



Oily wastewater treatment using ultrafiltration

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ABSTRACT

Treatment of the oily and greasy wastewater of Tehran refinery using an ultrafiltration (UF) system was experimentally studied. In the experiments, a polysulfone (PS) (30 kDa) and a polyacrylonitrile (PAN) (20 kDa) and the API wastewater of Tehran refinery as membranes and feed were used, respectively. Effects of different operating parameters such as transmembrane pressure (TMP), cross flow velocity (CFV), temperature and pH on permeate flux, fouling resistance (R_f) and rejection were studied. According to the results, the optimum operating conditions of the UF process were found as following: TMP (3 bar), CFV (1 m/s), operating temperature (40°C) and pH (9). Performance of the both membranes for the wastewater treatment was compared. The PAN membrane showed higher rejection, permeate flux and less R_f than the PS membrane. Also, when using the PAN membrane, concentration polarization phenomenon and consequently gel layer formation took place quicker. A cleaning procedure was proposed using a metal chelating agent (EDTA) and an anionic surfactant (SDS) which was able to regenerate the fouled UF membranes effectively by optimizing chemical (pH) and physical (cleaning time, CFV and temperature) conditions. Analysis of the UF process showed 99.7%, 77.2%, 63.3%, 65.4%, 29.8%, 100% and 99.5% reductions of oil and grease content, TOC, COD, BOD₅, TDS, TSS and turbidity, respectively. Long term experiments confirmed that UF using the PAN membrane is effective for treatment of oily wastewater produced from refinery processes. A comparative study also showed that UF is more effective than the conventional biological method.

Keywords: Wastewater treatment; Ultrafiltration; Fouling; Chemical cleaning

1. Introduction

Large amounts of wastewaters are generated daily by a variety of industrial sources. An important fraction of these are oil/water emulsions for which current treatment technologies are often costly and ineffective [1]. Oily wastewaters are one of the major pollutants of the aquatic environment. This is due to the emission

of a variety of industrial oily wastewaters from sources such as refineries, petrochemical plants, and transportation [2]. The methods used throughout the world for treatment of oily wastewater can be categorized as creational: coalescence, coagulation, filtration, adsorption, gravity separation, chemical d-emulsification and modern methods based on membrane technologies such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) [1,3]. Wastewater treatment reduces environmental pollution in

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Table 1
Characteristics of the polymeric membranes

Membrane					Recommended operating limits		
Series	Name	Material	MWCO (kDa)	Contact angle (°)	pH range	Pressure range (bar)	Temperature range (°C)
PAN350	PAN	Polyacrylonitrile	20	4	1.5–10.5	1–10	0–100
UFPHT 20-6338	PS	Polysulfone	30 kDa	44	1–13	1–10	0–75

a great extent furthermore, treated wastewater can be used or discharged to the water or the ground more trustily. Oil and grease in wastewater can exist in several forms: free, dispersed and emulsified. The differences are based primarily on size [4]. UF has been successfully used in oil-in-water separations [5,6]. The most successful UF separation performances are obtained when discrete and stable emulsion particles of oil that are larger than the membrane pore size are rejected. The basis for selecting membrane material and membrane operating condition is to achieve significant reduction of emulsified oil and chemical oxygen demand (COD) in the permeate, while, high permeation flux can be achieved largely empirical [1]. Several researchers have reported the effectiveness of UF process on treatment of oily wastewaters. Karakuleski et al. reported oil content less than 15 ppm and COD reduction of 92–96% using UF of a bilge water [2]. Marchese et al. reported pilot oily wastewater treatment data using UF, with achieving up to 90% and 99.7% reduction of COD and hydrocarbon (HC), respectively [1]. As mentioned, UF membranes are widely used in wastewater treatment and other industrial applications. However, a major impediment in applications of UF technology for oily wastewater reclamation is membrane fouling. Depending on the membrane type, materials in the feed and process conditions, the membrane loses its performance during operation. Flux as a measure of the membrane performance is affected by two phenomena, concentration polarization and fouling. As a result, control of fouling is of utmost importance. Techniques involved are pretreatment of feed which reduces the particulate density, optimization of operating conditions, e.g. pH, pressure, cross flow velocity (CFV) and temperature and membrane regeneration, i.e. backwashing and cleaning. An important and final technique for membrane regeneration is chemical cleaning of fouled membranes. Chemical cleaning means removing impurities by means of chemical agents [7–9]. In this paper, it was focused on oily wastewater treatment of Tehran refinery by UF with emphasis on process fundamentals and operating conditions. Also, fouled

membranes were washed with chemical agents such as chelating agents and surfactants. The best procedure for the membrane cleaning was finally proposed.

2. Material

2.1. Membrane

In all the experiments, polyacrylonitrile (PAN) from Sepro membranes of USA and polysulfone (PS) from DOW Co. of Denmark were used as UF membranes. Characteristics of the membranes are presented in Table 1.

2.2. Chemical cleaning agents

Chemical cleaning agents used were NaOH, certified grade ethylene diamine tetra acetic acid disodium salt-2-hydrate (EDTA) as a metal chelating agent and certified grade sodium dodecyl sulfate (SDS) as an anionic surfactant. NaOH, EDTA and SDS were purchased from Fisher Scientific, Merck and Acrös Organics, respectively.

