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Wastewater treatment of raisins processing factory using micellar-enhanced ultrafiltration

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ABSTRACT

In this work, the treatment of raisins processing wastewater using micellar-enhanced ultrafiltration (MEUF) with two cationic surfactants, hexadecyl pyridinium chloride and Cetyl trimethyl ammonium bromide, has been investigated. The effect of process parameters, such as transmembrane pressure (TMP), temperature, and surfactant concentration, on permeate flux and rejection of the wastewater pollutants have been studied. COD, turbidity, TDS, and electrical conductivity were selected as the indicators of wastewater pollution. The obtained results show that rising TMP or temperature led to rejection decrease and flux increase. However, rejection of pollutants increased and flux decreased with increasing surfactant concentration. Applying surfactants enhanced the rejection of the pollutants, thereby a considerable amount of wastewater pollution was omitted and the turbidity of the wastewater was decreased to a high extent through this process. As a result, the MEUF process can be applied as an efficient method for the treatment of raisins factories' wastewater.

Keywords: Wastewater; Raisin; Micellar-enhanced ultrafiltration; Flux; Rejection

1. Introduction

The growing population, improved living standards, and industrial and agricultural developments are the causes of increased water consumption and as a result, increased wastewater production which leads to environmental pollution. There are several methods for wastewater treatment, one of which is the micellar-enhanced ultrafiltration (MEUF) process. MEUF process was initially developed and used for the treatment of heavy metals in wastewater in the 1970s [1]. Since then, this novel method has been successfully used for the removal of phenol [2], aniline [3], pigments like methylene blue [4], phosphates [5], nitrates [6], and heavy metals [7,8] from wastewaters.

In MEUF process, a surfactant is applied as a complex forming agent. In this process, a surfactant is added to the solution containing contaminants such as metal ions until it reaches a critical micelle concentration (CMC). When the surfactant concentration exceeds the CMC value, the surfactant monomers are assembled, forming aggregates (often spherical) referred as micelles. In this stage, due to the electrostatic forces between the solutes and micelles surfaces,

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the solutes are adsorbed on micelles. These bounded solutes cannot pass through membrane pores because of the large diameter of the micelles [9–12]. In fact, this method combines the high efficiency of separation using reverse osmosis and nanofiltration membranes and the high flux of the ultrafiltration membranes [12–14].

MEUF method has been performed in laboratory-scale several times and the successful results have been reported. However, it seems necessary to perform these experiments in pilot scale in order to investigate the exact effectiveness of this method. In this article, a pilot scale MEUF process was applied for the first time to treat a raisins processing wastewater using two different surfactants. Firstly the CMC of the two surfactants were determined and then the influence of transmembrane pressure (TMP), temperature, and surfactant concentration on permeate flux and retention of pollutants was investigated comparing the process performance using these two surfactants.

2. Materials and methods

2.1. Materials

Hexadecyl pyridinium chloride (CPC) and hexadecyl trimethyl ammonium bromide (CTAB) were obtained from Merck. polyacrylonitrile (PAN)-350 membrane (Sepro, USA) was chosen for the experiments because of its chemical stability which makes it suitable for different experimental conditions. As reported by the supplier, this membrane has provided 80% rejection for 20 KDa polyethylene glycol. Further information about the characteristics of the membrane is listed in Table 1.

The wastewater used in this work was the effluent of a raisins processing factory. The result of the wastewater analysis after sedimentation is shown in Table 2.

2.2. Ultrafiltration set-up

A schematic diagram of the cross-flow ultrafiltration pilot plant is shown in Fig. 1.

