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Factorial experimental design for treatment of an industrial wastewater using micellar-enhanced ultrafiltration

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ABSTRACT

In the present study, micellar-enhanced ultrafiltration (MEUF) using linear alkylbenzene sulfonate (LAS) surfactant was applied in order to treat soft drink processing wastewater. The effects of two parameters of LAS surfactant concentration and transmembrane pressure (TMP) on the separation performance and flux were studied by applying a full factorial design. It was found that LAS concentration and TMP had negative and positive effect on the flux, respectively. The results showed that the optimum TMP for rejection of pollution indices of the wastewater was equal to 3.5 bars at the surfactant concentrations above critical micelle concentration (CMC). In addition, the stable flux and rejections were precisely predicted by the full factorial design models.

Keywords: MEUF process; Surfactant; Critical micelle concentration; Full factorial design

1. Introduction

Food industry is one of the biggest contributors of wastewater contamination, so that high load of organic compounds is one of the main disadvantages of the wastewater discharge from this industry [1,2]. The wastewaters resulting from food processing industries such as wastewater of soft drink industry usually have high concentrations of contaminant. Various treatment techniques have been developed to improve the quality of soft drink wastewater. Treatment of this wastewater has been studied by using the anaerobic and aerobic treatment systems, such as anaerobic biological fluidized bed reactors, anaerobic up-flow packed bed reactor, and two-stage aerated lagoons [3].

The advances in membrane technology have had benefits for treatment of food industry wastewater such as reuse of one or both the output streams [4]. In some of the most important types of membrane filtration such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), the driving force can be created by a difference in pressure [5,6]. Among these membrane separation processes, UF and NF have the characteristics between those of MF and RO and have recently gained noticeable interest due to their effective role in removal of natural organic matter (NOM) and synthetic organic compounds (SOCs) while still maintaining a high permeate flux [5]. In NF and RO operations, the membrane pore size is smaller than that of UF and MF; thus, they are able to retain metal ions and small organic molecules, but their applications in wastewater treatment is limited due to three reasons. First of

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all, high operating pressure is required. Secondly, the permeate flux tends to be generally low and the last, the decline in the permeate flux occurs due to concentration polarization and membrane fouling [7–9]. Unfortunately, MF and UF also have deficiencies such as low rejection potential [9]. In order to defeat the problems, an alternative approach i.e. micellar-enhanced ultrafiltration (MEUF) has been introduced [10]. MEUF is a promising technology to remove organic and inorganic contaminants simultaneously using surfactant under mild conditions. A surfactant is a substance including hydrophilic head and hydrophobic tail. Surfactant monomers form a micelle above critical micelle concentration (CMC). Organic compounds are solubilized into the core of micelle and inorganic contaminants can be bound on the surface of oppositely charged micelle [11]. At this condition, the hydrodynamic diameter of pollutants is significantly large, so they can be retained by an UF membrane system which has higher permeate flux and lower energy consumption than NF or RO membrane systems. In other words, this method combines high selectivity of RO and high flux of UF [12,13].

Many researchers have proved that MEUF process has shown an excellent performance in the separation of different contaminants from synthetic wastewaters. However, few papers have discussed the treatment of real wastewaters by MEUF process. Therefore, in the present study, an attempt was made to investigate the effect of transmembrane pressure (TMP) and linear alkylbenzene sulfonate (LAS) surfactant concentration on the flux and removal efficiency of chemical oxygen demand (COD), total dissolved solids (TDS), and turbidity of soft drink processing wastewater using MEUF process. A full factorial design was also applied for this purpose.

2. Experimental

2.1. Materials

The anionic surfactant used, LAS ($C_{12}H_{25}C_6H_4SO_3Na$, MW 348.48), was obtained from Sigma-Aldrich. The CMC of this surfactant is 1.2 mM [14]. The wastewater was sampled from a local soft drink industry unit. Three pollution indices of the wastewater i.e. turbidity, COD, and TDS were in the range of 2,000–3,000 NTU, 6,900–7,500 mg/l, and 900–1,800 mg/l, respectively. PAN-350 flat membrane, supplied from Sepro, was used in the experiments. As reported by the supplier, this membrane has provided 80% rejection for 20 kDa poly (ethylene glycol). Maximum process temperature for this membrane is 100˚C. The membrane thickness is 0.165 mm. Distilled water, NaOH, and HCl were applied for the membrane cleaning.

