15 min at 300 rpm. Eventually, a mixture of 0.1 l surfactant solution and 7.9 l of the dairy wastewater was stirred at 110 rpm for 30 min to prepare the final feed solution before subjecting to the membrane setup.

With the start of the process, permeate flux was measured at 1 min intervals with respect to Eq. (2).

$$\text{Flux} = \frac{V}{A \cdot t} \tag{2}$$

where V is the permeate quantity (l), A is the membrane surface area (m^2), and t is the sampling time (min). It should be mentioned that both retentate and permeate were continuously recycled to the feed reservoir in a closed-loop to ensure a constant feed concentration of solutes, and permeate collecting was done after it reached to a plateau.

To evaluate the filtration efficiency in removal of three pollution indices, i.e. COD, TDS, and turbidity from the feed solution, the following equation was used:

$$R\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{3}$$

where R is the rejection percent and C_f (mg/L) and C_p (mg/L) are the concentrations of COD, TDS, and turbidity in the permeate and feed, respectively.

After each experiment, the membrane was washed for about 10 min in each of the following solutions to recover the membrane permeability: distilled water, 1% NaOH solution, 0.1-M HCl solution, and distilled water. To verify the effectiveness of each cleaning process, the pure water flux of the membrane was measured using distilled water and if it was different from its original value, a new membrane was applied. Furthermore, the setup was washed thoroughly with distilled water after each experimental run.

The performance of the MEUF process was evaluated at different TMPs and surfactant concentrations. To observe the effect of these parameters, four TMPs in the range of 2–3.5 bars and five concentrations for each surfactant in the range of 0–4 mM were examined. Tables 4 and 5 show the details of the experimental design.

2.5. Analysis

A thermoreactor (RD125) was applied for the digestion of COD vials solution with COD photometer from Lovibond Tintometer (Germany). Electrical conductivity meter of Extech EC-400 (USA) was used for measuring the TDS and Lutron electronic turbiditymeter (model TU-2016, Taiwan) was used so as to measure the turbidity.

Table 3
Ultrafiltration membrane properties

Membrane	Material	MWCO (kDa)	Thickness (mm)	P_{max} (MPa)	T_{max} (°C)	Company
PAN-350	Polyacrylonitrile	20	0.165	8.3	100	Sepro

Table 4
Experimental runs with TX-100

Experiment no.	TX-100 concentration (mM)	TMP (bar)
1	2	2
2	2	2.5
3	2	3
4	2	3.5
5	0	2
6	0.2	2
7	1	2
8	2	2
9	4	2

Table 5
Experimental runs with LAS

Experiment no.	LAS concentration (mM)	TMP (bar)
1	2	2
2	2	2.5
3	2	3
4	2	3.5
5	0	3
6	1	3
7	2	3
8	3	3
9	4	3

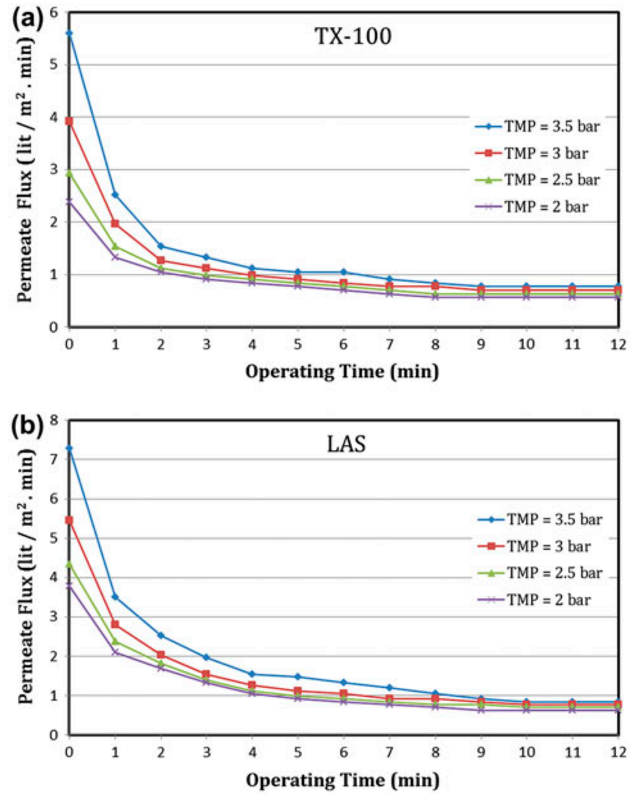

Fig. 2. Effect of TMP on the permeate flux as a function of operating time at surfactants concentration of 2 mM, (a) TX-100 and (b) LAS.