Table 1
Membrane characteristics

Membrane	Material	Thickness (mm)	P_{max} (Mpa)	T_{max} (°C)
PAN-350	PAN	0.165	8.3	100

Table 2
Analysis of the raw wastewater after sedimentation

pH	TDS (ppm)	Electrical conductivity (μs/cm)	COD (mg/l)	Turbidity (NTU)
4.25	2030	3,380	2,670	430

The wastewater was introduced to the stainless still feed tank with a volume of 62.8 L. Then it passed through a 20 cm diameter and 50 cm length tubular heat exchanger by a high pressure pump (Diamond OS-30A) operating with 2–3 kW power. After the wastewater passed through the disk-shaped membrane module which had an effective membrane area of 113 cm^2, permeate and retentate were recycled to the feed tank to establish a constant concentration of the feed tank solution during the experiment. The tangential flow rate of the feed in the membrane module was kept constant at 6 L/min. In order to determine the TMP, two pressure gauges (Indumart Co.) were used. In addition, there were two thermometers (Wiekie Co.) installed on permeate and retentate lines and a flowmeter installed on permeate line.

2.3. Experimental procedure

Prior to initiating the main experiments, primary experiments were implemented using distilled water (without further addition of chemicals) to identify the probable system problems as well as module sealing. Then, the wastewater was poured into the feed tank, and the specified amount of surfactant (CPC or CTAB) was added to the feed. After that, the solution was mixed using a magnetic stirrer at 1,500 rpm. Once the ultrafiltration process was started, permeate flux was recorded until it reached a plateau. Ensuring the

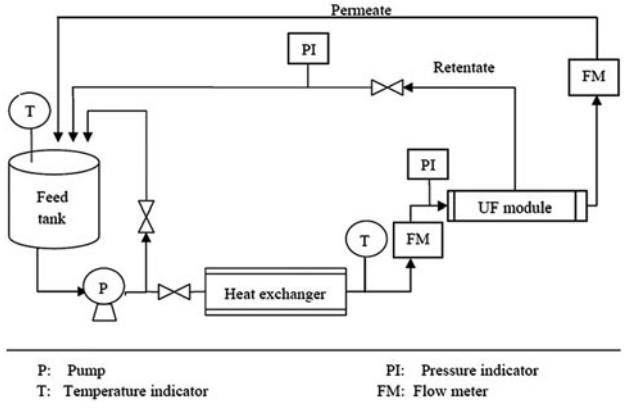

Fig. 1. Schematic diagram of the experimental setup.

Table 3
Experimental layout design

Experiment number	Temperature (℃)	Surfactant concentration (mM)	TMP (bar)
1	20	0.5	2.5
2	20	5	2.5
3	20	15	2.5
4	20	25	2.5
5	20	20	2
6	20	20	2.5
7	20	20	3
8	20	20	3.5
9	30	20	2.5
10	40	20	2.5
11	50	20	2.5
12	20	0	2.5

steady state in permeate flux, permeate was sampled. Ultrafiltration experiments were performed at TMP ranges of 2–3.5 bar, temperature ranges of 20–50% ℃, and surfactant concentration ranges of 0.5–25 mM. The range of TMP was chosen relatively small because some pollutants leak through the membrane module at TMPs greater than 4 bar. The experimental layout design is listed in Table 3.

After each experiment, chemical cleaning of the membrane was done using NaOH solution (0.1 N) and all parts of the set-up were thoroughly cleaned using HCl solution (0.1 N) and distilled water.

2.4. Analysis

In order to investigate the process efficiency, samples were analyzed after each experiment and the pollution indicators including COD, TDS, turbidity, and conductivity were determined. Conductivity measurements were performed by JENWAY conductometer. Concentration of total dissolved solids in the solution was measured by JENWAY. Samples turbidity was determined using TURB WTW353ir turbidimeter. An AQUALYTIC AL800 spectrophotometer was applied to measure the COD of the solution.

To evaluate the filtration efficiency in removing the pollutants from the feed, the rejection rate (R) was determined using the equation below:

$$R = 100\left(1 - \frac{I_p}{I_f}\right) \quad (1)$$

where R is the rejection percent, I_p and I_f are the pollution indicators in permeate and feed, respectively.

