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Application of nanofiltration as a tertiary treatment in a polyester production industry for wastewater reuse

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ABSTRACT

Membrane technology is one of the most efficient approaches for the treatment of industrial wastewater and reuse. In this study, the influence of influential parameters, including pH, feed pressure, sulfate concentration, and chemical oxygen demand (COD) on the simultaneous removal efficiency of pollutants in Polyacryl Iran Company, were investigated by applying a commercial TFC polyamide nanofilter. The three leveled factors of sulfate and COD concentration, feed pressure, and pH were considered in the range of 550–1,283 mg L^{-1}, 85–198 mg L^{-1}, 0.5–0.9 MPa, and 5–9, respectively. By increasing pH from 5 to 9, the sulfate and COD removal efficiency increased up to 90%, and also by increasing feed pressure from 0.5 to 0.8 MPa, the removal rate of COD increased to 92%, whereas the effect of feed pressure on the sulfate removal was found insignificant. Results also indicated that an increase in the COD concentration resulted in a reduction in the removal efficiency of COD from 96 to 82%. On the other hand, by increasing the sulfate concentration to 800 mg L^{-1}, an increase in the sulfate removal efficiency from 94 to 96% was observed. A further increase in the sulfate concentration resulted in the reduction of sulfate removal efficiency.

Keywords: Nanofiltration; Reuse; Textile wastewater; Sulfate; Wastewater treatment

1. Introduction

Population growth, alongside with a significant increase in the industrial water demand, has made wastewater reuse essential. This is the particular case of textile industries, which are characterized by their high water consumption rate and pollution level. Wastewater of textile industries is contaminated with high values of conductivity, chemical oxygen demand (COD), color, and turbidity. The physical and chemical treatments typically used to treat the textile wastewater are not sufficient enough to purify the wastewater to the standard level of reuse, and further treatment is usually necessary. While biological processes generate a large amount of sludge and are not able to remove water salinity, membrane processes provide a chance for a significantly better water treatment and reuse [1,2].

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Membrane technology is considered as one of the most efficient processes to treat industrial effluents for water reuse. Among the membrane processes, nanofiltration (NF) is a suitable choice for wastewater reuse in textile industry, since it operates at medium pressures but has relatively high fluxes, excellent removals of dyes, COD, and divalent ions. Comparing to NF, reverse osmosis (RO) is able to purify water even better than NF by removing the monovalent ions and organic compounds with the expense of higher operational pressures and energy consumption rate [3,4].

A previous study conducted by Barredo-Damas et al. [5] on the treatment of textile wastewaters by tubular ceramic ultrafiltration (UF) membranes at different operating conditions (transmembrane pressure and pH) showed that at low pH values the COD removal increased with the enhancement of operating pressure. A considerably high COD removal was achieved (>70%), together with a complete turbidity removal (>93%). Therefore, the ceramic ultrafiltration process can be considered suitable as a pretreatment for NF and RO processes. However, they did not investigate the influence of COD concentration on COD removal. In another study, a comparison between RO and NF membranes on COD removal was investigated by Liu et al. [6] They reported that a very high reduction of COD (up to 90%) could be achieved using RO and NF membranes.

According to Liu et al., NF, membranes have shown higher COD removal efficiency due to the sieving exclusion mechanism [6]. They found that the formation of a second layer from dye molecules and the Donnan effect can significantly improve the COD removal efficiency. Similar behavior was also observed by Madaeni and Mansourpanah [7]. However, changes in operating conditions were not investigated.

Current wastewater treatment in Polyacryl Iran Co. is based on an activated sludge process followed by sand filters, which are designed to discharge its output into the surrounding green space. However, due to the recent drought and legislations, the factory has encountered a shortage of water resources and has been looking for a solution to recycle its wastewater.

In this work, a lab-scale membrane system was used for the treatment of real textile wastewater in order to obtain water with enough quality to be reused in the mentioned industry. The waste water samples were characterized and then were treated by a microfilter (MF) and NF process.

The effects of pH, feed pressure, and feed concentration were studied through continuous measurement of sulfate removal and COD retention. This was aimed to obtain the optimum conditions and observation of system behavior in different operating conditions.

2. Materials and methods

2.1. Wastewater characteristics

The study was conducted with a textile wastewater sample provided from Polyacryl Iran Company. Generally, the wastewater comes from the wet and dry spinning of polyester production steps which was treated with activated sludge and sand filters. But, the amount of sulfate concentration in the wastewater is not in compliance with the Iranian standard of wastewater discharge to environment. The physical–chemical characteristics of wastewater entrance to NF are given in Table 1.

