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Treatment of biodiesel production wastewater by a commercial nanofiltration system

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ABSTRACT

In the present study, treatment of biodiesel production wastewater by a commercial nanofiltration membrane (NE-90) has been investigated for the first time. The wastewater was the water washing effluent of the biodiesel production pilot plant. The effect of feed flow rate and operating pressure on the COD, BOD and TDS removal was studied. The results showed that by an increase in feed flow rate, the rejection percentage for COD and BOD is increased due to lowering the effect of concentration polarization. Moreover, with an increase in the operating pressure, the rejection percentage for BOD and COD is also increased due to an increase in rejection from the surface of the membrane. A maximum removal percentage for BOD and COD was obtained as 74.1% and 77.9%, respectively at 14 bar feed pressure and 250 L/h feed flow rate. At this condition, TDS removal was measured as 86.5%. The obtained results showed that the current nanofiltration system is able to treat the biodiesel's water washing effluent successfully and reduces the COD, BOD, and TDS, considerably.

Keywords: Biodiesel's water washing; Wastewater treatment; Nanofiltration; Permeate flux; Flux decline

1. Introduction

Currently, the world energy crisis resulting from fossil fuel depletion and also increasing concern for the environment, have motivated scientists to find alternative fuels as eco-friendly sources of energy. Extensive studies have been conducted by many countries to solve this problem [1]. Biodiesel which is a biodegradable and nontoxic fuel derived from natural resources is one of the proposed solutions [2]. The most common method to synthesize biodiesel is through transesterification of a fatty ester or an organic fatty acid with a low molecular weight alcohol like methanol or ethanol. The general term of transesterification is used to describe a class of organic reactions in which the transformation of an ester from one form to another form is performed by the exchange of the alkoxide groups. Based on the oil or ester origin used, it is possible to obtain biodiesel with similar physicochemical characteristics to diesel fuel. After completion of the reaction, the mixing is interrupted and the reaction products mixture is allowed to rest and decant in two phases. The organic phase is composed mainly of the biodiesel (reaction esters), glycerides, unreacted fatty acids and soaps while the aqueous phase which has higher density, consists mainly of glycerol, soaps, unreacted alcohol, residues of transesterified triglycerides and catalysts [3].

After removal of the aqueous phase (glycerin rich phase), the raw biodiesel contains low amounts of alcohol, catalyst, free fatty acids, glycerin, water, soap, etc., which is necessary to be removed before the stabilization and the finishing steps. Therefore, it is essential to use the purification and drying processes so that the final biodiesel specifications meet the standards [4].

Purification of raw biodiesel is usually performed through multiple water washing by hot water, followed by

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decantation which is called wet scrubbing (wet washing). This method consists of using hot water due to the high solubility of these impurities in water, along with the low cost, high efficiency, abundance, and simplicity. The disadvantage of the method, besides the formation of the emulsion, which allows the formation of free fatty acids and soap and prevents the separation of esters, is the generation of a large volume of wastewater [3,4]. The generation of a large amount of wastewater by the commonly used wet-washing process has attracted the attention of researchers.

In practice, the washing process is normally repeated two to five times depending on the impurity levels in the product methyl ester which generates about 20–120 L of wastewater per 100 L of biodiesel produced [5]. In addition to generating a highly polluting emulsion effluent, containing free fatty acids, soaps, etc. with high chemical and biological oxygen demand (COD and BOD) as well as high total dissolved and suspended solids (TDS and TSS, respectively) it is an extra threat to the environment [6]. Discharge of biodiesel wastewater and residual oils into the public sewage system could cause several problems such as plugging of the system, reduction of the microbial activity, etc. [7]. Up-to-date, some individual treatments on biodiesel production wastewater have been reported such as coagulation [8], electrocoagulation [5], biological processes [9], adsorption [10] and microbial fuel cell systems [11]. The effectiveness of the above-mentioned methods in the reduction of BOD and COD is presented in Table 1.

Membrane separation processes have shown that they are very effective in the treatment of various wastewaters. Currently, commercialized and matured membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis are used widely for the treatment of water and wastewaters. As the pore size of the membrane becomes smaller, the filtration output is reduced while the quality of the product increases. Then there is a trade-off between the product quality and output. Recently, nanofiltration (NF) has attracted much attention because of the acceptable product flow rate along with high product quality. Usually, the NF membrane filtration system is used for the removal of low molecular weight soluble organic compounds from liquid streams. NF membranes, similar to RO membranes, are able to separate inorganic salts and small organic molecules. The key characteristics of NF membranes which distinguish them from reverse osmosis membranes are higher fluxes, high rejection of divalent and low rejection of monovalent ions. These properties have allowed NF to be used in niche applications in many areas especially for water and wastewater treatment, biotechnology and pharmaceutical and food engineering [12–16].