3. Results and discussion

3.1. Determination of critical micelle concentration

The determination of CMC was carried out through conductivity measurements. With respect to Fig. 2, the conductivity measurements have provided a linear diagram with two different slopes for both of the surfactants. The left hand side of the diagram refers to the region in which the surfactant concentration is lower than CMC. In this region, only the monomers of the surfactant are present in the solution. The right hand side of the diagram with lower slope than the previous one refers to the association of surfactant monomers to form larger units called micelles [15]. The intersection of these two lines shows the CMC. Therefore, the CMC of CPC and CTAB are 0.9 and 0.92 mM, respectively (Fig. 2).

3.2. Permeate flux

While TMP, temperature, and surfactant concentration were changed individually, permeate flux was being recorded within the first 14 min of process and its variation is shown in Figs. 3–5, respectively. The tests were implemented using each of the surfactants, CPC and CTAB, to compare the performance characteristics of these systems. With respect to the figures, there was a desirable high flux during the initial minutes of process. However, the permeate flux dropped with time because of the concentration polarization and membrane fouling. In the real-life filtration process, the fouling problem could be minimized and a large amount of challenge solutions could be used by modification of the membrane surface and increasing cross-flow velocity of feed on the membrane in order

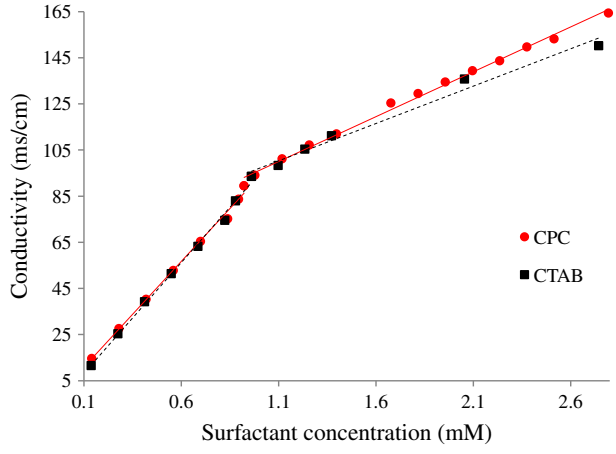

Fig. 2. Determination of CMC for CPC and CTAB through conductivity measurement.