2.2. Materials

All the chemicals including NaOH, HCl (%37), $K_2Cr_2O_7$, H_2SO_4, $Hg(NO_3)_2$, and Ag_2SO_4 were purchased from Merck.

2.3. Pilot setup

As schematically presented in Fig. 1, a continuous NF system installed in the factory was applied in this study. A Korean spiral-wound polyamide membrane was used in a nanofilter module. The membrane characteristics are presented in Table 2. The applied pumps were diaphragm type, which were installed in a series arrangement. The pumps output flow and pressure were set to 1.6 L min^{-1} and 8.5 bar, respectively. The membranes were cleaned before each cycle by back-washing for half an hour [9,10]. Also, to reduce the membrane fouling, the feed was prefiltered by a (MF, 5 μm) before entering into the NF stage.

The isoelectric point of the membrane is the pH point at which the surface does not have charge. By adjusting the pH above or under the isoelectric point, surface can have negative or positive stream potential. As it is mentioned in the study, our operating pH

Table 1
Characteristics of wastewater entrance to NF

Parameter	Range	Permitted level*
pH	6.5–7.5	6–8.5
Conductivity at 25˚C (μS/cm^2)	2,000–4,000	–
COD (mg L^{-1})	80–200	<200
TDS (mg L^{-1})	5,100–5,600	–
HCO_3^- (mg L^{-1})	400–500	–
Nitrate (mg L^{-1})	50	–
Sulfate (mg L^{-1})	500–1,300	500

*According to Iranian standard for agriculture reuse [8].

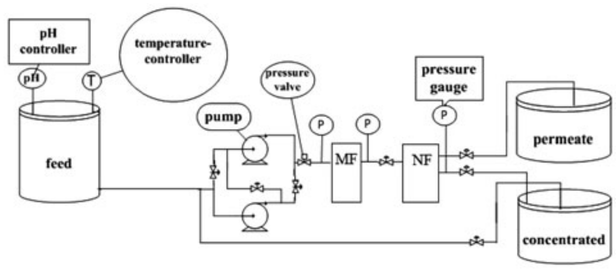

Fig. 1. Schematic view of the pilot system used in this study.

Table 2
Commercial polyamide TFC membrane specifications

Skin layer	Polyamide
Maximum tolerable pressure	20 bar
pH range	2–11
Isoelectric point	4.5
Surface electrical charge	Negative
Active surface (m^2)	0.35

range (5–9) is above the isoelectric point of the membrane, so the membrane surface charge is negative.

2.4. Experimental procedure

The removal efficiency of COD and sulfate after each experiment was determined using the following equation:

$$R\ (\%) = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100 \quad (1)$$

where C_p and C_f represent the measured parameters of COD and sulfate, respectively, in the permeate and in the feed solution. Each experiment was repeated three times to generate standard deviations and to check the reproducibility of the results. The feed temperature was set at 25 ± 1°C, and the recovery percentage was set to about 50 ± 3% [11,12].

2.5. Analysis

All the measurements were performed based on the water and wastewater examination standard methods [13]. Conductivity and pH were measured using a conductivity meter (model MC 226) and a pH meter (model MP 220), respectively. In order to measure the sulfate concentration, a spectrophotometer (UV–Vis model spectronic, USA) was applied. As well as, the basis to measure COD is that nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions. Potassium dichromate is a strong oxidizing agent in acidic conditions. Potassium dichromate is reduced, forming Cr^{3+}. The amount of Cr^{3+} is determined after oxidization is completed and is used as an indirect measure of the organic contents of the wastewater sample.

2.6. Response surface methodology

Response surface methodology is an effective method for response optimization [14]. The Box–Behnken design was used to optimize the response. The design includes three trihedral factors and presents 15 experiment runs. Design Expert software (version 8.0.1) was applied for the experimental design and statistical analysis. To avoid possible errors due to the systematic bias, the confidence level of 95% was considered as well as experiments were conducted randomly. The objective was to obtain the maximum removal efficiency of sulfate and COD as the responses. In this work, samples were taken from three wastewater tanks which were located in the factory (Table 3).