2.2. Experimental design and procedure

The experimental setup used in the MEUF experiments consists of a feed tank, a cross-flow module, a pump, two pressure gauges, two thermometers, two flow meters, and a heat exchanger. The schematic of experimental setup applied in this research can be found elsewhere [15]. The effective membrane area in the module is 70.88 cm^2. In order to make 8,000 cm^3 feed solution, first of all, required amount of the surfactant was calculated and added to 1,000 cm^3 fresh soft drink wastewater. Then, the solution was stirred using a magnetic stirrer for about 10 min at a constant speed of 600 rpm to provide complete mixing. After being fully mixed, the solution was added to 7,000 cm^3 wastewater and stirred for about 10 min at a constant speed of 110 rpm, and settled down for about 1.5 h after complete blending to ensure formation of micelles. Then, the solution was poured into the feed tank and pumped to the membrane module.

At the beginning of the process, pure water flux (PWF) was measured and this value was used as the basis value for the membrane PWF. After each run, in order to overcome the membrane fouling, the membrane was perfectly washed with distilled water, 1% NaOH solution, distilled water, 0.1 M HCl solution, and distilled water. Then, the membrane was placed into the ultrasonic bath of model PS-30A for sonication. After the cleaning process, the membrane PWF was checked to ensure that it remains nearly constant between sequential runs.

The flux was determined via division of permeate flow rate by effective membrane area in the module. To evaluate the filtration efficiency in removal of pollution indices of COD, TDS, and turbidity of the wastewater, their values in the feed and permeate were measured. The COD was measured by using thermoreactor of RD125 for the heating and digestion of COD vials contents along with COD photometer from Lovibond Tintometer (Germany). Conductivity meter of Extech EC-400 (USA) was used for measuring the TDS. Lutron electronic turbidity meter (model TU-2016, Taiwan) was used in order to measure the turbidity.

In the present study, a full factorial design was employed with the aid of Design Expert version 8.0.7.1 statistical software. In statistical sciences, a factorial design consists of two or more factors at discrete possible levels, and the experimental runs take on all possible treatment combinations of these levels across all factors [16,17]. Basically, factorial designs are used to determine which factors are significant and screen them, but when the number of factors is smaller than five, full factorial design can also be used successively to model and refine a process [17,18]. The advantage of this design is that the maximum information regarding the factors is obtained. It is also possible to identify the interactions between separate experimental factors and the effect that such interactions have on the experimental response [17]. Thus, the experiments in the present study were designed to investigate the effects of two important factors in MEUF process i.e. TMP and feed LAS concentration on the permeate flux and rejection of COD, TDS, and turbidity of soft drink wastewater. The feed surfactant concentration and TMP were varied from 0 to 5 mM and 2 to 4 bars, respectively. Table 1 represents the all possible factor-level combinations which are considered in this study.

3. Results and discussion

3.1. Effect of operating time, surfactant concentration, and TMP on permeate flux

The permeate flux is one of the most significant factors in the evaluation of performance of a MEUF system. In this regard, Fig. 1 displays the permeate flux variations vs. operating time. As shown in this figure, the flux variations followed similar trends at different LAS concentrations. The permeate flux was decreased with the increase of operating time. This phenomenon is related to the membrane fouling and concentration polarization in which the accumulation of surfactant and retained solutes on the membrane surface gradually increase over time. The accumulation will continue until a gel layer is formed on the membrane surface and acts as an additional resistance to permeate. Thus, the permeate flux was decreased until it reached a stable flux in which the flux change was negligible [19,20].

Fig. 2 illustrates variations of the stable flux at several TMPs vs. various concentrations of LAS. As shown in Fig. 2, a decrease in the stable flux is observed by increasing LAS concentration. When the surfactant concentration is below CMC, the flux reduction is attributed to the following three main reasons [20,21]. First of all, the presence of precipitates of the contaminant and surfactant, which aggregate to form a cake on the membrane surface and in the membrane pores. Second of all is adsorption of the contaminants and surfactant on the membrane surface. The last reason is the formation of a deposited layer close to the membrane surface due to concentration polarization phenomenon. At the LAS concentrations above CMC, the deposited micelle layer presents more resistance against the flux through the membrane [21], hence the flux is reduced.