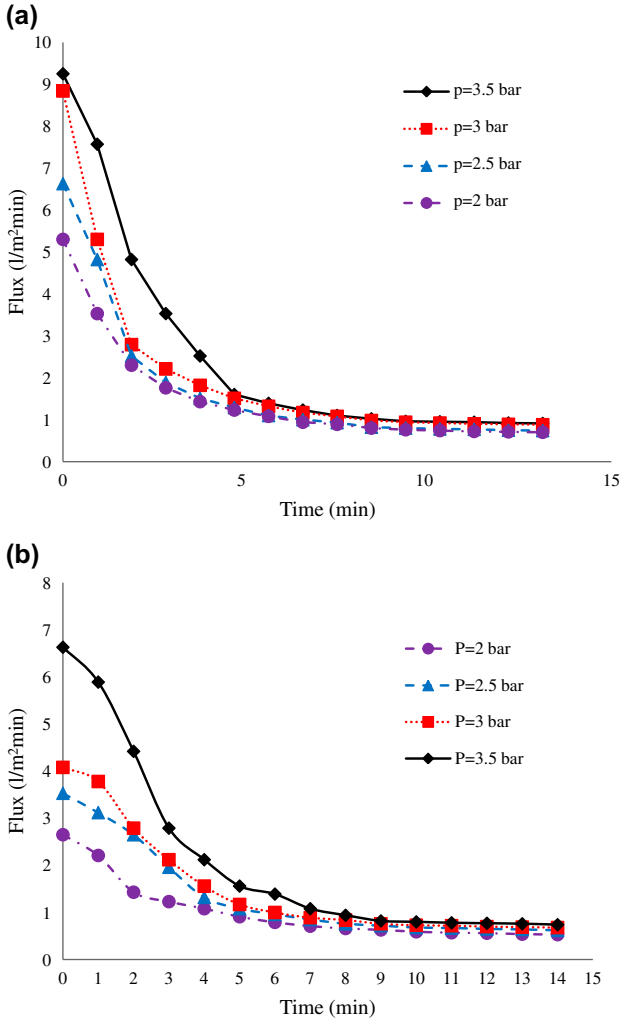

Fig. 3. Time variation of flux at different TMPs using: (a) CPC and (b) CTAB.

to decrease concentration polarization. The flux continued to decrease until it reached a rather steady state in which either no more change in flux was observed or the change was insignificant. The required time to reach this steady state depends on feed properties, membrane characteristics (material, pore size, etc.), and operating conditions (temperature, TMP, and surfactant concentration in feed phase). The results of these experiments showed that the steady state occurred almost after the 9th minute of process. Comparing CPC and CTAB, it is obvious that the initial flux was higher when CPC was applied. However, the rate of flux decline was more severe when CPC was used since both systems reached the plateau of almost 1 L/m^{2}h after 9 min. In addition, the effect of process parameters on the rate of flux decline was different in these two systems of surfactants. The detailed analysis of the flux behavior is discussed in sections 3.2.1–3.2.3.

3.2.1. Effect of TMP on permeate flux

To assess the effect of TMP on process performance, experiments were performed at temperature of 20 °C, surfactant concentration of 20 mM, and TMPs of 2, 2.5, 3, and 3.5 bars. CPC was used in the first set of experiments and CTAB was used in the second set and the corresponding flux variations can be seen in Fig. 3(a) and (b), respectively.

According to the figures, increasing TMP increased permeate flux because TMP is the effective driving force for process, the increase of which could force more solution to filter through the membrane, leading to a higher permeate flux [10,13]. Comparing the two surfactants, CPC and CTAB, it is concluded that TMP increase was more effective in increasing the flux when CPC was used.

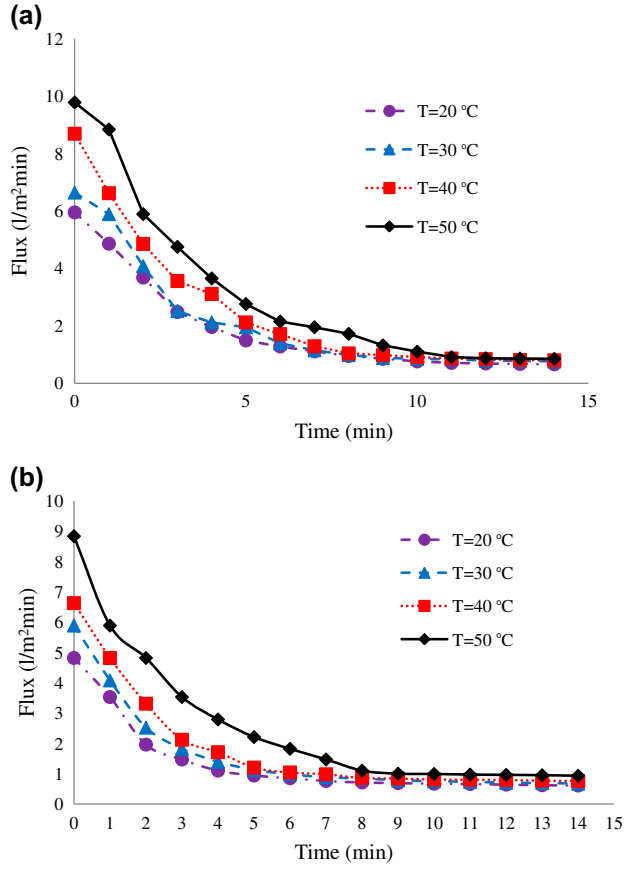

Fig. 4. Time variation of flux at different temperatures using: (a) CPC and (b) CTAB.