3. Results and discussion

The measured sulfate removal efficiency and COD reduction from the wastewater based on the

Table 3
Factors and their selected levels

Factors	Level 1 code* (−1)	Level 2 code (0)	Level 3 code (+1)
COD (mg L^{-1})	85 ± 2	174 ± 4	198 ± 4
Sulfate (mg L^{-1})	550 ± 11	858 ± 17	1,283 ± 26
Feed pressure (MPa)	0.5 ± 0.1	0.7 ± 0.1	0.9 ± 0.1
pH	5 ± 0.1	7 ± 0.1	9 ± 0.1

*The code (−1), (0), and (+1), respectively, represent the minimum, moderate, and maximum pollution values.

Box–Behnken method and the analysis of variance for the results are presented in Tables 4–6.

The regression factor (R^2) is used to recognize the agreement of the experimental response value and the calculated value by the Box–Behnken method. The results demonstrated that the regression value for the sulfate removal and COD reduction are about 0.91–0.93, respectively, which show that the response surface methodology is an acceptable method, as the regression value is close to one.

Each experiment is repeated twice apart from itself, which means that there are three runs for each experiment to generate standard deviations.

In this study, the experiments were conducted at constant flux by fixing the flux recover at 50% over the experiments. To avoid the contributory effect of concentration polarization and fouling on the next experiments, the membranes were back-washed after each run to assure that the experimental conditions are consistent all across the experiments.

According to Tables 5 and 6, the *F*-values show the importance of each parameter. The parameter with larger *F*-values has more impact on the response. Thus, for sulfate removal, pH has the maximum effect on the removal efficiency, while for COD reduction, COD concentration, pH, and feed pressure are the most

Table 4
Box–Behnken method results

Exp. no.	Sulfate (mg L^{-1})	COD (mg L^{-1})	pH	Feed pressure (MPa)	Sulfate removal efficiency (%)	STDEV. of Sulfate removal	COD removal efficiency (%)	STDEV. of COD removal
1	858 ± 17	174 ± 4	7 ± 0.1	0.7 ± 0.1	96.2	1.75	89.58	1.72
2	550 ± 11	85 ± 2	5 ± 0.1	0.7 ± 0.1	91	1.56	90.52	1.69
3	550 ± 11	85 ± 2	7 ± 0.1	0.5 ± 0.1	95.50	2.10	88.94	1.64
4	1,283 ± 26	198 ± 4	7 ± 0.1	0.9 ± 0.1	92.21	2.10	80.79	1.54
5	858 ± 17	174 ± 4	7 ± 0.1	0.7 ± 0.1	96.25	2.65	91.25	1.68
6	858 ± 17	174 ± 4	9 ± 0.1	0.5 ± 0.1	98.54	0.95	87.38	1.59
7	1,283 ± 26	198 ± 4	7 ± 0.1	0.5 ± 0.1	93.54	2.11	78.65	1.37
8	858 ± 17	174 ± 4	7 ± 0.1	0.7 ± 0.1	94.10	1.75	84.94	2.12
9	1,283 ± 26	198 ± 4	5 ± 0.1	0.7 ± 0.1	90.30	1.85	80.11	1.58
10	858 ± 17	174 ± 4	9 ± 0.1	0.9 ± 0.1	98.12	0.80	93.12	1.02
11	858 ± 17	174 ± 4	5 ± 0.1	0.9 ± 0.1	93.45	1.70	87.50	1.44
12	858 ± 17	174 ± 4	5 ± 0.1	0.5 ± 0.1	93.88	2.05	73.33	1.46
13	550 ± 11	85 ± 2	9 ± 0.1	0.7 ± 0.1	98	0.75	99	0.58
14	550 ± 11	85 ± 2	7 ± 0.1	0.9 ± 0.1	94.80	1.91	93.35	1.10
15	1,283 ± 26	198 ± 4	9 ± 0.1	0.7 ± 0.1	98	0.65	88.28	1.41

Table 6
Analysis of variance for COD removal efficiency

Model terms	Mean square	Sum of squares	d.f.	*F*-value	*P*-value	Status
Model	63.82	574.34	9	7.39	0.0201	Significant
A: COD	240.46	240.46	1	27.85	0.0033	Significant
B: pH	167.63	167.63	1	19.42	0.0070	Significant
C: Pressure	90.72	90.72	1	10.51	0.0229	Significant
A × B	0.093	0.093	1	0.011	0.9214	Not significant
A × C	1.89	1.89	1	0.22	0.6595	Not significant
B × C	17.77	17.77	1	2.06	0.2109	Not significant
A × A	0.85	0.85	1	0.098	0.7668	Not significant
B × B	0.86	0.86	1	0.10	0.7645	Not significant
C × C	51.68	51.68	1	5.99	0.0582	Not significant
Lack of fit	7.26	21.79	3	0.68	0.6414	Not significant
Pure error	10.69	21.38	2	–	–	–