Table 1
Removal efficiencies of biodiesel wastewater using different methods

Methods	Removal (%)		Refs.
	BOD	COD	
Coagulation	97.2	97.5	[8]
Electrocoagulation	–	55.4	[5]
Biological processes	–	97	[9]
Adsorption	76	90	[10]
Microbial fuel cell systems	–	60	[11]

Nanofiltration is an extremely complex process which is dependent on the interfacial interactions between the chemical components of the system at the membrane surface and within the membrane pores and also the micro hydrodynamics of the liquids through the pores. Rejection of the solutes from NF membranes is attributed to a combination of steric, dielectric, Donnan and transport effects. The transport of neutral solutes through NF membranes is performed by the steric mechanism (or size based exclusion) which has been well described through several studies of UF membranes [17].

Treatment of biodiesel production wastewaters by membrane systems is completely new and novel. Only a few experiences have been reported for using membrane processes in the treatment of biodiesel production wastewaters. Shirazi et al. used a superhydrophobic electrospun polystyrene MF system for treatment of biodiesel wash water. They reported that the use of this type MF membrane could reduce BOD and COD effectively but reduced TDS partially [18]. In another study, Jaber et al. reported an effective method for treatment of biodiesel's water washing by a combination of a filtration system equipped with commercial hydrophobic polypropylene membranes followed by adsorption on activated carbon [19].

In the current research, treatment of biodiesel's water washing effluent by a commercial nanofiltration membrane is considered for the first time. The effect of operating parameters such as feed pressure and flow rate on COD, BOD and TDS removal from biodiesel's water-washing wastewater is examined and the results are reported.

2. Materials and methods

2.1. Materials

Biodiesel wash-water was kindly received from the Biofuel Research Team (Karaj, Iran). The raw biodiesel was produced from the reaction of waste cooking oil (WCO) and commercial methanol (1:6 molar ratio) using potassium hydroxide (1 wt.%) as the alkaline catalyst for the transesterification reaction. After decantation of the reaction product, the light phase (raw biodiesel) was washed with hot water three times and the resulting wastewaters were collected, mixed and used as the feed for the nanofiltration experiments. Then average specification of the water washing effluent (after the pre-filtration stage) which was used as the feed is shown in Table 2.

Table 2
The average specifications of the water washing effluent after pre-filtration step

EC (μS/cm)	1,820
pH	7.10
COD (mg/L)	15,190
BOD (mg/L)	12,685
TDS (mg/L)	2,432

2.2. Apparatus

The commercial NF membrane, NE-90, was supplied from CSM Co., Korea. It was a polyamide thin film composite NF spiral wound membrane. The rejection for NaCl was reported by the manufacturer as 90%. The module was split and some flat sheets were cut and used in the experiments. The active area of the flat membrane was 78 cm^2 ($W = 5.2$ and $L = 15$ cm).

A high-pressure membrane filtration test system was set-up for the experiments. Fig. 1 presents the schematic of this membrane filtration system. This system consisted of a 25 L feed reservoir, a low-pressure pump, a pre-filtration housing including a 5 µm polypropylene cartridge filter, a vertical multistage high- pressure centrifugal pump, and a cross-flow flat sheet membrane module. Different pressure gauges (Bourdon Sedeme, 0–16 bar and Sangan Sanat, 0–40 bar), needle and globe valves, and a flowmeter (Fischer and Porters, Germany) were used for adjustment and controlling the system at the desired set-points. All of the materials in contact with the process fluids were made of high-quality AISI-316 L stainless steel.

2.3. Procedure

The feed tank was filled with wastewater (about 25 L). A low pressure pump was used to pass the feed through the 5 µm polypropylene cartridge depth filter entering the main high-pressure pump to remove the insoluble materials and clarify the feed to reduce the nanofiltration membrane fouling. In all experiments, the feed temperature was controlled at 30°C using a cooling coil placed in the feed tank. The feed temperature was controlled by cold water as the cooling medium through an external cooling coil placed into the feed tank. This was because the feed was circulated by a 36-stage centrifugal pump that increases the feed temperature to higher than 60°C. An external cooling coil was placed in the feed tank to control the temperature and prevent excessive increase of feed temperature. The feed temperature was adjusted at 30°C by controlling the cold water flow rate. This temperature was selected according to our previous experiences on biodiesel production and washing of the produced biodiesel by hot water. It should be noted that biodiesel is usually washed by hot water (about 60°C), therefore the resulted wastewater is warm and considering the heat loss through the transferring and storage stages, the wastewater temperature entering the treatment section has a temperature of about 25°C–35°C depending on the climate and storage condition. Therefore, we used 30°C as the normal temperature for the feed. Of course, the feed temperature affects the performance of the membrane such as permeate flow rate and salt rejection, but an attempt was made to use real conditions for the experiments as much as possible.