3.2.2. Effect of temperature on permeate flux

The effect of temperature on MEUF process was investigated at TMP of 2.5 bars and surfactant concentration of 20 mM. The obtained results using CPC and CTAB as the MEUF surfactants are shown in Fig. 4(a) and (b), respectively.

A simple model of liquid flow through UF membranes is to describe the membranes as a series of cylindrical capillary pores of diameter d. The liquid flow through a pore (q) is given by Poiseuille's law as [16]:

$$q = \frac{\pi d_4}{128 \mu l} \Delta p \quad (2)$$

where Δp is the pressure difference across the pore, μ is the liquid viscosity and l is the pore length. It is clear that at low temperatures, liquid viscosity is higher. With respect to Eq. (2), viscosity increase resulted in less liquid flow through the membrane pores which means less permeate flux. However, two phenomena occurred, when the temperature was increased; when the temperature was increased, the feed viscosity decreased and therefore, an increase in its permeability was observed [17]; furthermore, membrane pores expanded at higher temperatures and permeate flux was enhanced [12,17,18]. In a comparative analysis, temperature increase had more positive effect on flux when CTAB was applied.

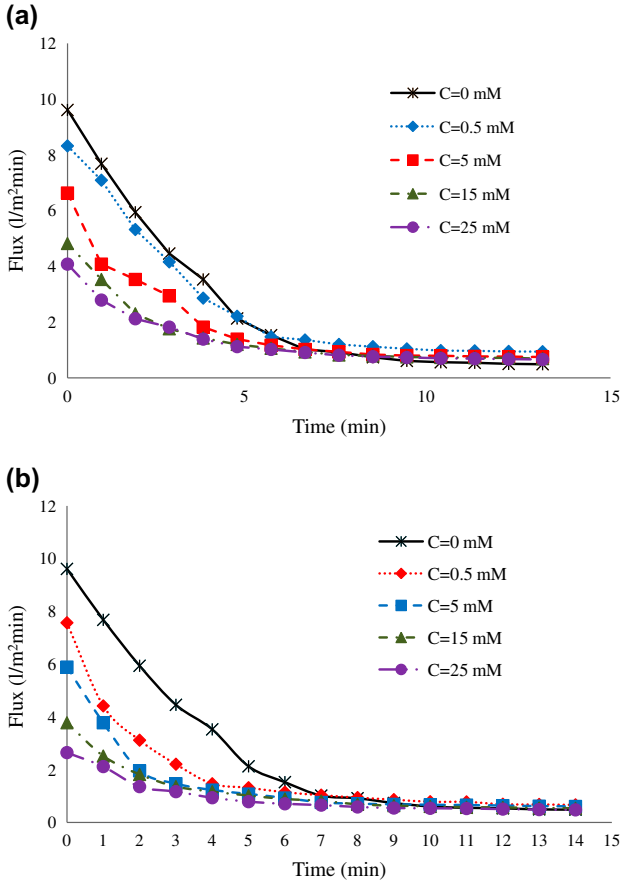

Fig. 5. Time variation of flux at different surfactant concentrations: (a) CPC and (b) CTAB.

3.2.3. Effect of surfactant concentration on permeate flux

Flux variation with surfactant concentration was studied at temperature of 20°C and TMP of 2.5 bars. The results belonging to CPC and CTAB can be seen in Fig. 5(a) and (b), respectively. Results show that applying each of the surfactants led to flux decline. Even when the surfactant concentration was increased, flux decreased. The reason is the increased number of micelles formed in the solution because of the increased surfactant concentration. In fact, the deposited layer of micelle aggregates offered more resistance against the permeate flux through the membrane [4,13,19]. It should be noted that the flux decline at surfactant concentrations below the CMC was due to the concentration polarization effects which led to the formation of micelles next to the membrane surface [4,13].