Table 5
Analysis of variance for Sulfate removal efficiency

Model terms	Mean square	Sum of squares	d.f.*	*F*-value	*P*-value	Status
Model	9.84	88.52	9	5.26	0.0412	Significant
A: Sulfate	3.06	3.06	1	1.64	0.2569	Not significant
B: pH	73.99	73.99	1	39.54	0.0015	Significant
C: Pressure	1.04	1.04	1	0.55	0.4902	Not significant
A × B	0.25	0.25	1	0.13	0.7297	Not significant
A × C	0.099	0.099	1	0.053	0.8270	Not significant
B × C	0.02	0.02	1	0.009	0.9972	Not significant
A × A	8.88	8.88	1	4.75	0.0813	Not significant
B × B	0.70	0.70	1	0.37	0.5686	Not significant
C × C	0.40	0.40	1	0.213	0.9503	Not significant
Lack of fit	2.12	6.35	3	1.40	0.4416	Not significant
Pure error	1.51	3.01	2	–	–	–

*Degree of freedom.

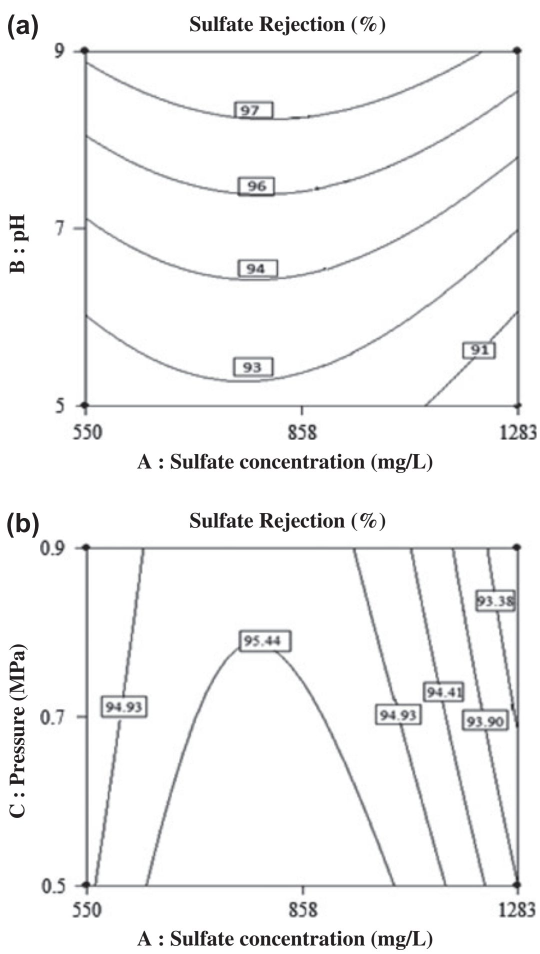

Fig. 2. Effect of parameters on sulfate removal efficiency; (a) the effect of sulfate concentration and pH on the removal efficiency of sulfate at constant feed pressure and (b) the effect of sulfate concentration and feed pressure on the removal efficiency of sulfate at constant pH.

important factors, respectively. It was also found that there was no interaction between the factors.

Response surface graphs for removal efficiency of sulfate as a function of sulfate concentrations, feed pressure, and pH are represented in Fig. 2.

The results of Fig. 2(a) and (b) showed that by increasing the sulfate concentration to about 800 mg L^{-1}, the sulfate removal efficiency slightly increased and then decreased. It could possibly be due to a slight change in the stream potential of the membrane surface. At higher concentration of sulfate, an increase in cation charge density can reduce the negativity of the membrane surface and thus repulsion forces. This leads to the reduction of sulfate removal.

The results demonstrate that by increasing pH from 5 to 9, the sulfate removal efficiency increased from 91 to 97%. Also, it was found that the feed pressure did not affect the sulfate ions removal. The observed results were consistent with previous researches [15,16].