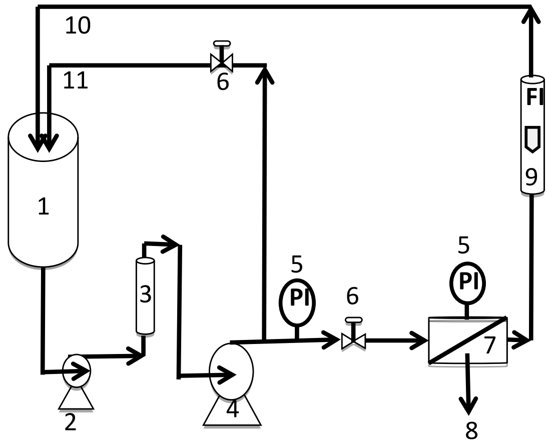

Fig. 1. Schematic diagram of the reverse osmosis set-up.
Note: 1-feed reservoir, 2-low-pressure pump, 3-prefilter, 4-high-pressure pump, 5-pressure gauge, 6-pressure control valve, 7-membrane module, 8-permeate stream, 9-flow meter, 10- reject stream, 11- pump bypass flow.

For each experiment, the membrane was soaked in distilled water for 48 h and then placed in the membrane module. Then the feed pressure and flow rate were adjusted at the desired values using the related valves and controlling devices. The rate of permeation was measured on a weight basis by a digital balance and then converted to the volume basis using the density of the permeate.

The effect of feed flow rate (100, 150, 200, and 250 L/h) and feed pressure (6, 8, 10, 12 and 14 bar) on the rejection of different components were investigated. In each experiment, the retentate (rejected stream) was recycled into the feed tank to establish a nearly pseudo steady state condition. Sampling from the permeate stream was done until establishing the steady state condition. It was found that the time required for attaining steady state was different at different conditions (based on feed flow rate and pressure) but an average of 10 h recirculation was needed for attaining the steady state condition.

In order to minimize the error from sampling during the transient period, the collected permeate was returned to the feed tank after every sampling. Normally, every 30 min about 0.5–1 L permeate was collected which is inconsiderable (about 2%–4%) with respect to the volume of the feed (25 L). In fact, the volume of the feed was selected so high that the effect of the permeate volume during the samplings becomes negligible. Each sample was then returned to the feed tank. In each experiment, only the last sample (at the steady state condition) which had a volume of about 500 mL was taken for the desired analyses (determination of BOD, COD and TDS). For the next experiment, a fresh feed was used. Then the error from the sampling or cake layer deposition on the membrane surface was minimized by this manner. On the other hand, the amount of the deposited cake on the membrane surface in each experiment was not more than 1–2 g. Considering the COD of the feed which is about 15,000 mg/L, the total amount of organic matter in 25 L feed is 375 g and then the amount of the deposited cake is less than 0.5% which could be neglected. Then the feed concentration before and after steady state conditions could be considered nearly unchanged.

The permeate flux and solute rejection were then calculated using Eqs. (1) and (2) as follows:

$$J_P = \frac{Q_P}{A} \tag{1}$$

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100 \tag{2}$$

where Q_P is the volumetric permeate flow rate (L/h), A is the effective area of the membrane (m^2), and C_P and C_F are permeate and feed concentrations, respectively [20,21].

In each experiment, a new membrane sheet was used and the feed was replaced by a fresh feed. This was done for preventing the error in calculation of rejection at different operating conditions and the interference of the results especially for fouling and flux declines.

3. Results and discussion

3.1. Effect of feed flow rate on permeation flux

The effect of feed flow rate on the permeate flux at a constant feed pressure was examined. Fig. 2 shows the effect of feed flow rate (100, 150, 200 and 250 L/h) on the permeate flux at a feed pressure of 14 bar and temperature of 30°C. As shown, in each feed flow rate, a sharp flux decline is observed at the initial minutes of the experiment which is due to the concentration polarization layer and cake formation on the membrane surface. As time goes on, the development of concentration polarization and cake formation reaches stable values and a steady state condition is established. The experimental results showed that the feed flow rate affects the required time for establishment of the steady state condition. At the feed flow rate of 100 L/h, the flow rate is so low that the flow is laminar and nearly no turbulence is observed. Then the polarization and consequently cake build-up at the surface of the membrane take place quickly which results in a short transition time. By increasing the feed flow rate to 150 L/h, a transition state occurs, therefore the required time for attaining the steady condition increases. An increase of feed flow rate over 150 L/h, increases the turbulency and shear stress at the membrane surface. The applied shear stress at the membrane surface limits the growth of the polarization and cake layer's thicknesses which consequently limit the total resistance against permeation through the membrane. By increasing the feed flow rate, thickness of the polarized and cake layers becomes smaller which results in a higher permeation flux. Lower resistance against permeation and higher shear forces at the membrane surface would result in shorter transition time and attaining faster steady state conditions.

