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APPLICATION OF MEMBRANE PROCESSES TO SEPARATION OF HYDROCARBONS FROM WASTEWATER

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Oily water emulsions are the main pollutants emitted into water by industry and domestic sewage and are the major pollution problem because oilfield produced water has distinctive characteristics due to organic and inorganic matter. Mainly, it includes salt and hydrocarbons, which may be toxic to the environment. So far, there are several techniques for oil separation. Typical ones include chemical emulsification, pH adjustment, gravity settling, centrifugal settling, filter coalescence, heating treatment, electrostatic coalescence, membrane separation, etc. There are some advantages and disadvantages connected with each of these techniques. This paper reports the application of UF membranes for hydrocarbon wastewater separation. The aim of this study is to investigate the effect of membrane properties and the effect of operating conditions, i.e., the

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transmembrane pressure and the initial feed concentration on ultrafiltration of the synthesized oily water.

Introduction

Membrane separations are used in industrial processes and are utilized currently for oilfield produced water treatment. Some of the most promising methods based on the membrane separation processes are dehydration of oil emulsion by pervaporation, or by reverse osmosis, flocculation followed by microfiltration, microfiltration, membrane distillation and ultrafiltration. The advantages of membrane process such as lower capital cost, the non-requirement of any chemical addition and the capability of generating permeate of acceptable quality are well known. Among all these processes, ultrafiltration (UF) is considered to be a versatile separation process [1]. This pressure-driven process is widely used for separation, purification and concentration of water-soluble solutes or water dispersible materials.

Theory

Separation of Oily Water

Oily water emulsions are the main pollutants emitted into water by industry and domestic sewage and are the major pollution problem because oilfield produced water has distinctive characteristics due to organic and inorganic matter. Mainly, it includes salt and hydrocarbons, which may be toxic to the environment. So far, there are several techniques for oil separation. Typical ones include chemical deemulsification, pH adjustment, gravity settling, centrifugal settling, filter coalescence, heating treatment, electrostatic coalescence, membrane separation, *etc*. There are some advantages and disadvantages connected with each of these techniques.

Oil might be present in water as free (> 150 μm), dispersed (150-50 μm), emulsified (50-0.1 μm), and/or soluble (< 0.1 μm) form. Free and dispersed forms are efficiently removed by gravity in oil/water separator devices. An emulsified fraction consists of stable oil droplets, which have to be destabilized before removal [2].

One of the advantages of UF compared with the other separation processes is a high reduction of mineral oil and a good separation of heavy metals, such as Ni, Cr, Pb and Cd [3]. Because of its suitable pore sizes (usually in the range of 2-50 nm) and the capability of removing emulsified oil droplets without any de-emulsification processes, ultrafiltration has been demonstrated as an efficient method or a pretreatment step before nanofiltration and reverse osmosis in oil/water emulsions treatment [4-6].

In Series Resistance Model

Various models are proposed to analyze and predict the flux decline behavior during filtration. All of them can be classified in three broad categories, namely (a) osmotic pressure controlled, (b) gel layer controlled and (c) resistance in series models. According to resistance in series model, the flux decline is due to the combined effects of irreversible membrane fouling and reversible fouling (concentration polarization) over the membrane surface in addition to the membrane resistance [7,8].

In most of the industrial applications, the flux decline during UF is the cumulative effect of several mechanisms, including adsorption of solutes on the membrane surface, pore plugging, concentration polarization, *etc*. Minimization of membrane fouling is essential to make the membrane processes economically competitive.

The total resistance was assumed as a sum of membrane resistance, resistance due to reversible polarized layer (removable by low water flow rate), semi-reversible cake/gel layer (removable at high water flow rate or with easy cleaning) and irreversible fouling (mainly pore blocking, uncleanable). In the present study, a resistance in series model, quantification of total resistance, membrane resistance, external fouling (cleanable) and internal fouling (for our cleaning method irreversible fouling) were used for a preatretment of real waste water. An effort had been made to evaluate these resistances independently by conducting independent experiments.