Moreover, considering Fig. 2, increasing the TMP increases the stable flux at each LAS surfactant concentration. In pressure-driven membrane separation processes such as UF, TMP increase leads to an increase in the driving force across the membrane and consequently usually causes the stable flux increase [20,21].

Table 1
Experimental design layout

Standard run no.	Run no.	A: LAS concentration (mM)	B: TMP (bars)	Standard run no.	Run no.	A: LAS concentration (mM)	B: TMP (bars)
1	2	0	2	16	4	3	3
2	30	1	2	17	17	4	3
3	9	2	2	18	22	5	3
4	29	3	2	19	26	0	3.5
5	11	4	2	20	28	1	3.5
6	15	5	2	21	7	2	3.5
7	14	0	2.5	22	3	3	3.5
8	10	1	2.5	23	16	4	3.5
9	20	2	2.5	24	19	5	3.5
10	6	3	2.5	25	13	0	4
11	25	4	2.5	26	21	1	4
12	23	5	2.5	27	27	2	4
13	18	0	3	28	24	3	4
14	8	1	3	29	5	4	4
15	1	2	3	30	12	5	4

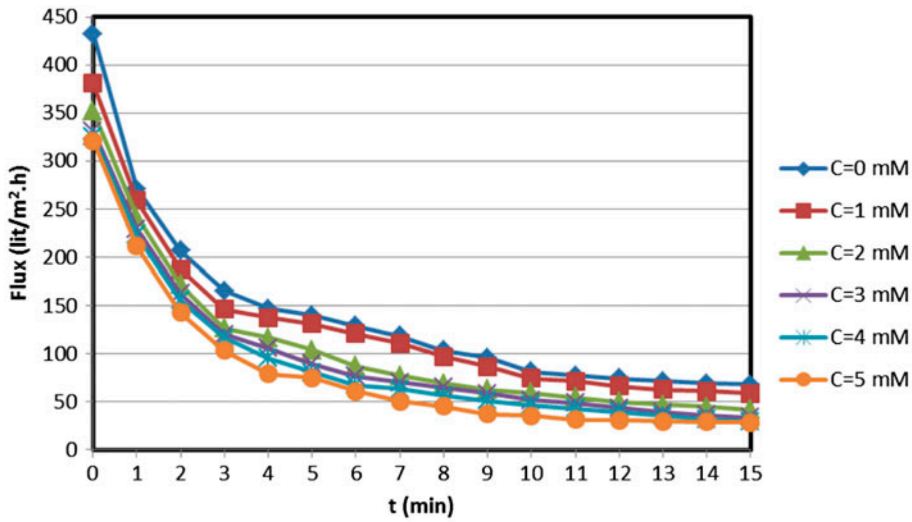

Fig. 1. Effect of time on permeate flux in various LAS concentrations and TMP = 3.5 bars.

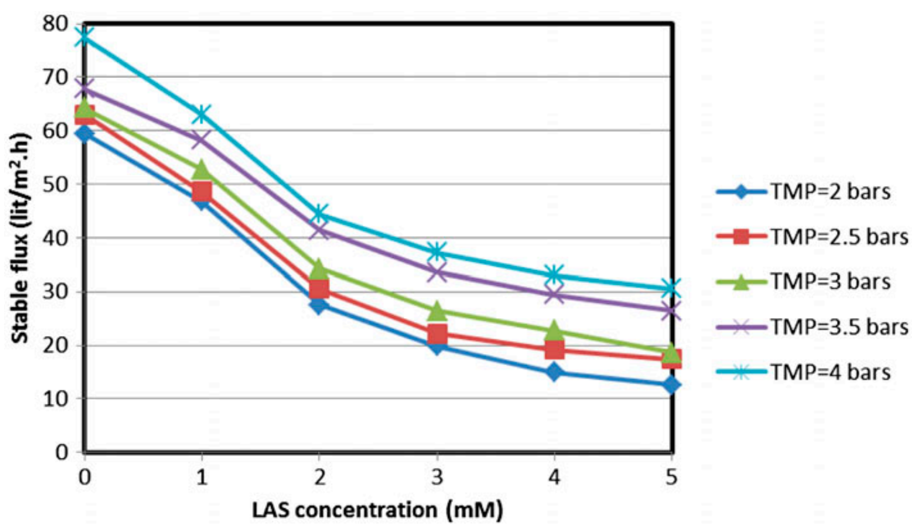

Fig. 2. Effect of LAS concentration and TMP on stable flux.