2.3. Process feed

Outlet of the API unit of Tehran refinery was used as the feed. The feed was taken daily and used immediately. Analysis of the feed taken from the wastewater of the API unit is presented in Table 2.

3. Experimental

3.1. Experimental method

In order to carry out the experiments almost close to an industrial scale, a pilot plant was designed. The pilot was operated in cross flow mode. According to Fig. 1, the cell was composed of two separate Teflon segments that were attached together with screws and nuts and its interior space was totally sealed using an O-ring. The membranes were placed between these two segments. At this condition, the membrane surface area in contact with the feed was equal to 64 cm².

Table 2

Characteristics of the wastewater and the treated wastewater (TMP = 3 bar, CFV = 1 m/s and $T = 40^{\circ}\text{C}$)

Treated wastewater					
Biological	Ultrafiltration		Feed	Unit	Parameter
	PAN	PS			
4	Trace	Trace	60	mg/L	Total suspended solids (TSS)
1540	1424	1560	2028	mg/L	Total dissolved solids (TDS)
5	0.2	2.2	78	mg/L	Content of oil and grease
32	48	48	124	mg/L	Chemical oxygen demand (COD)
20	18	30	52	mg/L	Biological oxygen demand (BOD ₅)
24	18.5	20	81	mg/L	Total organic carbon (TOC)
1.1	0.4	1.1	53	NTU	Turbidity

The feed was passed through the upper segment of the cell. The lower segment had a groove in order to hold a membrane retentive plate. The membrane was preserved against the fluid pressure by this porous metallic plate. A groove was made under the porous plate to collect the permeation.

The UF cell was installed in a system according to Fig. 2 and all the industrial reservations were considered during the experiments.

The system was simple and had no complexity, however, it was designed in such a way that all important operating parameters in the UF process such as temperature, operating pressure and linear flow velocity could be tuned and controlled. The system mentioned above had a vessel with a capacity of 15 L. This vessel had a heater to heat the feed or to keep it at a constant temperature and also a stirrer in order to

keep the feed uniform. The feed temperature was controlled by a digital thermometer with an accuracy of $\pm 0.1^{\circ}\text{C}$ and the feed pH was measured by a digital pH meter with an accuracy of 0.01. A shell-tube heat exchanger was used to control the feed temperature. Temperature, pressure, volume flow rate and pH were tuned and controlled simultaneously.

3.2. Analysis of samples

Scanning electron microscopy (SEM) used in this work was Philips model XL30. Samples for measurements of the feed and the permeate total suspended solids (TSS), biological oxygen demand (BOD₅), COD, oil and grease content, turbidity, total organic carbon (TOC), and total dissolved solids (TDS) contents were taken as necessary and analyzed by the procedure

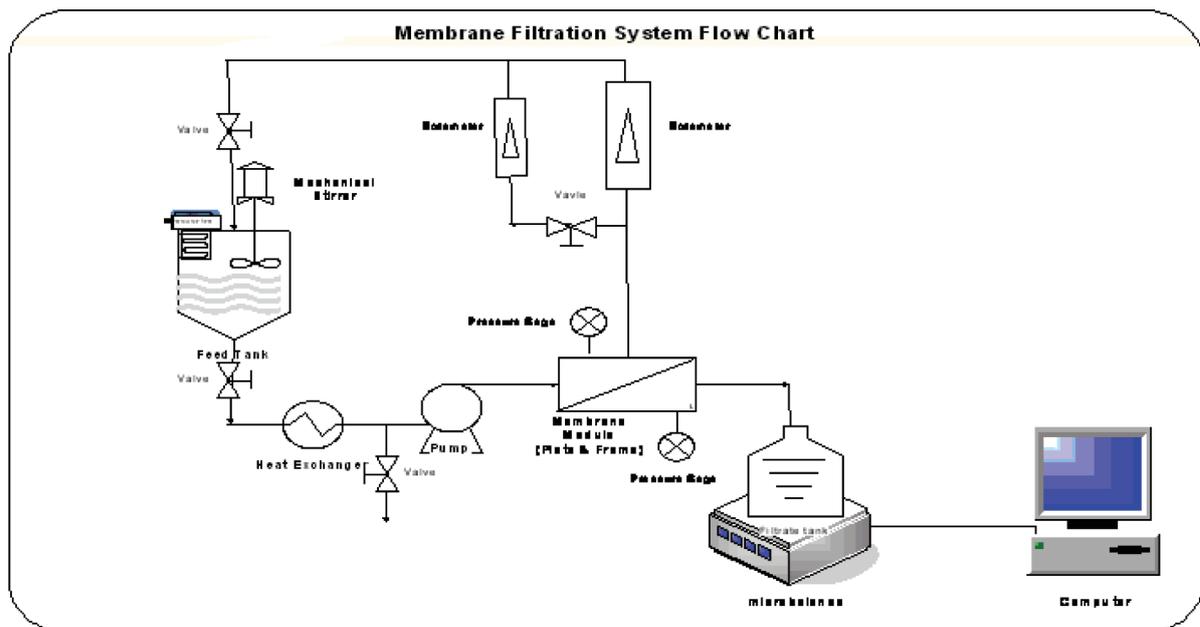


Fig. 1. Schematic of the UF system.