Response surface graphs for COD reduction efficiency as a function of COD concentration, feed pressure, and pH are presented in Fig. 3. The figure shows that with increasing pH from 5 to 9, COD removal efficiency increases from 82 to 96%. Therefore, higher COD retention was achieved at higher pH values. It could be due to the fact that the acidic environment at lower pH values can enhance the hydrolyzation rate of starch significantly.

The results of Fig. 3 illustrated that by increasing the feed pressure from 0.5 to about 0.8 MPa, COD removal efficiency reached about 92%. As the feed pressure increases, the water flux is increased and this results in the enhancement of COD reduction. However, with an increase in feed pressure above 0.8 MPa, COD removal efficiency decreases, since more solutes

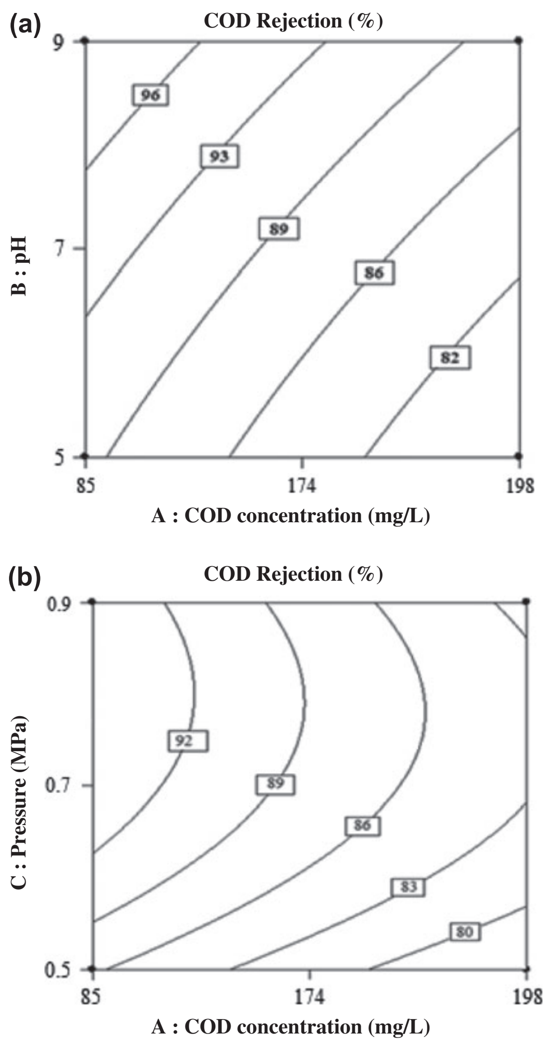

Fig. 3. Effect of parameters on COD removal; (a) the effect of COD concentration and pH on the removal efficiency of COD at constant feed pressure and (b) the effect of COD concentration and feed pressure on the removal efficiency of COD at constant pH.

are able to permeate through the NF membrane at a higher pressure.

According to Fig. 3, the removal efficiency decreases by increasing COD concentration. In fact, the concentration of organic compounds increases with COD concentration enhancement, and they pass through the membrane [17,18].

Similar behavior was observed by Zheng et al. on biologically treated textile effluent through submerged filtration. They found that increasing the transmembrane pressure in NF membrane can slightly increase the COD retention [19].

The optimum conditions for removal of sulfate and COD of the wastewater by Box–Behnken method are estimated in the concentration levels about 550 mg L^{-1} for sulfate and 85 mg L^{-1} for COD, at pH of 9, and feed pressure of 0.8 MPa. Thus, the maximum removal efficiency of sulfate and COD are 97 and 98%, respectively, which are consistent with the experimental results.

4. Conclusions

The results demonstrated that NF using a commercial spiral-wound polyamide nanofilter (TFC) has an acceptable efficiency in simultaneous reduction of sulfate concentration and COD from effluent Polyacryl factory to the standard level of reuse. Sulfate and COD concentrations, feed pressure, and pH have great impacts on the system performance, while interaction between the factors does not have a significant effect on the removal efficiency.

An increase in the pH values resulted in an increase in the removal efficiency of sulfate and COD up to 90%. While increasing the COD concentration, the COD removal efficiency was decreased. It was also found that by increasing feed pressure from 0.5 to 0.8 MPa, the removal efficiency of COD increased to about 92%. While, the feed pressure did not affect the removal of the sulfate ions. The results indicated that by increasing the sulfate concentration to 800 mg L^{-1}, the sulfate removal efficiency increased from 94 to about 96%, and then with enhancement of the concentrations of sulfate, the removal efficiency of sulfate was reduced.

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