3. Results and discussion

3.1. Effect of TMP on the permeate flux as a function of operating time

Fig. 2(a) and (b) shows the effect of TMP on the permeate flux for TX-100 and LAS, respectively. Accordingly, the experiments were carried out at constant concentration of 2 mM for both surfactants at room temperature.

With respect to this figure, the flux increases with increase in the TMP. This is due to the driving force enhancement and resistance stability. Separately, each curve is divided into two parts: first part is moved from beginning of the test up to 8 min in which the permeate flux is time dependent, while the second part is started after 8 min of the beginning of the process and it is continued to the end which is independent of the time flux. This phenomenon is related to resistance resulting in deposited micelles over the membrane surface. In the beginning, the number of micelles in the bulk is much more than those on the membrane surface, whereupon a thin layer of micelles is formed whose growth continued until establishing an equilibrium between them (micelles of the bulk and those of over the membrane surface) [22,26].

The nonionic surfactant diagram shows that the flux of this surfactant is less than the anionic one at the same time because the viscosity of nonionic solution is more than the viscosity of the ionic solution, and this factor caused more hydraulic resistance against the flux. Furthermore, nonionic surfactant micelle size is lower than the anionic one causing pore blocking [27].

3.2. Effect of TMP on the turbidity, COD, and TDS rejection

The turbidity, COD, and TDS rejection dependency on the TMP was evaluated by analyzing samples which are collected over the independent time flux part in the previous section.

It can be seen from Fig. 3 that the rejection of pollution indices decreases with increase in the TMP for the nonionic surfactant, while for the anionic one, the rejections are first ascending and then descending. This is due to the fact that the thickness of polarization layer increases and a gel layer is formed by increasing the TMP. Therefore, more pollutants adsorb

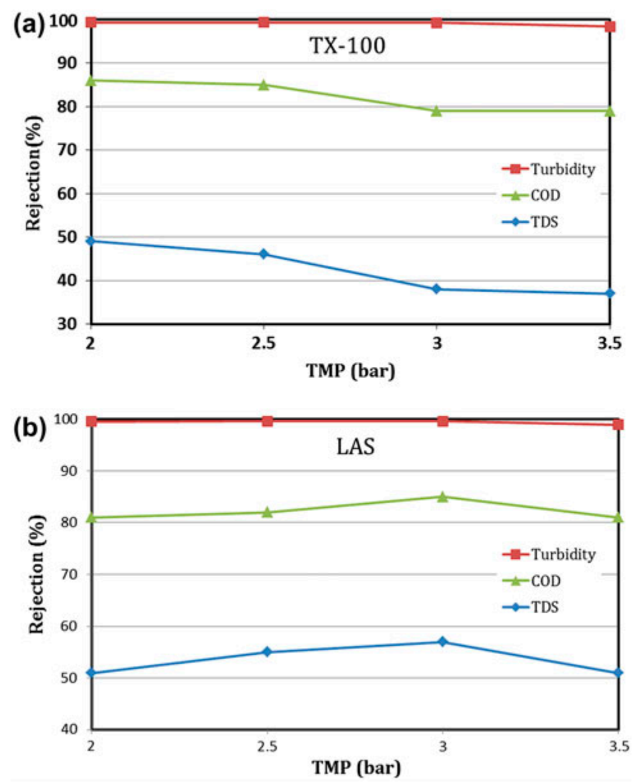

Fig. 3. Effect of TMP on the turbidity, COD, and TDS rejection at surfactants concentration of 2 mM, (a) TX-100 and (b) LAS.