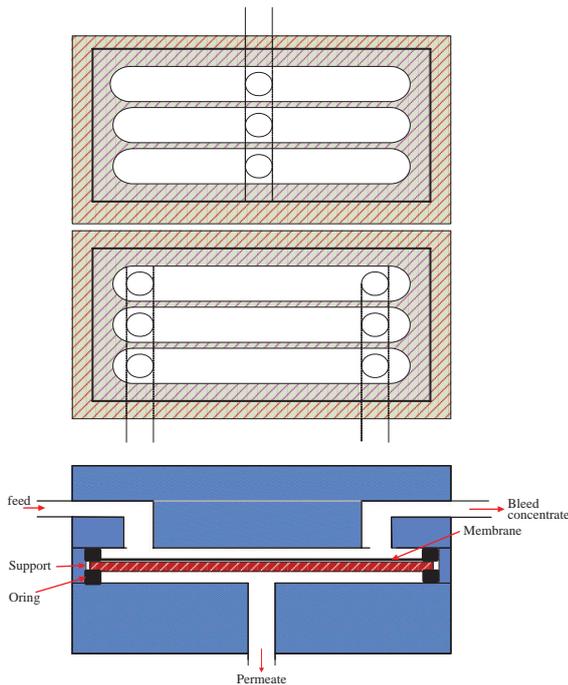


Fig. 2. Schematic view of the module.

outlined in standard methods [10]. TOC and Turbidity were estimated using TOC Analyzer (Model DC-190) and Turbidimeter (Model 2100A HACH), respectively.

3.3. Theory

Permeation flux, R_f , and rejection are important parameters in design and construction of UF separation processes. Permeation flux shows the amount of permeate and the product rate. R_f represents the amount of cake/gel layer formed on the membrane surface and the flux decline. To measure efficiency of UF for wastewater treatment, rejection is also utilized. The flux was measured gravimetrically with an electronic balance via weighting the permeation. The rejection of different components was calculated by comparing their concentrations in the permeate and in the feed, as follows:

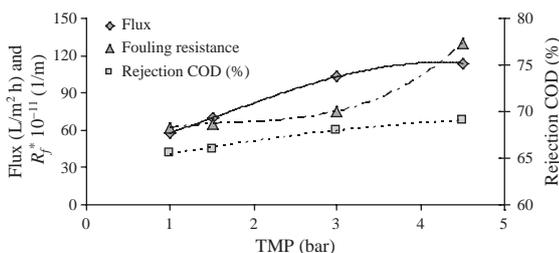


Fig. 3. Effect of TMP on permeation flux, R_f and COD rejection (CFV = 1 m/s, $T = 40^\circ\text{C}$ and $\text{pH} = 8$).

$$\text{Rejection (\%)} = [1 - (C_p/C_f)] \times 100$$

Where, C_p is the concentration in the permeate, and C_f is the concentration in the feed. R_f was calculated as follows [8]:

$$R_f = \left(\frac{\Delta P}{\mu J_{ww}} \right) - \left(\frac{\Delta P}{\mu J_{wi}} \right)$$

Where ΔP is the transmembrane pressure (TMP), μ is the feed viscosity, J_{wi} is initial water flux and J_{ww} is final water flux (after fouling).

Fouling and cleaning were quantified via measurements of the R_f before and after cleaning of the membranes. The resistance is due to the formation of a cake or gel layer on the membrane surface. Fouling and cleaning were evaluated using resistance removal (RR) and flux recovery (RF) as follows [9]:

$$\text{FR(\%)} = [(J_{wc} - J_{ww}) / (J_{wi} - J_{ww})] \times 100$$

$$\text{RR(\%)} = [(R_f - R_c) / R_f] \times 100$$

Where R_c is the resistance after chemical cleaning and J_{wc} is water flux after chemical cleaning.

4. Results and discussion

4.1. Effects of operation conditions on permeation flux, R_f and rejection

4.1.1. Effect of TMP

According to the Darcy's law, increasing TMP increases permeation flux, however, fouling restricts this fundamental law [1,11]. Increasing TMP makes the sediments more compact on the membrane surface and blocks the membrane pores [11–13]. Thus, at an optimum TMP, permeation flux is high, while tendency to cake/gel layer formation is low [13]. Effects of TMP on permeation flux, R_f and rejection are presented in Fig. 3. It can be observed that, with increasing TMP up to 3 bar, permeation flux increases linearly, however, at higher TMPs it is nearly constant. This can be due to compression of the cake/gel layer formed on the membrane surface at high pressures. As shown in Fig. 3, until a TMP of 3 bar, R_f increases slightly however, after that it increases severely. This can also be due to low tendency to cake/gel layer formation at TMPs up to 3 bar and as a result, the R_f growth is low,

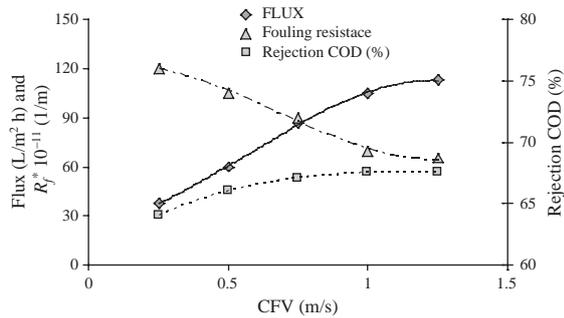


Fig. 4. Effect of CFV on permeation flux, R_f and COD rejection (TMP = 3 bar, $T = 40^\circ\text{C}$ and pH = 8).

however, after that the resistance increases sharply because the cake/gel layer becomes denser.