As the feed flow rate is increased, the permeation flux and consequently the total volume of the permeate also increase. This will result in a faster cake build-up and polarization layer development on the surface of the membrane. Although, at higher feed flow rates, the shear forces and flow turbulency at the membrane surface limit the growth of cake and polarization layers, their formation and growth rate depend on the permeation flux through the membrane. Therefore, by increasing the feed flow rate, the permeation flux and consequently the initial rate of cake build-up and polarization layer formation increases and then the flux decline is observed at shorter times.

Fig. 3 shows the effect of feed flow rate on the percentage of permeate flux decline at 14 bar operating pressure. As shown, the flux decline decreases almost linearly as the feed flow rate increases. As explained before, by increasing the feed flow rate, the shear forces acted on the membrane surface increase and the total resistance against permeation decreases.

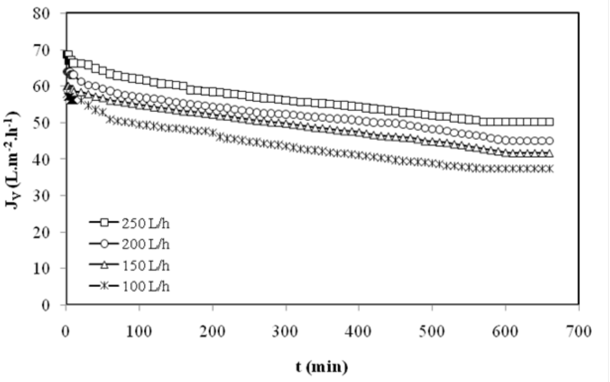

Fig. 2. Effect of feed flow rate on the permeate flux at P_F = 14 bar and T_F = 30°C.

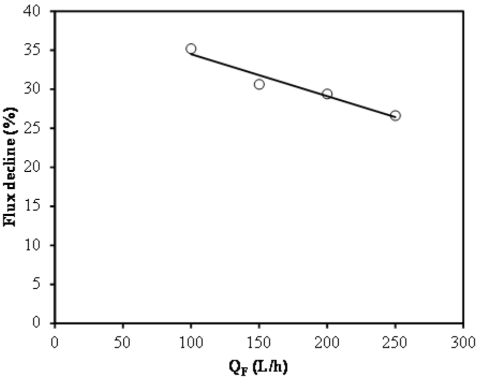

Fig. 3. Effect of feed flow rate on the flux decline at P_F = 14 bar and T_F = 30°C after 660 min.

It should be noted that both fouling and polarization reduce the permeation flux, considerably. Increasing feed flow rate lowers the polarization and fouling, but reduces the recovery rate per single pass, as well. In such cases, the fouling and polarization reduction (or mitigation) is more important. To compensate the low recovery rate per pass, it is customary to recycle a part of the retentate (reject) stream to the feed inlet. Then the overall recovery could be kept at higher levels.

3.2. Effect of feed flow rate on rejections

The effect of feed flow rate (100, 150, 200 and 250 L/h) on COD, BOD and TDS rejections at 14 bar operating pressure was shown in Fig. 4. Two different behaviors for rejection of organic and inorganic compounds were observed. By increasing the feed flow rate, the rejection of organic compounds (COD and BOD) was increased. Similar trends for BOD and COD rejections were observed and overall COD rejection was higher than that for BOD. This shows that the cake formation and adsorption on the membrane surface are the main reasons for organic compounds' transport through the membrane.

The presence of the soaps, unreacted fatty acids and metal ions (such as potassium, calcium...) in the cake and polarization layer may result in some interactions and formation of some bridges between the organic and inorganic species.

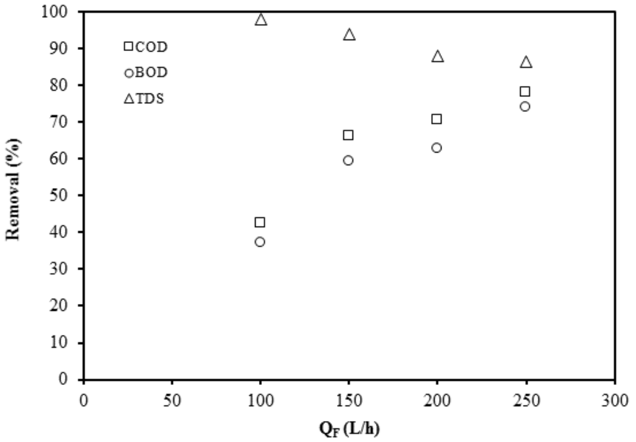

Fig. 4. Effect of feed flow rate on the COD, BOD and TDS rejection at P_F = 14 bar and T_F = 30°C after 660 min.