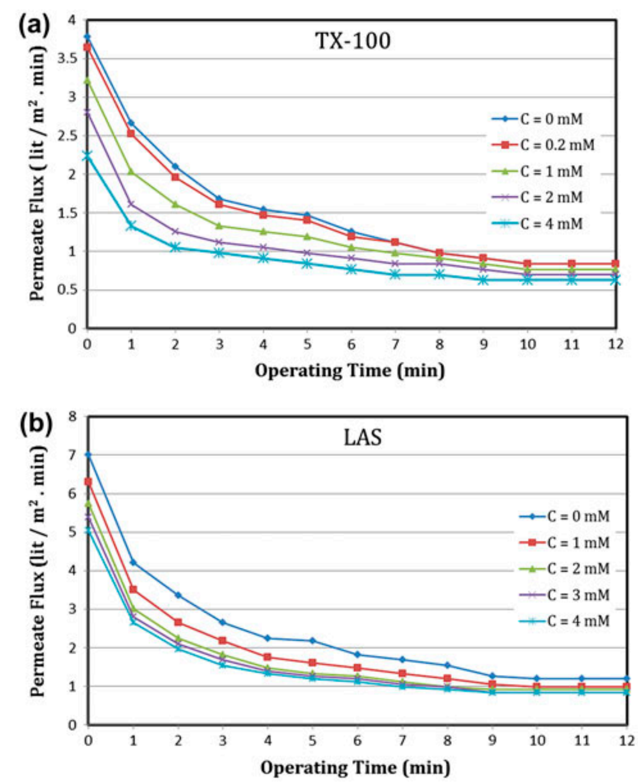

Fig. 4. Effect of surfactants concentration on the permeate flux for (a) TX-100 and TMP = 2 bars and (b) LAS and TMP = 3 bars.

onto the membrane surface and rejection is increased [10,28].

Two reasons for the rejection decline with TMP increment are acceptable: firstly, at higher pressure, the micelles may become compact and their solubilization capability decreases [21,29]. Secondly, at higher pressure, the convective transport of the solutes through the membrane will be higher leading to more penetration of them to permeate and lower rejection [21].

3.3. Effect of feed surfactant concentration on the permeate flux

According to previous tests, the best TMP for each surfactant was specified in which the rejection was maximum value. It should be noted that the best TMPs are 2 and 3 bars for TX-100 and LAS, respectively. Then, for each surfactant at constant TMP, the concentration variation experiments were performed at room temperature. As it can be seen from Fig. 4, for every curve, there is a descending manner similar to the TMP variation curves and the reasons mentioned there will be valid here. It is clear that permeate flux declines as surfactant concentration increases because fraction micelle formation is larger at higher concentration which causes more thickness micelle gel layer and in turn more resistance against feed flow [30]. It can be seen that permeate flux for the anionic surfactant is more than the nonionic one and its reason is similar to that of flux variation curves vs. TMP variation.

3.4. Effect of feed surfactant concentration on the turbidity, COD, and TDS rejection

The effect of the feed surfactant concentration on the rejection of pollution indices was carried out at the best TMPs (2 and 3 bars for nonionic and anionic surfactants, respectively). It is observed from Fig. 5 that the rejection of pollution indices at concentration below the CMC is greater than the case without the surfactant. Theoretically, at surfactant concentrations below CMC, surfactants are present in monomer form and there are no micelles in the bulk solution. However, a considerable rise in the rejections is observed when the surfactant concentration is below the CMC. The concentration polarization phenomenon