Fig. 3 also presents effect of TMP on COD rejection. The results indicated that the rejection increases slightly with increasing TMP. This can also be due to formation of the thicker cake/gel layer, where this layer traps oil drops among sediment pores and does not let them pass through.

To achieve an optimum design, obtaining the maximum outlet flow and considering the minimum investments and operating costs are needed and this means that it is very important to have a membrane with the most effective service time. Primarily, the membrane service time and its permeation flux are affected by concentration polarization (caused by accumulation of solutes) and fouling (formation of a sticky cake/gel layer and/or an irreversible cake/gel layer).

Thus, a TMP of 3 bar is the optimum operating pressure. Because at higher TMPs, R_f increases as TMP increases, while permeation flux and rejection does not change any more.

4.1.2. Effect of CFV

Increasing CFV increases mass transfer coefficient in the concentration boundary layer and also increases the extent of mixing over the membrane surface. This can reduce aggregation of the feed components in the gel layer, and as a result, the aggregated materials on the membrane surface diffuse back to the bulk solution, so the concentration polarization effects diminish. This increases the effective pressure difference consequently [13–17], and thus, permeation flux increases. In Fig. 4, effects of CFV on permeation flux, R_f and rejection are presented. It can be observed that permeation flux increases sharply until a CFV of 1 m/s and after that it does not change significantly. The influence of two different CFVs on permeation flux was also compared. At low CFV (0.25 m/s), there was a little turbulence so the cake/gel layer could be formed

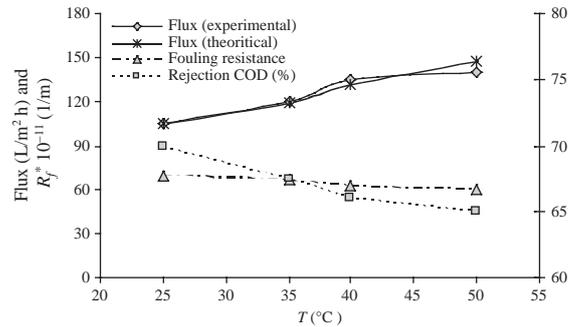


Fig. 5. Effect of temperature on permeation flux, R_f and COD rejection (TMP = 3 bar, CFV = 1 m/s and pH = 8).

easily. Therefore, maximum fouling was observed and permeation flux reduced consequently. At higher CFVs (up to 1 m/s), more turbulence was made so the aggregated materials on the membrane surface diffused back to the bulk solution and as a result there was no sediment formation. Thus, permeation flux increased. Further increasing CFV more than 1 m/s did not affect R_f and permeation flux.

The results indicated that increasing CFV slightly increases the rejection. This can also be due to the fact that increasing turbulence decreases residence time of the components on the membrane surface where there is a challenge between water and oil molecules to pass through the membrane and water molecules have more change to pass through so the rejection increases. Also, less fouling and high hydrophilic nature of the membrane surface increases the rejection.

Considering that higher CFVs leads to more power consumption for pumping so the choice of very high CFVs is not economically feasible. Therefore, the optimum CFV is 1 m/s.

4.1.3. Effect of temperature

As shown in Fig. 5, increasing operating temperature increases permeation flux. Osmotic pressure is the pressure required to stop the net flow of water across a semipermeable membrane separating solutions of different compositions. The van't Hoff equation [18] describes the osmotic pressure (Π) on one side of the membrane and is given by:

$$\Pi = RT(C_1 + C_2 + \dots + C_n)$$

Where R is the gas constant, T is temperature, and C_1, C_2, \dots, C_n are individual solute concentrations for solutes contained in the oily wastewater. As observed, increasing temperature increases osmotic pressure. It

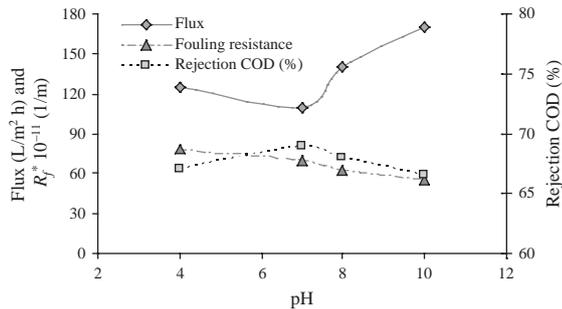


Fig. 6. Effect of pH on permeation flux, R_f and COD rejection (TMP = 3 bar, CFV = 1 m/s and $T = 40^\circ\text{C}$).