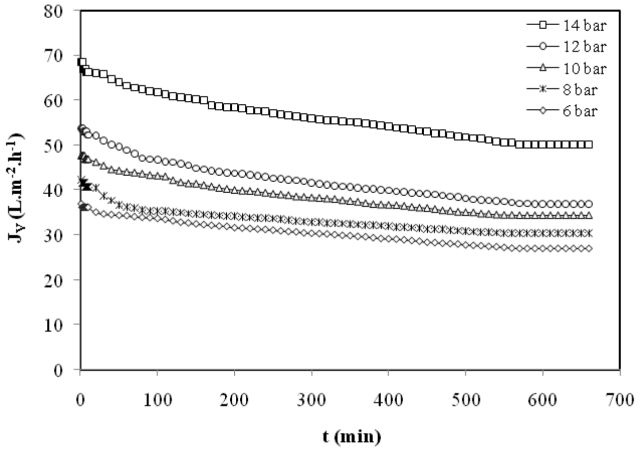

Fig. 5. Effect of feed pressure on the membrane permeate flux at Q_F = 250 L/h and T_F = 30°C.

In the feed solution, the concentration of the inorganic species is very low and therefore no considerable interactions are observed, while in the cake and polarization layers the concentration of the species are several times more than those in the free stream. Therefore, based on the law of mass action, the interactions increase considerably. This may promote the fouling tendency at the membrane surface by the bridging effect between organic and inorganic ion species.

Most of the organic materials in this study are heavy organic compounds such as soaps, unreacted fatty acids, and esters which have a high tendency for cake forming on the membrane surface. At constant pressure, as the feed flow rate is increased, the permeate flux increased because of a decrease in polarization boundary layer thickness, therefore, the residence time of the soluble compounds on the membrane surface decreases and the soluble materials could not be dissolved into the membrane surface effectively. An increase of the permeate flux increases the concentration of the solutes on the membrane surface and enhances the cake build-up. As soon as the cake is formed, the direct reach of the large organic species such as soaps and fatty acids become more difficult. Therefore, by an increase in the feed flow rate, the concentration of the organic species (BOD and COD) in the permeate decreases. COD and BOD rejections increased from 42.3% and 37.2% at 100 L/h to 77.9% and 74.1% at 250 L/h, respectively.

The removal of TDS showed a decreasing behavior with increasing feed flow rate. The TDS rejection at 100 L/h was measured as 97.9% while this value at 250 L/h was measured as 86.5%. It seemed a little strange at first because the rejections usually increase as the flow rate is increased. The reason could be explained as the occlusion of the ionic inorganic compounds in the cake layer and also their adsorption on the membrane surface. As it was explained before, the formation of inorganic cake layer on the membrane surface prevents the direct reach of the organic matters to the membrane surface but the inorganic soluble ions such as potassium ions which are considerably smaller in size than the organic species could pass easily through the porous cake. The accumulation of the inorganic ions in the porous cake increases their concentrations on the membrane surface which results in higher concentration of the dissolved solids in the permeate stream. On the other hand, the isoelectric point of the TFC polyamide nanofiltration membranes is observed at pH values in the range of 4–5. This means that at pH values higher than 4–5 the surface of the membrane is negatively charged and is susceptible for adsorption of positive ionic compounds and Ca ions. pH of the feed was measured as 7.1 and then the surface of the membrane is covered by the adsorbed cations which are the main constituent of TDS forming compounds. It is well-known that by increasing the feed flow rate, the permeation flux increases, as well. Although the flow regime at the feed side is turbulent (except for 100 L/h), a laminar sub-layer is present adjacent to the membrane surface. By increasing the feed flow rate, the thickness of this sub-layer decreases and therefore, the rate of flux increases. A higher permeate flux would result in higher concentration polarization. Since the thickness of the polarized layer is controlled by the flow turbulency, then only the concentration of the rejected salts at the membrane surface increases. Higher concentration of the salts at the membrane surface would further increase the adsorption of the solutes on the membrane surface and consequently increase the concentration of the permeate stream because the rejection coefficient of the membrane is almost constant. The presence of a permeable, porous cake would increase the concentration of the soluble salts at the membrane surface and consequently increase the permeate concentration even more. Then, the occlusion of the salts in the porous cake layer depends on the permeate flux which itself depends on the feed flow rate.

3.3. *Effect of feed pressure on permeation flux*

Fig. 5 shows the effect of feed pressure (6, 8, 10, 12 and 14 bar) on the permeate flux of the NE-90 nanofiltration membrane at 250 L/h feed flow rate and 30°C. The results showed that by increasing the operating pressure, the permeate flux increases accordingly. All of these experiments were performed at 250 L/h feed flow rate to minimize the polarization effects, therefore, lower flux declines were observed in comparison with the previous experiments for the effect of feed flow rate at constant pressure. Nearly after 600 min of operation, the steady state condition has been established. As the pressure is increased from 6 to 12 bar, the required time for attaining the steady condition increased which shows the effect of pressure on the development of polarization and the cake layers. At 14 bar, the time for attaining the steady condition decreases. It seems that the cake compaction and polarization layer development have reached a maximum value at 12 bar and increasing the operating pressure from 12 to 14 bar had a less effect on the total permeation resistances, then the time for attaining the steady condition decreased. The experimental data supports this claim because as the pressure is increased from 6 to 12 bar, the permeate flux at steady state condition increased linearly from 27 to 36.84 $L.m^{-2}.h$ (slope 1.67 $(L.m^{-2}.h)$/bar with a regression coefficient of 0.990) while by an increase of pressure from 12 to 14 bar, the permeate flux at steady state conditions increased from 36.84 to 50.23 $L.m^{-2}.h$ (slope 6.69 $(L.m^{-2}.h)$/bar).