3.2. Effect of surfactant concentration and TMP on COD removal

The effect of feed LAS concentration at various TMPs on COD rejection is displayed in Fig. 3. The results show that UF process alone cannot efficiently reduce COD of the wastewater, but by increasing TMP; the rejection of COD by this process can be enhanced. Fig. 3 also reveals that there is an initial rapid rise in COD rejection with increasing the concentration of LAS at each TMP. This behavior is due to the fact that in the concentrations below CMC, the possibility of micelles formation in the layer near to the membrane surface was increased due to concentration polarization. It means that a number of LAS monomers start to create the micelles at the concentration polarization layer because the surfactant concentration in this layer is more than that of the bulk solution [20]. Although COD rejection is improved by increasing the surfactant concentration above CMC, this improvement is not very significant, probably because the solubilization of organic compounds on the micelles is saturated [22]. Incidentally, COD rejection is decreased with increasing the feed LAS concentration at high TMPs and concentrations because the

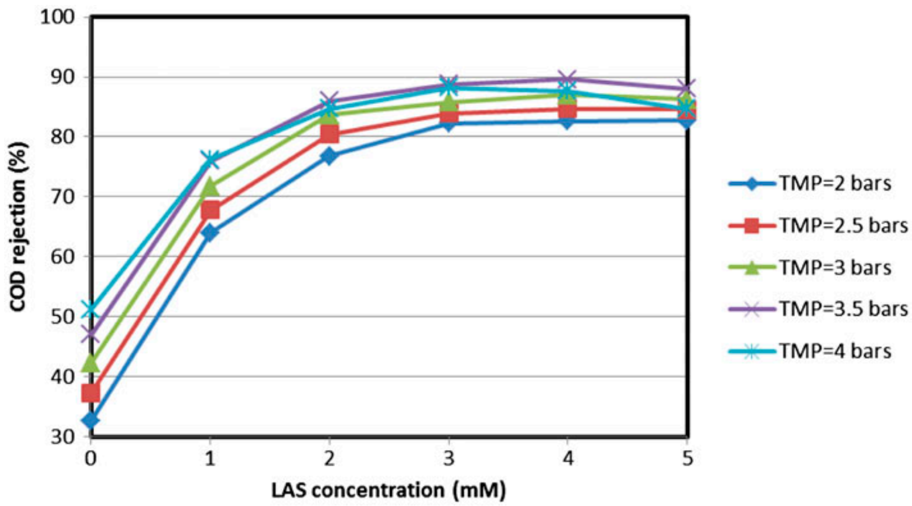

Fig. 3. Effect of LAS concentration and TMP on COD rejection.

micelles get compact and their solubilization capacity decreases [14,22]. The results show that maximum COD rejection is obtained at the TMP of 3.5 bars and the LAS concentration of 4 mM. At the LAS concentrations below CMC, the rejection at TMP of 4 bars is better than that of 3.5 bars, but with increasing the LAS concentration above CMC, the rejection at TMP of 3.5 bars shows the optimum condition due to the micelles compaction in higher TMPs.

3.3. *Effect of surfactant concentration and TMP on removal of TDS and turbidity*

Usually, turbidity of wastewaters using UF membranes is well reduced. As shown in Fig. 4, in the presence or absence of LAS surfactant, turbidity rejection is above 99%. Therefore, adding the surfactant does not have a considerable effect on turbidity removal.

With respect to Fig. 5, the trend of TDS rejection is almost similar to that of COD rejection. It means that TDS rejection is increased by increasing LAS surfactant concentration. The results reveal that UF process cannot be solely sufficient to reduce TDS of the wastewater. Moreover, an increase in the surfactant concentration over 2 mM has no important effect on the rejection. The optimum TMP for rejection of turbidity and TDS from soft drink wastewater is equal to 3.5 bars at the surfactant concentrations above CMC.