must be mentioned that Darcy's Law may be written as follows [11]:

$$J = \frac{\Delta P - \sigma_k \Pi}{\mu(R_m + R_f)}$$

Where σ_k and Π are reflection factor and osmotic pressure, respectively. According to the equation, increasing osmotic pressure decreases permeation flux. However, from another point of view, increasing temperature decreases viscosity, and as a result increases permeation flux [19]. Fig. 5 presents effects of temperature on permeation flux. Experimental and theoretical values can be observed. According to the observations and the calculations, permeation flux increases with increasing temperature. It must be mentioned that in calculation of osmotic pressure, oil and grease concentration was only considered. It was due to the fact that concentrations of other pollutants were not exactly known. As can be observed, increasing rate of permeation flux reduces above 40°C . In other words, temperature has a double effect on permeation flux [13,20]. Increasing temperature up to 40°C increases permeation flux because the viscosity effect is more significant than the osmotic pressure effect, however, further increasing temperature has a negligible effect on permeation flux and it remains almost constant. The osmotic pressure effect enhances and the viscosity effect diminishes at higher temperatures till these two effects are equilibrated finally. As observed in Fig. 5, increasing temperature decreases the membrane fouling and this is due to increasing the oil solubility. According to the results, increasing temperature decreases the rejection. This can also be due to the viscosity effect. At higher temperatures, oil and grease can more easily permeate through the membranes. The results show that the optimum temperature of 40°C can be recommended to achieve high permeation flux at low operating costs.

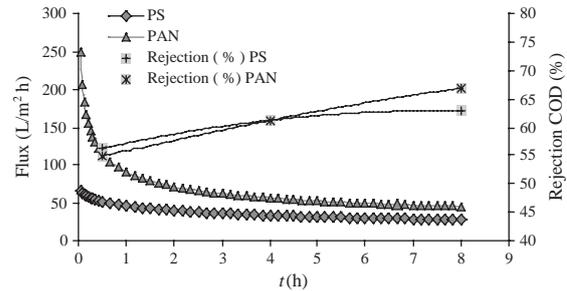


Fig. 7. Effect of time on permeation flux and COD rejection (TMP = 3 bar, CFV = 1 m/s, $T = 40^\circ\text{C}$).

4.1.4. Effect of pH

Fig. 6 presents effects of pH on permeation flux, R_f and the rejection. As observed, with acidic and basic solutions, permeation flux increases. This means that the feed chemistry is change at higher (to significant extent) and lower pH values and this causes R_f on the membrane surface to reduce and permeation flux of the membrane to enhance.

It can be also observed that the rejection with acidic and basic solutions decreases. This can be due to the fact that acidic and basic solutions can deform oil droplets and facilitate their transfer pass through the membrane.

The best pH should be selected according to maximum permeation flux, minimum R_f , suitable rejection and maximum chemical stability. Thus, a pH of 9 can be the optimum value.

4.2. Comparison of the membranes performances (PAN and PS)

The effect of time on permeation flux and COD rejection of the PS and PAN membranes under the same operational conditions is presented in Fig. 7. The results show that permeation flux of the PAN membrane is nearly constant with time after an initial significant decline, while that of the PS membrane is almost constant. Using SEM cross sectional images of the membranes as observed in Fig. 10, different permeation fluxes and rejections of the membranes can be explained by their different morphological properties, materials and hydrophilic natures. Permeation flux of the PAN is higher than that of the PS. This can be due to the fact that the PAN has thinner dense layer and more porous sub layer and is more hydrophilic (as can be observed in Table 1). COD rejections of the both membranes vary similarly with time, however, that of the PAN increases a little more sharply and this can also be attributed to the different morphologies and materials of the membranes. In Fig. 8, initial reduction

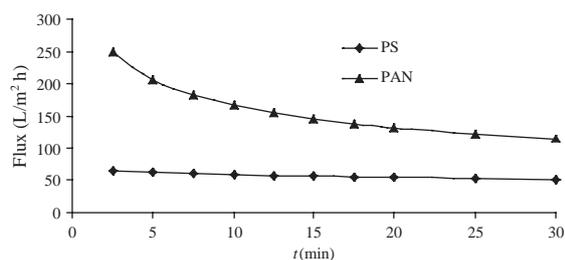


Fig. 8. Effect of time on permeation flux (TMP = 3 bar, CFV = 1 m/s, $T = 40^{\circ}\text{C}$).

of permeation flux in 30 min is presented for the both membranes. Percentage of flux decline for the PAN and the PS membranes is also presented in Fig. 9. According to the results, percentage of flux decline for the PAN is higher than that for the PS. As observed, final flux decline of the PAN is about 80%, while that of the PS is about 60%. However, infinite permeation flux of the PAN is about $45 \text{ L/m}^2 \text{ h}$, while that of the PS is about $28 \text{ L/m}^2 \text{ h}$. As mentioned, this is due to the fact that the PAN membrane is more hydrophilic, and as a result, a large volume of the wastewater is filtrated at the beginning of the filtration. Thus, concentration polarization takes place much quicker and then a cake/gel layer is formed much earlier. It means that, at the end of the process, the amount of precipitated materials on the PAN membrane surface is greater than that on the PS (Figs. 10 and 11). As mentioned, due to the more hydrophilic nature, permeation flux of the PAN is higher, and this causes a reverse effect on rejection. Lots of hydrophilic groups on the PAN membrane surface cause high water permeation, and as a result, some oil passes through the membrane and this causes its initial rejection to be low, however, after formation of the cake/gel layer and reduction of permeation flux, some of the hydrophilic groups become inactive and this causes lower water permeation, and as a result, higher rejection. Rejection of the PAN membrane is more than that of the PS as presented in Table 2. Oil and grease removal performance of the PAN and the