The effect of operating pressure on the flux decline is shown in Fig. 6. The flux decline was increased as the operating pressure is increased. Nearly a linear dependency between flux decline and operating pressure was observed but the slope is so small that it could be considered as constant. The reason could be explained as the effect of operating pressure at a constant flow rate on the development of concentration polarization and cake layers. By increasing the feed pressure, the permeate flux also increases, which results in faster movement of soluble ingredients toward the membrane surface. Therefore, by an increase in feed pressure, the development of the polarized layer becomes faster and the thickness of the polarized layer would increase. Moreover, more compaction of the cake layer will result as the feed presuure is increased. All of these effects would decrease the permeation flux but the increase of the driving force (trans-membrane pressure) has overcome these resistances and the flux increased but not linearly with pressure. This means that as the pressure is increased, the resistance against permeation also increases but the permeation flux increases, too. The presence of high feed flow rate limits the increase of polarization and cake layer thickness by the shear stresses acting on the membrane surface. As the pressure is increased, the thickness of the polarized and cake layer also increased and more compacted cake with lower permeability would result and the flux declines more. The flux decline increased from 26.8% at 6 bar with a slope of nearly 0.154% per bar, which seems to be so low that it is ignorable (Fig. 6). Therefore, it could be concluded that feed pressure has a slight effect on the flux decline.

3.4. Effect of feed pressure on rejections

The effect of operating pressure (6, 8, 10, 12 and 14 bar) on COD, BOD and TDS rejections at 250 L/h feed flow rate and 30°C is shown in Fig. 7. The results showed that by increasing the operating pressure, BOD and COD rejections increased but TDS rejection decreased. Both COD and BOD rejections followed similar trends. As the feed pressure is increased, the cake layer becomes more compact which results in higher rejections for BOD and COD compounds. Moreover, by increasing the feed pressure, the permeate flux has also been increased which in turn increases the rejection of the soluble and insoluble species from the surface of the membrane. On the other hand, TDS rejection decreased as the feed pressure is increased. The reason could be explained as the occlusion of the soluble salts and ions in the porous cake layer which limits the influence of shear forces acting on the membrane surface. As the pressure is increased, the concentration of the solutes at the membrane surface is increased. The occlusion of the soluble salts within the porous cake increases the amount of the adsorbed ions on the membrane surface and consequently increases the passage of the ions through the membrane and decreases the apparent rejection coefficient for the positive charge ionic species. By increasing the feed pressure from 6 to 14 bar, the rejection for the COD and BOD increased from 42.3% and 45.8% to 77.9% and 74.1%, respectively while the TDS rejection decreased from 96.8% to 86.5%.

3.5. SEM

Fig. 8 shows the images have taken from the top surface of the clean and fouled membranes with different magnifications by a KYKY-EM3200 (KYKY Technology Development Ltd., Beijing, China) scanning electron microscope (SEM) at an accelerating voltage of 26 KV.

The left-hand image shows the surface of a clean membrane and the right-hand image shows the fouled membrane.

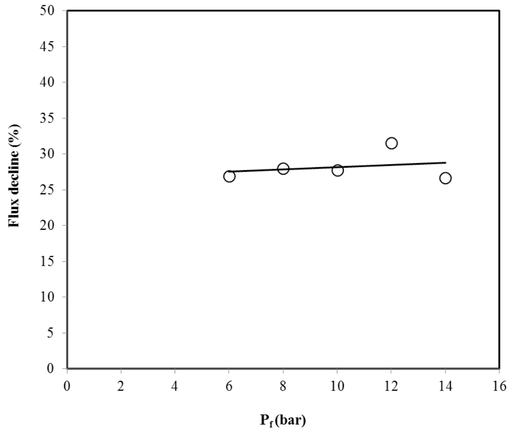

Fig. 6. Effect of operating pressure on the permeate flux decline at Q_F = 250 L/h and T_F = 30°C after 660 min.