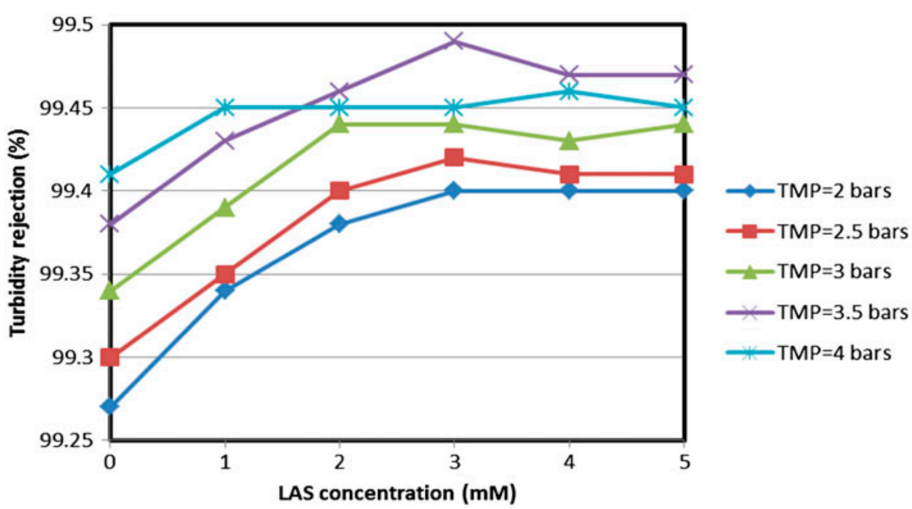

Fig. 4. Effect of LAS concentration and TMP on turbidity rejection.

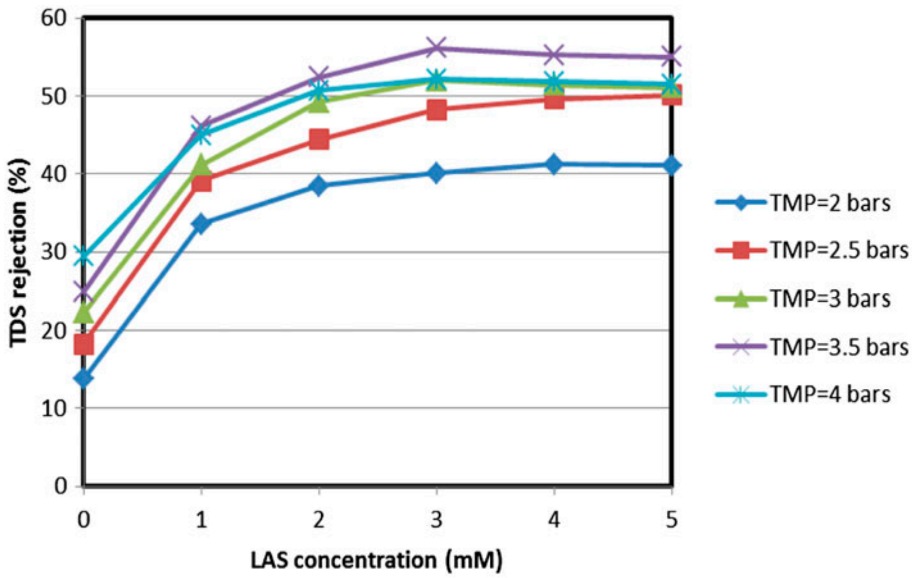

Fig. 5. Effect of LAS concentration and TMP on TDS rejection.

3.4. Statistical analysis

Various statistical parameters can be found in Tables 2 and 3. The model F values for the responses i.e. stable flux and rejection of COD, TDS, and turbidity were 806.93, 161.50, 178.36, and 33.94, respectively. These values indicate that the models are statistically significant, and there is only less than 0.01% probability that these levels of fit can occur due to