Membrane resistances can be evaluated using the following formulas (see Eqs (1)-(3))

$$R_m = \frac{\Delta P}{\mu_P J_W} \tag{1}$$

where μ_P is dynamic viscosity of the permeate, J_W is the permeate flux for deionised water, and ΔP is the transmembrane pressure

$$R_{M,IF} = \frac{\Delta P}{\mu_P J_{W,mech.cleaned}} \tag{2}$$

where $J_{W,mech.cleaned}$ is the steady state permeate flux of membrane after mechanically cleaning

$$R_T = \frac{\Delta P}{\mu_P J_\infty} \tag{3}$$

where J_∞ is the steady state permeate flux of membrane during separation experiment.

The difference between this resistance and the membrane resistance with internal fouling $R_{M,IF}$ is external fouling resistance R_{EF}.

Experimental

Materials

Demineralized water with electrical conductivity below 10 µS cm^{-1}, light fuel oil and model wastewater after separation (both obtained from company ASIO) were used. Model wastewater consists of Light fuel oil, ARVA (emulgator), suspended solids ($CaCO_3$, kaolin) and water. Real wastewater was obtained from a car wash station in city transport company Pardubice.

Table I Characteristics of car wash wastewater

Parameters	Zaneti *et al.* [2]	Bhatti *et al.* [9]	Experimental wastewater
pH	7.1-8.3	7.89-8.75	8.4
Conductivity, µS cm^{-1}	508-758	1159.7-1289.6	980
TSS, mg l^{-1}	49-87	110-5855.66	36-52
Oil contents, mg l^{-1}	5-7	1.3-83.7	2-15

The solution of wastewater is presented in Table I. There are given only important factors for our separation method. For comparison, the values given in literature are also shown in Table I.

We have chosen ten flat sheet membranes, eight membranes for UF a two membranes for MF. The membranes were obtained from company ASIO, Brno (producer is Microdyn-Nadir). The basic characteristics are listed in Table II. The membrane area was 130 cm^2.

Table II Basic characteristics of membranes tested
UF membranes:

Name	Material	MWCO kDa	Permeability A $\mathrm{l\ m^{-2}\ h^{-1}\ bar^{-1}}$
US005	PSH	5	4.9
US100	PSH	100	13.7
UP005	PES	5	16.6
UP020	PES	20	97.9
UP150	PES	150	498.8
UH004	PESH	4	7.4
UH050	PESH	50	106.4
UV150	PVDF	150	524.9

MF membranes:

Name	Material	r_p µm	Permeability A $\mathrm{l\ m^{-2}\ h^{-1}\ bar^{-1}}$
MP005	PES	0.05	522.5
MV020	PVDF	0.2	2301$^{1)}$

Note: $^{1)}$ at 25 °C

Experimental System

The microfiltration/ultrafiltration experimental apparatus used is shown schematically in Fig. 1.

The circulating loop was constructed of stainless steel and contained a ten litre feed suspension reservoir, pump and the membrane module. This loop was also equipped with a pressure and flow monitoring system. The crossflow velocity was controlled using the speed of the pump, and the operating pressure (and hence transmembrane pressure) in the loop was controlled by a needle valve at the module outlet; both parameters were varied independently. The loop was also equipped with a temperature regulating system.

In the separation experiments, model solutions or real wastewater from a car wash were used. During all the tests, the filtration was run at the constant retentate flow rate of 150 l h^{-1} and the constant pressure of either 2 bar for UF or 1 and 0.5 bar for MF.

Before each filtration experiment, the demineralised water flux of membrane was measured. The membrane was placed into the membrane module, and deionised water was circulated in the test loop at different pressures (from 0.5 bar to 3 bar for UF membranes and 0.25 bar to 1 bar for MF membranes) to reached stable conditions (pressure and temperature 20 or 25 °C). After this time, a stable value of the permeability of the membrane to water was observed and next value of pressure was set. From the measured permeate flow rate, the membrane resistance R_M can be calculated from Eq. (1).