Comparing CPC and CTAB, the flux decline was more severe with CTAB when a similar surfactant concentration increase was applied to both systems of surfactants.

3.3. Rejection of wastewater pollutants

The effect of TMP, temperature, and surfactant concentration on the rejection of wastewater pollutants were investigated. COD, TDS, turbidity, and conductivity of the wastewater were used as the indicators of wastewater pollution. The tests were implemented using each of the surfactants, CPC and CTAB to compare the performance characteristics of these systems and the results are shown in Figs. 6–8. According to the figures, the most and least rejection percent belonged to turbidity (up to almost 98%) and COD, respectively, showing that the microorganisms and colloidal particles that cause turbidity were well removed by this process. The percentage of rejection of TDS and conductivity were almost the same. Comparing the two surfactants, CPC and CTAB, rejection was slightly higher when CPC was applied.

3.3.1. Effect of TMP on rejection behavior

To study the effect of TMP on rejection percent of pollutants, experiments were performed at temperature of 20°C, surfactant concentration of

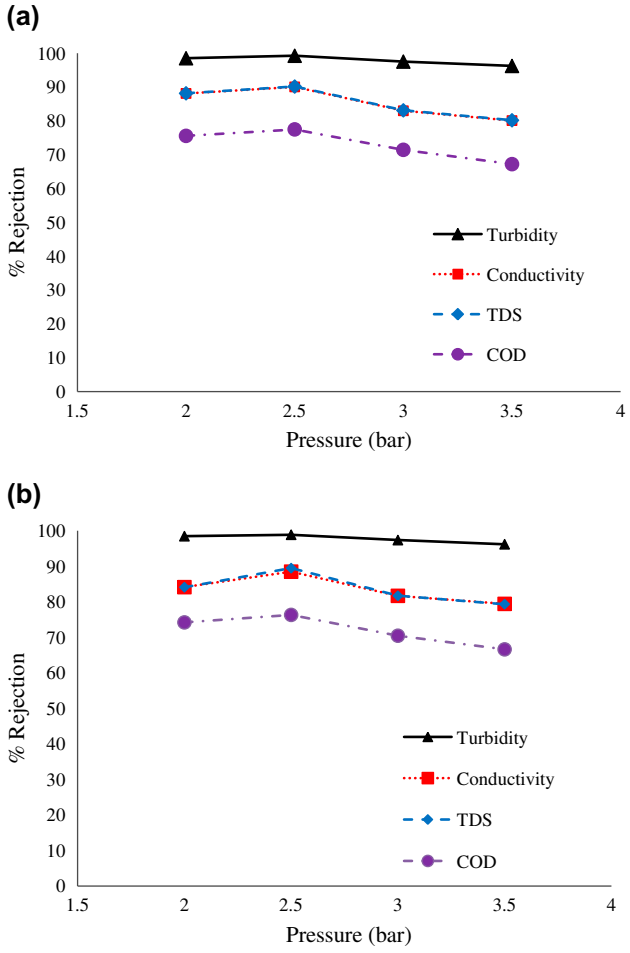

Fig. 6. Effect of TMP on rejection percent of pollution indicators using: (a) CPC and (b) CTAB.