Table 2
Analysis of variance (ANOVA) for selected factorial models

Source of variation	Sum of squares	Degree of freedom	Mean square	*F*-value	*P*-value Prob > *F*	
Model for stable flux	9,438.22	9	1048.69	806.93	< 0.0001	Significant
A-LAS concentration	8,247.41	5	1,649.48	1,269.22	< 0.0001	
B-TMP	1,190.81	4	297.70	229.07	< 0.0001	
Residual	25.99	20	1.30			
Cor total	9,464.21	29				
Model for COD rejection	7,843.28	9	871.48	161.50	< 0.0001	Significant
A-LAS concentration	7,489.04	5	1,497.81	277.58	< 0.0001	
B-TMP	354.24	4	88.56	16.41	< 0.0001	
Residual	107.92	20	5.40			
Cor total	7,951.20	29				
Model for TDS rejection	3,753.62	9	417.07	178.36	< 0.0001	Significant
A-LAS concentration	3,059.64	5	611.93	261.69	< 0.0001	
B-TMP	693.98	4	173.49	74.19	< 0.0001	
Residual	46.77	20	2.34			
Cor total	3,800.39	29				
Model for turbidity rejection	0.072	9	7.954E-003	33.94	< 0.0001	Significant
A-LAS concentration	0.038	5	7.526E-003	32.12	< 0.0001	
B-TMP	0.034	4	8.488E-003	36.22	< 0.0001	
Residual	4.687E-003	20	2.343E-004			
Cor total	0.076	29				

Table 3
Statistical parameters used to test goodness of fit of the factorial models

Statistical parameter	Stable flux	COD rejection	TDS rejection	Turbidity rejection
Std. Dev.	1.14	2.32	1.53	0.015
Mean	38.12	75.48	43.18	99.41
CV%	2.99	3.08	3.54	0.015
R^2	0.9973	0.9864	0.9877	0.9386
Adjusted R^2	0.9960	0.9803	0.9822	0.9109
Predicted R^2	0.9938	0.9695	0.9723	0.8617
Adequate precision	95.172	39.699	47.344	20.932

random chance [16]. Values of "Prob > F" less than 0.05 indicate the model terms are significant. Thus, both terms in the models have a significant effect on the responses, because all *P*-values are less than 0.0001.

Coefficient of determination (R^2) is used to assess how well a model explains and predicts responses. It is proposed that R^2 should be close to 1 for an acceptable model. The predicted model for each response has a proper R^2 value as shown in Table 3. But this statistical parameter always increases as terms are added to the model. In order to solve this problem, adjusted-R^2 is used, because it is adjusted for the model size, more specifically the number of factors [16]. Table 3 shows that the R^2 and adjusted-R^2 values for the models do not differ considerably, indicating significant terms of LAS concentration and TMP have been included in the models. Predicted-R^2 measures the amount of variation in the new data explained by the model [23]. Regarding Table 3, the values of predicted-R^2 are almost close to the values of adjusted-R^2. Adequate precision measures the signal-to-noise ratio [23]. The values greater than 4 are desirable to indicate adequate model discrimination [24]. With respect to Table 3, the value of this statistical parameter is well above 4 for all the responses. Coefficient of variation (CV) is the standard deviation expressed as a percentage of the mean and is calculated by dividing the standard deviation by the mean value and multiplying by 100. As a general rule, it should not be greater than 10% for a good fit to the selected model [23]. It is less than 10% for all the responses.

The residuals from a factorial experiment play an important role in evaluating the final model adequacy. The normal probability plot of the studentized residuals is used to check this adequacy. As shown in Fig. 6 for COD rejection response, the points on this plot lie reasonably close to a straight line, confirming that the errors are normally distributed with mean zero and constant [16]. The same results for the other responses were obtained.

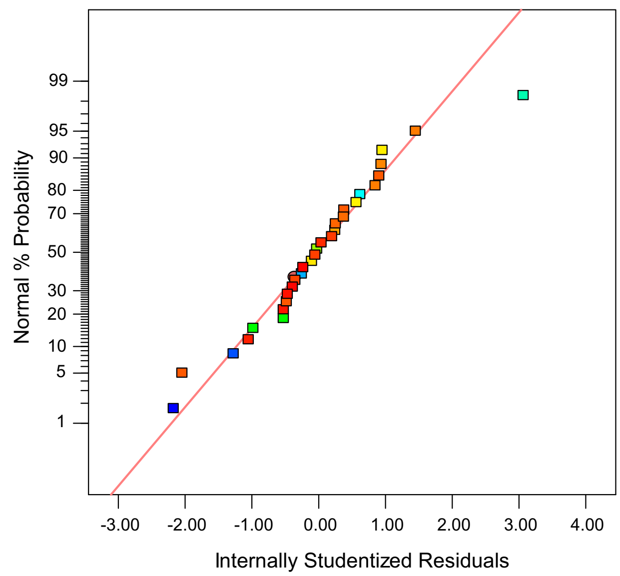

Fig. 6. Normal probability plot of residuals for COD rejection in MEUF process.