After this measurement, the dispersion was placed into the reservoir and the filtration, the operating pressure as well as feed velocity were adjusted by the regulation system. The stock dispersion was kept at the constant temperature of 25 °C. The flux through membrane was measured by weighing permeate and timing the collection period (by use of a balance interfaced with a computer). Both the retentate and permeate were recirculated back into the reservoir. Therefore, the concentration in the recirculation loop remained virtually constant.

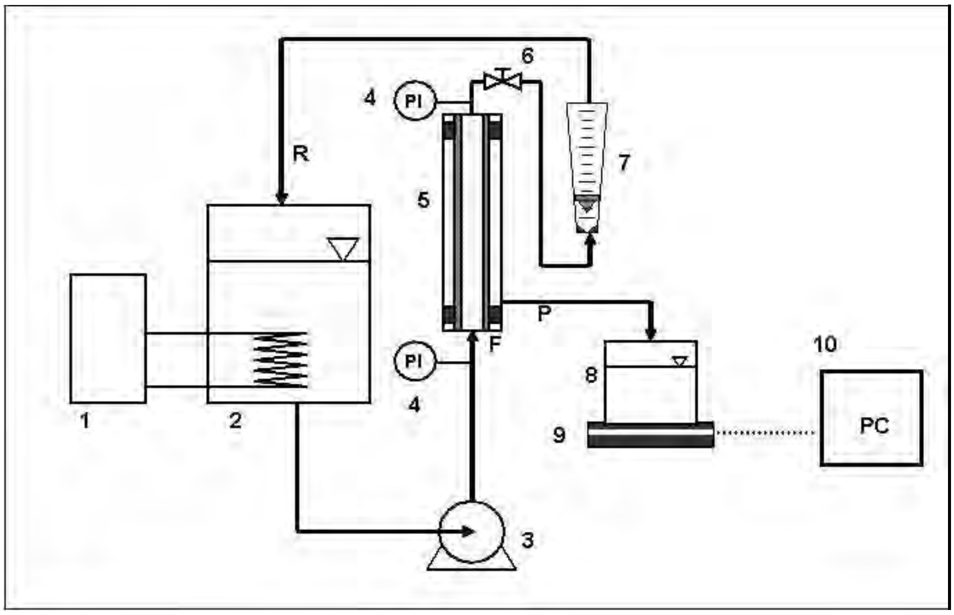

Fig. 1 Schematic diagram of crossflow microfiltration system: 1 – system for maintaining constant temperature, 2 – stock tank, 3 – pump, 4 – sensor of pressure, 5 – membrane module, 6 – needle valve, 7 – rotameter, 8 – beaker for permeate, 9 – scale, 10 – output on PC. F – feed, P – permeate, R – retentate

The experiment was stopped after obtaining a constant permeate flux. After each experiment, the membrane was mechanically cleaned, and the unit was rinsed with deionised water, and the pure water flux was measured again under the conditions of the initial test until the steady state was attained. From this value, the membrane resistance was calculated again. The internal fouling of the membrane can be calculated from the difference between the two resistances (that is the "before" and "after" filtration resistances).

The filtration resistance after mechanical cleaning $R_{M,IF}$ was calculated from Eq. (2).

The difference between this resistance and the membrane resistance R_M is internal fouling resistance R_{IF}.

The total resistance can be calculated from the steady state permeate flux during separation experiments (Eq. (3)). This resistance includes all fouling mechanisms.

Analysis

Conductivity and pH were measured by means of portable a WTW Cond 340i conductometer and Hanna HI 9126 pH/ORP meter, respectively.
TSS was analyzed using filter with the nominal diameter of pores 0.8 μm and weighting this dry filter before and after filtering of wastewater.

Oil content was analyzed by gas chromatography (Shinadzu GC-2010). Extraction with *n*-hexane must be done before this analysis, and this extract was used as input for gas chromatography.