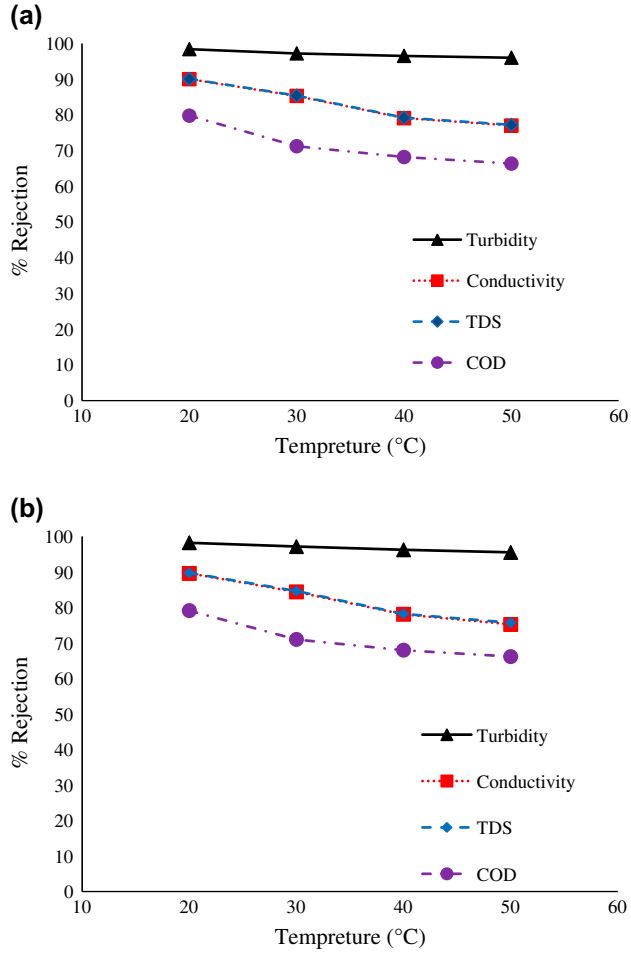

Fig. 7. Effect of temperature on rejection percent of pollution indicators using: (a) CPC and (b) CTAB.

20 mM, and TMPs of 2, 2.5, 3, and 3.5 bars. CPC was used in the first set of experiments, and CTAB was used in the second set and the corresponding variations in pollution indicators reduction are shown in Fig. 6(a) and (b), respectively.

When TMP was increased, rejection slightly enhanced initially because permeate flux increases with pressure resulting in more solvent and solute passing through the membrane. However, solute flux remains lower than that of solvent which leads to rejection increase. Further increase in TMP reduced rejection due to the following reasons: at higher operating pressure, micelles might be compacted, thereby decreasing the micelle solubilization capability, and therefore, a lower quantity of pollutants would be solubilized within the micelles [10,20,21]; in addition, the increase in driving force causes the increment of the convective transport of solutes through the membrane [13]. Moreover, micelles degrade at high operating pressure which leads to the reduction in effective bonding positions [10]. With respect to the figures, the adverse effects of TMP increase were more dominant in this system.

Comparing CPC and CTAB, the decreasing effect of TMP increase was slightly more when CPC was applied.

3.3.2. *Effect of temperature on rejection behavior*

The effect of temperature on rejection was investigated at TMP of 2.5 bars and surfactant concentration of 20 mM. Fig. 7(a) and (b) show the obtained results using CPC and CTAB as the MEUF surfactants, respectively. Rejection of pollutants decreased with temperature because of the increased diffusion of solutes through the membrane [10] and also the expansion of pores at higher temperatures [10,12,17,18]. Furthermore, CMC of surfactant is a function of temperature and it rises as temperature is increased due to the de-micellization process. In fact, at high temperatures, the micelles dissociate easily and