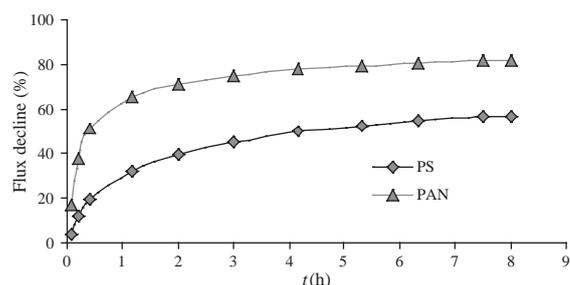


Fig. 9. Effect of time on flux decline.

PS membranes are 99.7% and 97.2%, respectively. This is due to the smaller pores and the more hydrophilic nature of the PAN membrane which significantly rejects oil emulsion drop lets. As can be seen in Table 2, in all the experiments, the PAN membrane performs better than the PS membrane, and regarding NTU, TOC, BOD₅ and COD values, the differences are more considerable. The TSS removal is perfect for both the membranes. With respect to all the above mentioned facts and the results listed in Table 2, it can be concluded that the PAN membrane is more suitable than the PS because of its higher rejection and permeation flux for the API wastewater treatment of Tehran refinery.

4.3. Comparison of UF with the conventional biological treatment method

Table 2 presents the results of two different treatment methods (UF and biological). Currently, a conventional biological method is being used in Tehran refinery for the wastewater treatment. As shown, the results of UF for all analysis are better than the results of biological method. This better preference is more considerable in TSS and especially in oil and grease content removals. The oil and grease content reduces using UF and biological method to 0.2 and 5 ppm, respectively. However, TOC content removal using UF is approximately less and this is due to the existence

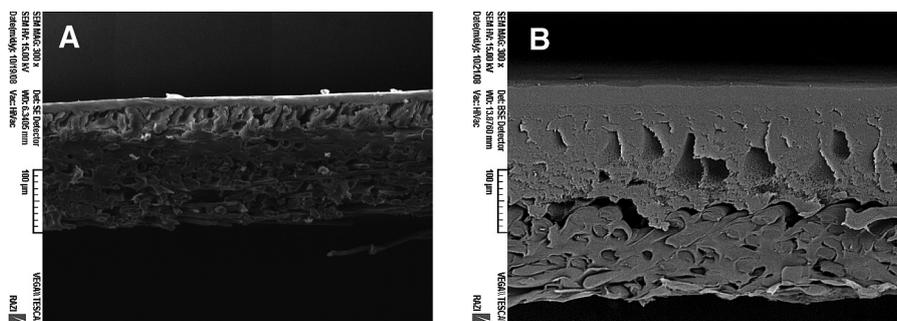


Fig. 10. Cross sectional SEM of the membranes (a) PAN and (b) PS before fouling.

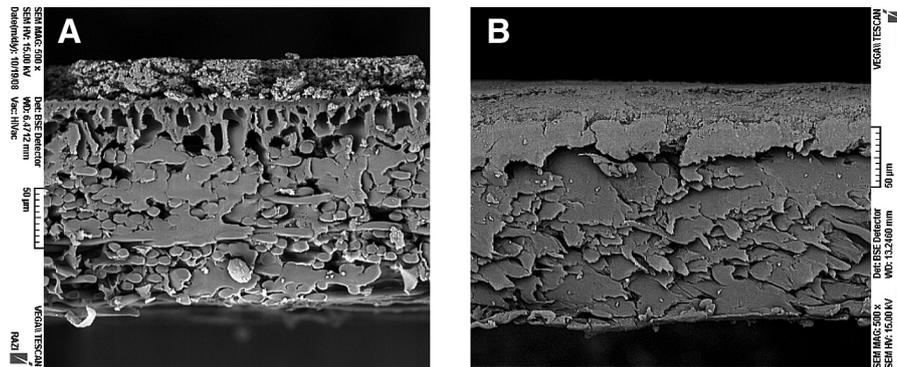


Fig. 11. Cross sectional SEM of the membranes (a) PAN and (b) PS after fouling.

of volatile organic compounds in the feed. It seems that more residence time in the API unit is necessary for all of these components to be removed.

4.4. Cleaning of the PAN membrane

4.4.1. Effect of cleaners

Based on the analysis of the feed and also the cake/gel formed on the membrane surface, two cleaning agents (SDS and EDTA) were selected. Fouling of UF membranes in oily wastewater treatment is mostly due to precipitation of oil and grease, suspended solids, colloidal materials and minerals on the membranes surfaces. The analysis of the feed is presented in Table 2. Cleaning experiments were performed using cleaning solutions containing different concentrations of SDS and or EDTA, as presented in Figs. 12 and 13, respectively. The results clearly show that cleaning efficiency using SDS and EDTA increases with increasing cleaning agent concentration. It can be observed that cleaning efficiency increases sharply until a concentration of 4 mM SDS and 30 mM EDTA and after that it does not change significantly. Using more concentrated EDTA cleaning solution can be due to the chemical reaction between EDTA and the deposited materials to break down cake/gel layer network.