Results and Discussion

Pure Water Flux

Water permeability is one of the basic characteristics of membranes. The pure water permeability of the ten membranes was determined by measuring the deionized water flux at different operating pressures. According to Darcy´s law, the permeate flux is directly proportional to the pressure difference across the membrane. The slope of this line corresponds to the water permeability (A). Permeability A is given in Table II. The comparison of UF membranes is given in Fig. 2. It can be seen that the membrane with similar MWCO reached similar values. For the separation are suitable membranes with higher values of permeate fluxes, and for this reason, membranes US005, UH004 and UP005 are the least suitable from among the tested membranes (if we consider only this criterion). On the other side, membranes with higher MWCO (usually have the highest flux) can have small rejection for separated solute (in our case, light fuel oil).

Separation of „Binary“ Mixture of Light Fuel Oil-Water

The performances (i.e., the concentration of oil in the feed, the concentration of oil in the permeate, permeate flux, and oil rejection) of all the three membranes under the constant (same for all membranes) process parameters (pressure 2 bar,

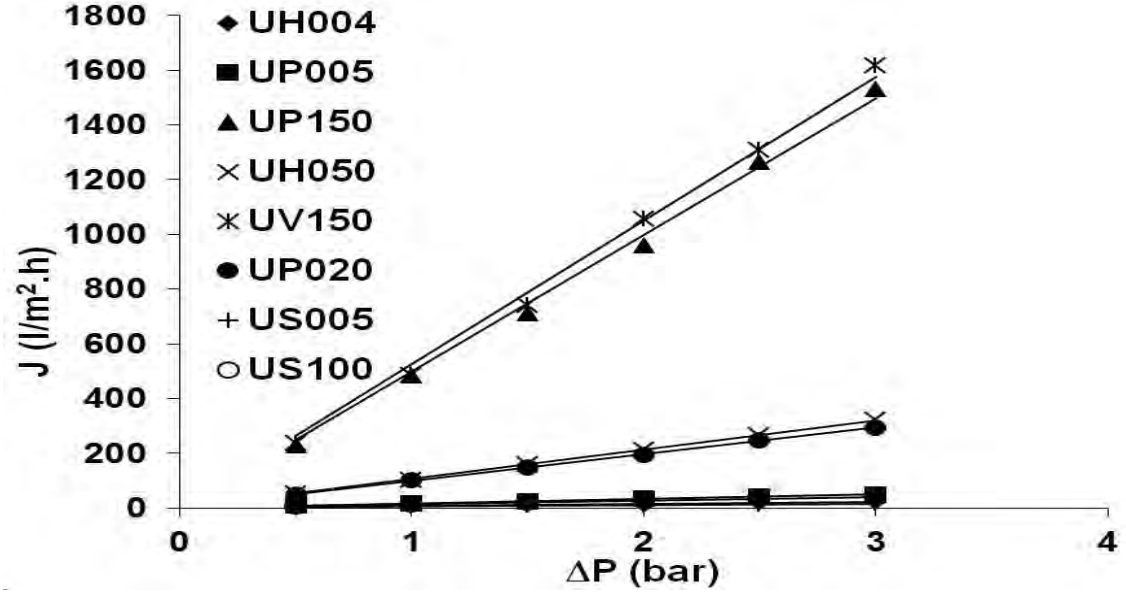

Fig. 2 Demineralised water flux as function of applied pressure

temperature 20 °C, cross flow velocity 1.1 m s^{-1}) are shown in Table III. In order to study the feasibility of ultrafiltration, separation experiments with three membranes with different cut off values and oil rejection were performed with wastewater. The difference in performance of these membranes can be assigned to many factors, like the variation of membrane pore size distributions, the difference in the interaction between the membrane material and the feed, formation of any temporary or permanent fouling layer, *etc*. From Table III, it is found that all the membranes except US100 show more than 95 % oil rejection within the feed concentration range. The clear difference in the values of permeate flux of different membranes under similar operating conditions can be observed from the Table III with UP020 and US005 membranes exhibiting the highest flux (77 l m^{-2} h^{-1}) and the lowest flux (9 l m^{-2} h^{-1}), respectively. The feed concentration decrease during experiment was due to adsorption of oil on all walls and due to cake formation. This cake layer improves separation efficiency as it can be seen from Table III. The decrease is not only due to cake formation because it was observed in the experiment without membrane too. This explanation means that oil (mainly free oil) is adsorbed on feed tank walls and all tubes. For this reason, permeate and retentate samples must be taken at the same time. This procedure eliminated time dependency of the feed concentration and its effect on rejection.