The independence of the errors is analyzed by plotting the residuals vs. different independent variables [16]. The plot of the studentized residuals vs. the predicted values is depicted in Fig. 7 for turbidity rejection response. The similar results for the other responses were obtained. Regarding this figure, there is no unusual structure showing a certain pattern for the variance, so there is no reason to suspect any violation of the independence or constant variance assumption [16].

The predicted values vs. the actual data are shown in Fig. 8 for stable flux response. The same results for the other responses were obtained. This plot represents how the model predicts over the range of data. The line goes through the middle of the data over the whole range of them. As it can be seen from Fig. 8, the full factorial design provides the results very close to the experimental measurements. The scatters show

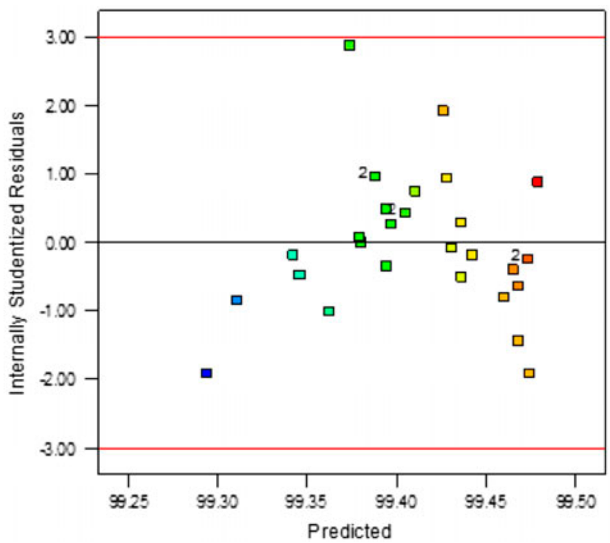

Fig. 7. Plot of studentized residuals vs. predicted response for turbidity rejection in MEUF process.

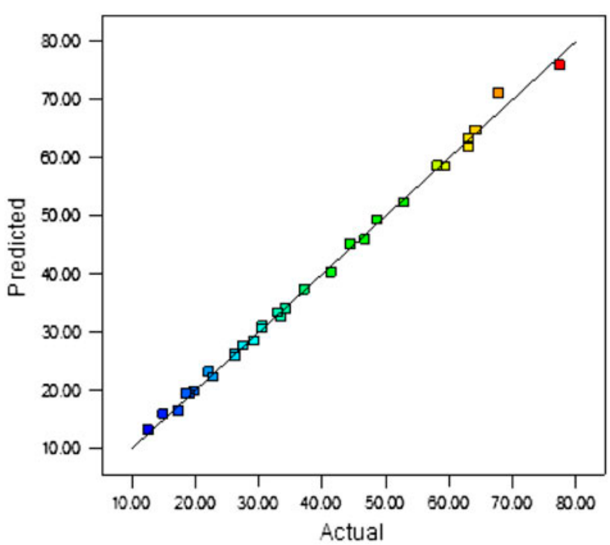

Fig. 8. Correlation between experimental data and predicted values for stable flux in MEUF process.

that the stable flux and rejections can be predicted very precisely by the full factorial design models.

4. Conclusion

The effect of significant factors of LAS concentration and TMP was investigated on the performance of MEUF process in treatment of soft drink wastewater. The results indicated that UF process alone cannot efficiently reduce COD and TDS of the wastewater. The rejection values were increased with increasing the surfactant concentration, but they were not increased effectively at the LAS concentrations above CMC. Furthermore, the optimum TMP was 3.5 bars for the removal of contaminants at the LAS concentrations above CMC. The flux was increased by decreasing feed LAS concentration and increasing TMP. The full factorial models were interpreted by analysis of variance. The comparison of the predicted values with the experimental data showed that there was a satisfactory agreement between them. Generally, the results proved that the application of MEUF process is useful in treatment of soft drink wastewater.

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