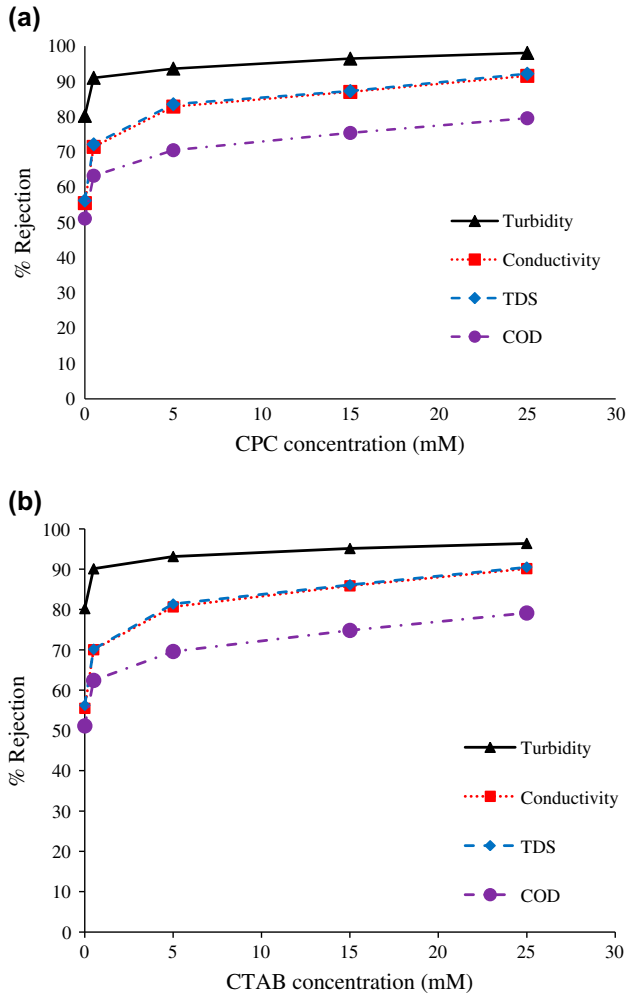

Fig. 8. Effect of surfactant concentration on rejection percent of pollution indicators: (a) CPC and (b) CTAB.

micelle number as well as its size decrease. It results in the passage of more surfactant monomers through the membrane resulting in rejection decline [17]. Analysis of rejection results shows that the variation of rejection was the same in both systems surfactants.

3.3.3. Effect of surfactant concentration on rejection behavior

Effect of surfactant concentration on rejection was studied at temperature of 20 °C and TMP of 2.5 bars. The results related to CPC and CTAB can be seen in Fig. 8(a) and (b), respectively. It is clear that the pollution indicators retention increased sharply after each of the surfactants was added to the system. From the figures, even when the surfactant concentration was lower than its CMC, although the surfactant micelles formation was almost negligible, the pollutants removal efficiency was enhanced which was similar to the literature data [13]. The reason was the concentration polarization effect, leading to a deposited layer on the membrane surface, in which the surfactant concentration might have exceeded the CMC value and therefore had formed micelles which would possibly solubilize some pollutant molecules [22]. The rejection continued to increase significantly with surfactant concentration increasing to 5 mM, and then, it increased slowly at higher surfactant concentrations. This result was attributed to an increase in the aggregation number of micelles. In fact, as the surfactant concentration increases, the number of micelles will increase, so more pollutant molecules should dissolve in micelles leading to more recovery and higher rejection [4,13]. However, at surfactant concentrations higher than CMC, micellar shape changes from spherical to cylindrical or plate like and thereby it could be easily crossed through the membrane pores causing the formation of more micelles less effective [13,23]. Comparing CPC and CTAB, increasing CPC concentration provided a slightly higher rejection enhancement for the process.

4. Conclusion

Raisins processing wastewater was treated in an MEUF process using PAN membrane. The permeate flux as well as the rejection of pollutants based on indicators such as COD, TDS, turbidity, and conductivity has been investigated under variable operating conditions (TMP, temperature, and surfactant concentration), using CPC and CTAB as surfactants. Although the permeate flux decreased when each of the surfactants were added to the process, pollutants rejection was enhanced compared with the surfactant-free system. 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, increasing the tangential speed of the feed on the membrane surface in order to decrease concentration polarization, etc. In this way, adding surfactants would be more advantageous.

According to the results, turbidity and COD showed the highest and lowest rejections, respectively. Rising TMP or temperature led to the rejection decrease and flux increase. However, rejection of pollutants increased and flux decreased with increasing surfactant concentration. Comparing CPC and CTAB, it is concluded that CPC provided higher rejection of pollutants. Moreover, the initial flux was higher when CPC was applied.

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