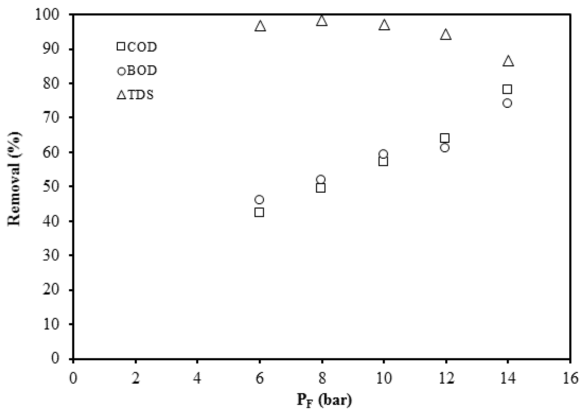

Fig. 7. Effect of feed pressure on COD, BOD and TDS rejections at Q_F = 250 L/h and T_F = 30°C after 660 min.

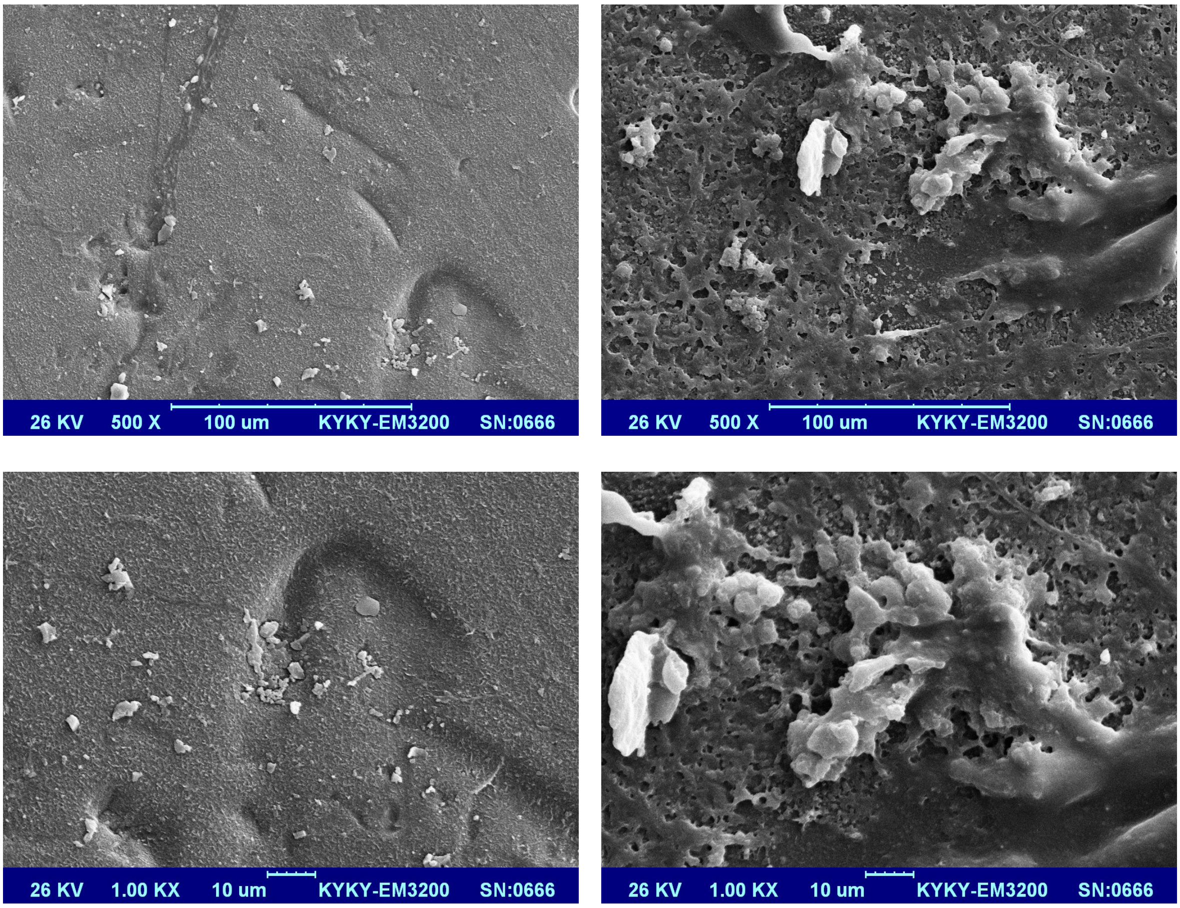

Fig 8. SEM images of the clean and fouled membranes with different magnifications. Clean (left) and fouled (right) membrane surfaces with two magnifications of 500X and 1,000X.

Small crashes on the surface of the clean membrane are due to the effect of feed side spacer on the membrane surface during the spiral wounded module wrapping. A thick, heavy and sticky fouling is observed on the fouled membrane surface which has been formed during the membrane filtration of the wastewater. This layer which is named the cake layer is comprised of the insoluble soapy materials, esters, unreacted oils and gums.