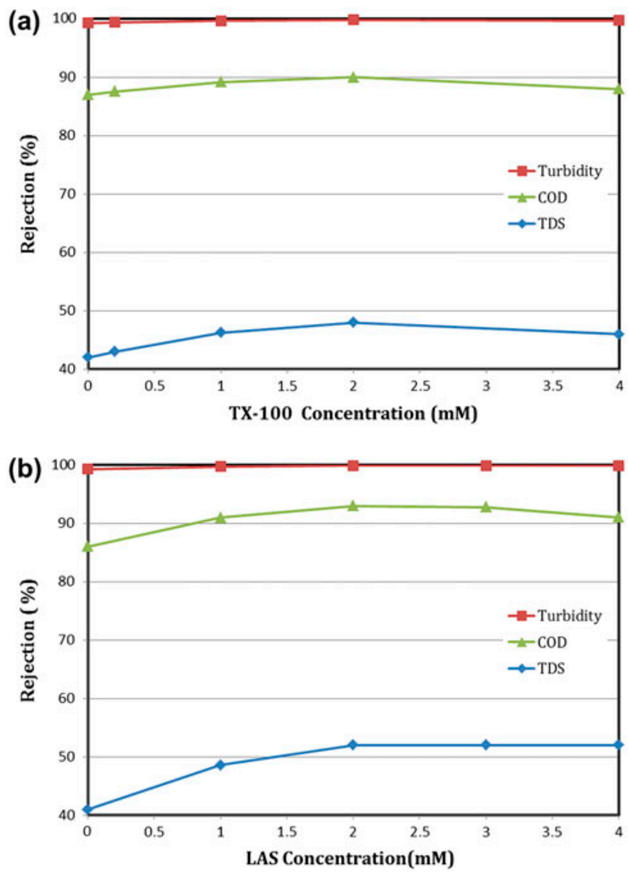

Fig. 5. Effect of surfactants concentration on the turbidity, COD, and TDS rejections for (a) TX-100 and TMP = 2 bars and (b) LAS and TMP = 3 bars.

contributes to such unusual behavior, whereupon accumulation of surfactant monomers occurs in the layer adjacent to the membrane surface. Thus, its concentration reaches above the CMC in this layer and the micelles formed trap the pollutants [16,22,25]. Up to the concentration of 2 mM for both surfactants, which is slightly higher than CMC, the rejection progress is significantly ascending because of the enhancement of micelles formation and more solubilization of pollutants on them [21,23]. However, at surfactant concentrations much higher than CMC, the rejection improvement reduces due the aggregation of the micelles and change in shape, but not the number of effective binding sites [16,25,31,32]. As it can be seen from Fig. 5, the turbidity is sufficiently eliminated by stand-alone UF whose rejection is more than 99%. Hence, adding the surfactant cannot have a considerable effect on the turbidity removal. Furthermore, the potential of MEUF process is more efficient in TDS removal compared to COD elimination. With regard to Fig. 5, the ionic surfactant has been more effective than the nonionic one. Under the applied experimental conditions, the best result has been achieved using LAS at TMP and concentration of 2 bars and 3 mM, respectively. As a result, turbidity, COD, and TDS rejection are 99.9, 93, and 52%, respectively.

4. Conclusion

In this research, the potential of MEUF process was examined to treat a real dairy wastewater and its performance was compared with stand-alone UF. LAS and TX-100 were used as anionic and nonionic surfactants, respectively. The effects of TMP (2–3.5 bars) and feed surfactant concentration (0–4 mM) on the permeate flux as a function of operating time were investigated. Furthermore, the effects of TMP and feed surfactant concentration were studied on the rejection of pollution indices including turbidity, TDS, and COD.

According to the results, for both surfactants, the permeate flux increased with a rise in the TMP, while it declined with an increase in the surfactant concentration. Moreover, at low surfactants concentration, a considerable rise in the rejection of pollution indices including COD and TDS was observed with an increase in their concentration, while turbidity rejection remained relatively unchanged. However, the rejection efficiency was not necessarily improved at high TMP.

Under the applied experimental conditions, the best concentration for both surfactants was 2 mM which is slightly more than their CMC values, while the best TMP occurred in 2 and 3 bars for TX-100 and LAS, respectively. Applying these conditions, it was concluded that permeate flux and rejection for LAS is better than TX-100. With respect to the results, the potential of MEUF process is more efficient in TDS removal compared to the COD elimination, while UF alone is sufficiently capable of removing the turbidity.

Acknowledgments

The author wishes to thank Mr A.S. Asgari, M. Khandan, M.R. Skandari, and Mrs S. Sharifi for their kind helps.

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