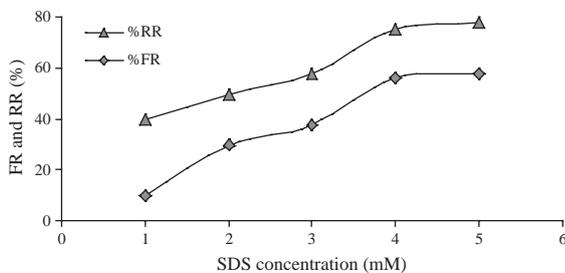


Fig. 12. Effect of the SDS concentration on FR and RR (cleaning instruction: CFV = 1.25 m/s, $T = 25^{\circ}\text{C}$, pH = 10, $t = 20$ min).

Cleaning efficiency of the different cleaning solutions (4 mM SDS and 30 mM EDTA and combination of 4 mM SDS and 30 mM EDTA) are compared in Fig. 14. The results show that cleaning with a combination of EDTA and SDS is relatively more effective. This is due to the fact that SDS has both hydrophobic and hydrophilic groups, and is semi soluble in both organic and aqueous solvents. Surfactants can solubilize macromolecules by forming micelles around them, and help to remove the precipitated materials from the membrane surface. Also EDTA can remove divalent cations from the complex organic molecules and improve cleaning efficiency of the fouled membrane. In other words, SDS is more responsible for removing oil and grease while EDTA removes minerals from the membrane surface.

4.4.2. Effect of CFV

Effect of CFV on cleaning efficiency was also investigated, as shown in Fig. 15. As can be observed, cleaning efficiency increases with increasing CFV till 1.25 m/s and then it remains almost constant. Increasing CFV which causes higher shear rates enhances mass transfer of the cleaning agent through the deposited materials on the membrane surface and this increases the cleaning efficiency.

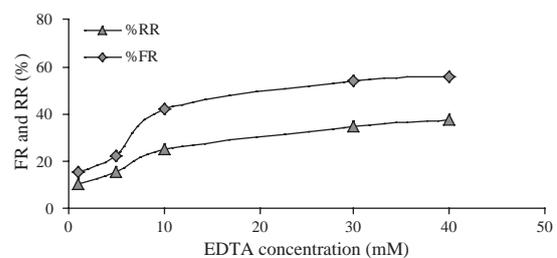


Fig. 13. Effect of EDTA concentration on FR and RR (cleaning instruction: CFV = 1.25 m/s, $T = 25^{\circ}\text{C}$, pH = 10, $t = 20$ min).

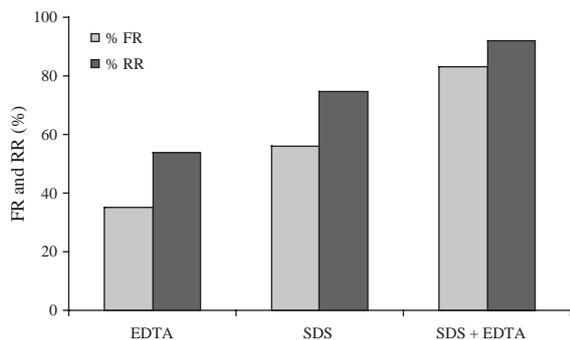


Fig. 14. Effect of cleaning agent on FR and RR (cleaning instruction: CFV = 1.25 m/s, $T = 25^{\circ}\text{C}$, pH = 10, $t = 20$ min).

4.4.3. Effect of pH

Effect of pH on cleaning efficiency of the cleaning agent (a combination SDS and EDTA) is illustrated in Fig. 16. It is shown that cleaning efficiency increases with increasing pH from 8 to 11. Higher chelating ability of EDTA with increasing pH results in a more effective ligand-exchange reaction between EDTA and alginate-metals complexes within the alginate cake/gel layer. Consequently, the alginate cake/gel layer is broken down relatively more easily, and this thus results in higher cleaning efficiency.

The best pH should be selected according to higher cleaning efficiency and more chemical stability. Thus, a pH of 10 can be an optimum value.

4.4.4. Effect of temperature

The results of the cleaning agent (a combination SDS and EDTA) at different temperatures are presented in Fig. 17. Cleaning efficiency increases dramatically with increasing temperature. This is due to the fact that both the rate of chemical reaction between the cleaning agent and the deposited materials and the rate of diffusive transport of the deposited materials from the cake/gel layer back to the bulk solution increase as

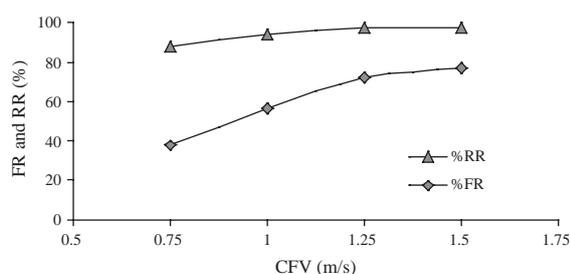


Fig. 15. Effect of CFV on FR and RR (cleaning instruction: $T = 25^{\circ}\text{C}$, $t = 20$ min, pH = 10).