Based on Fig. 8, severe fouling is observed on the membrane surface which is unusual for nanofiltration and reverse osmosis membranes. This fouling should not be neglected, if so, permanent damage of the membrane will occur. Two strategies could be considered for future studies: fouling mitigation and cleaning. Two methods for fouling mitigation are proposed as: pulse-feeding and gas sparging. In the first method, the feed is introduced to the membrane module pulse-wise which removes the formed cake from membrane surface and in the second method which seems to be more effective, an inert gas is sparged at the surface of the membrane which introduces mechanical force (shear) and mitigates the fouling [22,23]. Cleaning of the membranes is a well-known technique for recovery of flux after fouling of the membranes. Chemical compounds such as acids, bases, surfactants and buffers are usually used for this purpose. It should be noted that chemical cleaning is generally either expensive or reduces the effective life time of the membranes. Therefore, chemical cleaning is not recommended unless other physical methods could not recover the flux.

4. Comparison of different methods for treatment of biodiesel water-washing wastewater

The results show that treatment of biodiesel water-washing wastewater by the nanofiltration system is a versatile, reliable and cost effective method. Comparing the previously reported efficiencies of the wastewater treatment systems applied for biodiesel wastewater treatment (Table 1) shows that coagulation system has the highest efficiencies both for BOD and COD removal followed by biological digestion systems, adsorption, microbial fuel cell systems and electrocoagulation process.

Nanofiltration is a fast treatment method without requiring stringent pretreatment. The residence time in this system is usually less than 1 min while all of the mentioned methods have relatively higher residence times. Higher residence times mean larger systems and higher investment costs.

In coagulation systems (both ordinary and electrocoagulation) it is necessary to add some chemicals to the wastewater such as aluminum compound, PAC, ferric chloride, etc. Of course, these processes produce some by-products which should be disposed. An introduction of metal ion containing the compounds, such as aluminum compounds, results in some sludge that has environmental limitations for disposal.

Biological digestions (both activated sludge and MBR) systems are environmental friendly systems, but they are very slow and therefore require long residence times and need to be performed at controlled conditions such as temperature and pH for attaining high efficiencies. Usually, large aeration ponds are needed for these operations and for situations in which there are limitations for construction of such large ponds, the use of these methods are not possible suitable.

Adsorption onto the suitable adsorbents is relatively faster than the mentioned methods but it needs large amounts of adsorbent such as activated carbon (because of low adsorption capacities) and regeneration of the loaded adsorbent. Therefore, this method could be suitable only for low COD and BOD contained wastewaters. Also, regeneration of the loaded adsorbents is usually performed by chemicals such as acids which produces some other wastewaters. The total cost of an adsorption system is relatively high because of replacing the used and inactivated adsorbent by the fresh one and consumption of chemicals for regeneration.

Microbial fuel cell systems are relatively new systems but they suffer from the growth of biofilm on the membrane surface which causes severe polarizations. The efficiency of this system is relatively low.

In comparison with these methods, nanofiltration seems to be a better system choice for treatment of the biodiesel's water-washing wastewater because it is very simple, fast and is able to remove nearly 78% of COD and 86.5% of TDS in a single pass system within a few seconds without using any chemicals or producing a second wastewater. It should be noted that nearly none of the mentioned methods in Table 1 could remove TDS while the NF removes TDS with high efficiency.

Among the mentioned methods, only biological systems (activated sludge, MBR and microbial fuel cell systems) eliminate the organic pollutants. Other methods including NF only remove the organic pollutants from the main wastewater stream physically and produce a waste stream having higher concentration than the initial feed. Therefore, it is more logical that a hybrid system including a NF and a biological system such as MBR could be more effective. The use of such a hybrid system will have much smaller footprints than a standalone MBR. In this hybrid system, the wastewater initially enters the NF system in which nearly 70% of the initial wastewater volume is recovered as the permeate with acceptable specifications for recycling through the biodiesel production plant and the remainder (reject or retentate stream) is sent to the MBR system in which the organic pollutants are digested by the microorganisms and the treated stream is sent to the main process after passing through a suitable RO system in order to decrease the TDS.

5. Conclusion

An effective and fast method for treatment of the biodiesel water washing effluent without the addition of chemicals has been introduced. In this method, a commercial nanofiltration membrane was effectively applied for reducing COD, BOD, and TDS of the waste water. The effect of feed flow rate and pressure was studied and the following results were obtained:

- An increase in feed flow rate increases the rejection for COD and BOD due to lowering the adverse effect of concentration polarization.
- An increase of the operating pressure increases the rejections for BOD and COD due to formation of the cake layer which is nearly impermeable to the high molecular weight organic species.
- A maximum removal percentage for BOD and COD was obtained as 74.1% and 77.9%, respectively at 14 bar feed pressure and 250 L/h feed flow rate.

The present method could be considered as part of the strategies for commercialization of biodiesel production through water recycling in biodiesel production plants to minimize water consumption and wastewater generation. Certainly, one of the most challenging problems for commercialization of this method is biofouling of the applied NF membranes that should be considered in future researches.

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