Separation of Model Mixture of Wastewater

The third step of experimental work was focused on separation of model wastewater after sedimentation pretreatment. This type of water was obtained from company ASIO. This model water was prepared using mixture of solution (based

Table III Efficiency of separation of „binary“ mixture light fuel oil-water

Membrane	c_F, mg l^{-1}	c_P, mg l^{-1}	J, l m^{-2} h^{-1}	R
UP020	29	1.3	77	0.955
	20	0.7		0.965
	18	0.6		0.966
US100	18	1.4	25	0.922
	12	0.9		0.925
	10	0.7		0.930
US005	25	1	9	0.960
	15	0.3		0.980
	10	0.1		0.990

on oil) and water. The final mixture before sedimentation pretreatment must contain 4 ml oil fraction in 1 liter water. This is much higher than normally occurs in car wash wastewater (see Table I) but this is typically water for testing efficiency of this type of separators. The oil fraction consists of light fuel oil, emulgator (commercial name ARVA) and suspended solids, like limestone, kaolin. For this experiment, we chose four UF membranes. Membranes US005 and US100 were not used because these membranes reached very low permeate flux. For the same reason, we excluded membranes UP005 and UH004. However, this decision was based on measurements of demineralised water permeability. The best results can be obtained for membranes with high water permeability, high permeate flux, and high oil rejection. Theoretically, we can assume high concentration in permeate as compared with binary system (note that here emulsifier is added). As it can be seen in Table IV all the membranes reached the concentration in permeate equal to 0.2 mg l^{-1}, i.e., near the detection limit of analytical method. It is caused by the time between the end of pretreatment and final separation method, UF. Some biological de-emulsification process operates and produces flocs, which themselves decrease the concentration of oil and secondly adsorb other oil on surface, and droplets can be coalesced. The nature of flocculation during this process was oil adsorption on flocs and increasing of oil droplets, which improve separation ability of membranes [10]. Before UF, the flocs were separated with stainless steel filter (mesh size 0.5 mm). This experiment can, therefore, exhibit mainly a fouling tendency of tested membrane, not separation efficiency. This means that the intensity of permeate flow is influenced by concentration of oil in feed. Membrane fouling is a main drawback in the practical application of UF to oil-water separation. It has been generally agreed that enhancement of the hydrophilicity of a UF membrane could reduce its fouling. Much research on the hydrophilization of UF membrane materials has been carried out [11]. The largest resistance is just concentrated in this layer.

Steady-state values of intensity of permeate flow can be expected approx. after 2 hours of the experiment. The experiments with membranes UH050 and UV150 confirmed it, because the values after 2 and 3 hours were the same. From Fig. 3 one can see firstly a rapid decreasing from values similar to those obtained with pure water, second stage of a long time decreasing and last part of stable values of intensity permeate flow. All the membranes reached similar values of intensity of permeate flow in the range of 45-55 l m^{-2} h^{-1}. Membrane UH050 reached this value with the highest feed oil concentration (259 mg l^{-1}). If we assume influence of the oil concentration on flux, we can recommend this membrane. The results from separation of model wastewater are summarized in Table IV.