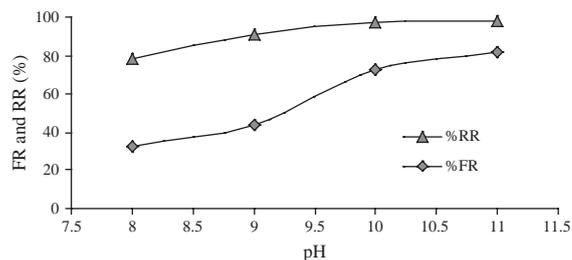


Fig. 16. Effect of pH on FR and RR (cleaning instruction: CFV = 1.25 m/s, pH = 10, $t = 20$ min).

temperature increases. Cleaning temperature of 45°C can be recommended for the cleaning procedure.

4.4.5. Effect of cleaning time

Effect of cleaning time on the cleaning efficiency is presented in Fig. 18. According to these results, the longer cleaning time the higher cleaning efficiency. This is due to the favorable chemical reaction between the cleaning agent and the deposited materials in the cake/gel layer which needs some time to proceed. Cleaning time of 30 min can be recommended for the cleaning procedure.

4.4.6. Cleaning mechanism

Investigation of fouling and cleaning mechanisms leads to better understanding of the cleaning process and provides a basis for tailor – made chemicals and procedures. As mentioned, a cross-linked fouling layer is formed on the membrane surface in presence of minerals and/or ions, which are bonded to organic materials and they form bridges between adjacent deposited materials. The cleaning agent diffuses into the deposited cake/gel layer on the membrane surface. Diffusion rate depends on different factors including turbulency. A chemical reaction occurs between the cleaning agent and the deposited materials at the membrane surface.

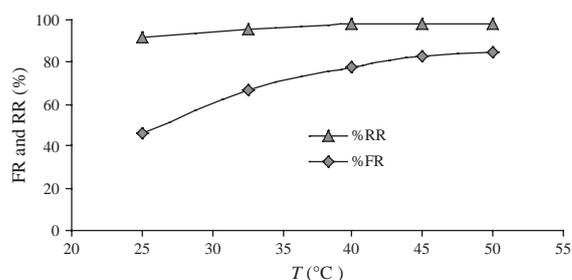


Fig. 17. Effect of temperature on FR and RR (cleaning instruction: CFV = 1.25 m/s, $T = 25^{\circ}\text{C}$, $t = 20$ min).

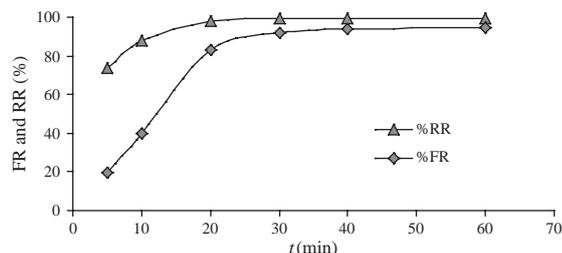


Fig. 18. Effect of cleaning time on FR and RR (cleaning instruction: $T = 45^{\circ}\text{C}$, $\text{CFV} = 1.25 \text{ m/s}$, $\text{pH} = 10$).

The cleaning agent reacts with the attached deposited materials in the fouling layer yielding to weaken them. The chemical reaction between the cleaning agent and the deposited materials in the fouling layer takes place and then the products diffuse from the membrane surface back to the bulk solution. The reaction may be hydrolysis, dissolution or dispersion. These finally results in removal of the deposited materials from the membrane surface.

5. Conclusion

In this work, treatment of an oily wastewater, with the PS and the PAN membranes were investigated. According to the results, it can be concluded that UF is a feasible and advantageous method for treatment of Tehran refinery wastewater effluent.

The results indicated that the PAN membrane performs higher permeation flux and rejection rather than the PS membrane. The results also showed that the UF treatment is very effective in reduction of oil and grease content, TSS and turbidity, while it is relatively less effective in reduction of COD, BOD_5 , TOC and TDS. The results showed that a TMP of 3 bar, a CFV of 1 m/s, a temperature of 40°C and a pH of 9 are the best operating parameters. Comparison of performances of the UF process and the conventional biological method showed that UF is more preferred rather than the conventional method. The UF permeate is suitable to discharge into the environment, even in the special regions in accordance with obligatory international laws. Overall, UF as a valuable process can be recommended for the refinery wastewater treatment.

The best cleaning agent to enhance cleaning efficiency of the PAN membrane was found to be a combination of SDS and EDTA. A combination of SDS (as a surfactant) and EDTA (as a chelating agent) as a powerful cleaning agent performed very effectively. EDTA is able to combine with metals. Effect of SDS can be attributed to the cleaning strength of emulsifiers due to their ability to alter interfacial tension of water.

Cleaning efficiency of the recommended cleaning agent was further improved by optimizing the cleaning condition. The results showed that a CFV of 1.25 m/s, a temperature of 45°C , a cleaning time of 30 min and a pH of 10 are the best cleaning conditions.

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