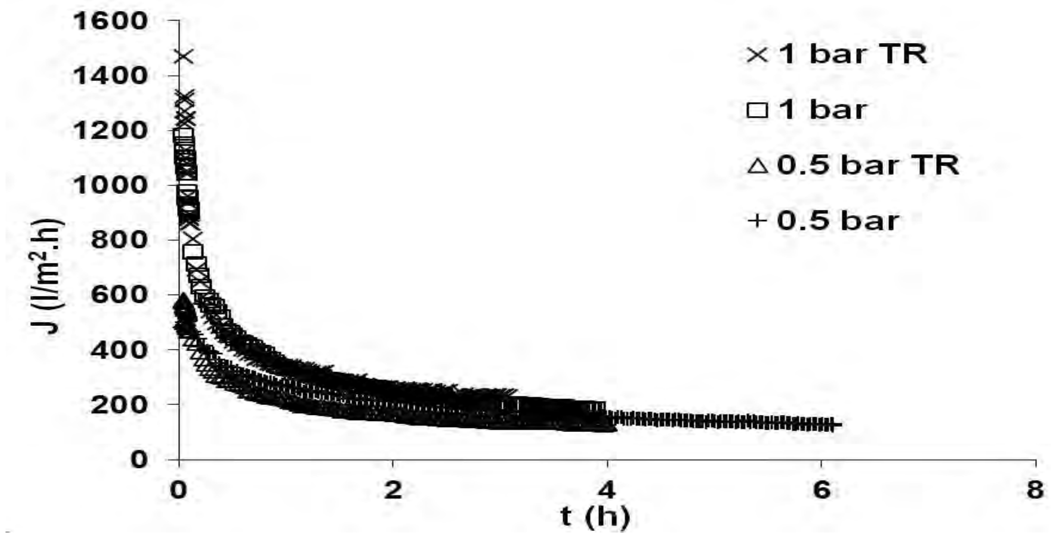

Fig. 3 Time-dependent fluxes of tested membrane during separation of model wastewater

The stability of mixture, i.e., the independence of area where feed sample is taken, was tested taking samples from different areas in the feed tank. All the samples had the same concentration, which shows that the mixture is not separating *via* sedimentation during our UF experiment.

Pretreatment of Real Wastewater

The last part of the experimental work was focused on separation of real wastewater using MF membrane (MV020). It will be the first stage of the membrane separation in a real separator. We want to decrease fouling potential of feed for UF stage. MF is able to minimally retain TSS. It means mainly dust, sand, *etc.* with a small diameter, which cannot be removed during sedimentation. Real

Table IV Feed concentration of oil and permeate flux during separation of model solution

Membrane	Permeate flux J, l m^{-2} h^{-1}			Oil feed concentration c_F mg l^{-1}			Oil permeate concentration c_P mg l^{-1}
	0.5h	1h	2h	0.5h	1h	2h	
UP020	59.0	52.6	45.7	92.3	84	65.4	≤ 0.2
UP150	62.3	53.8	49.8	179	148	124.6	≤ 0.2
UH050	78.1	58.2	47.9	259	246	217.6	≤ 0.2
UV150	73.5	62.1	54.8	76.6	67	66	≤ 0.2

wastewater was firstly filtered with a classical in line filter with the pore diameter of 50 μm (OPERA, washable CRL filter). This pretreated water was used for MF experiments. We do not assume any change in the oil content. Membrane MV020 was used because it reached the highest demineralised water flux, and we want to obtain the separation ability of this membrane for light fuel oil. Process parameters during these experiments were 0.5 bar or 1 bar and 25 °C. The cross flow velocity was the same as in UF experiments (1.1 m s^{-1}). Because there exist some adsorption effects, not only a total recycle mode (TR) was used. The second operation mode, like feed and bleed, was used. This mode simulates normal operating mode in a real treatment station. The permeate stream was replaced with new waste water, and the liquid level in feed tank was held constant.

Figure 4 clearly shows that the time-dependent flux curves for experiments at 1 bar are similar. This means that a small change in oil content does not change the flux. During the experiment with a smaller applied pressure difference a small deviation exists. The flux decreases slowly in feed and bleed mode. This behavior can be explained by small values of TSS (48.9 vs. 36.7 mg l^{-1}) and, due to this reason, slowly increasing thickness of the particles layer on the membrane. The steady state of permeate flux is independent of the type of operating mode, because hydrodynamics conditions influence these values. The results are summarized in Table V. Oil rejection with this membrane was poor, max. 72.2 %.

Resistance in Treatment of Real Wastewater

On the basis of Eqs (1)-(3), the resistance of each layer was calculated. The membrane resistance was calculated from the value of permeability for new membrane. Similar procedure was used for the evaluating membrane resistance with internal fouling. The difference was in the fact that here intensity of the mechanically cleaned membrane (after experiment with real waste water) is measured. The total resistance is calculated from steady-state values of the per-

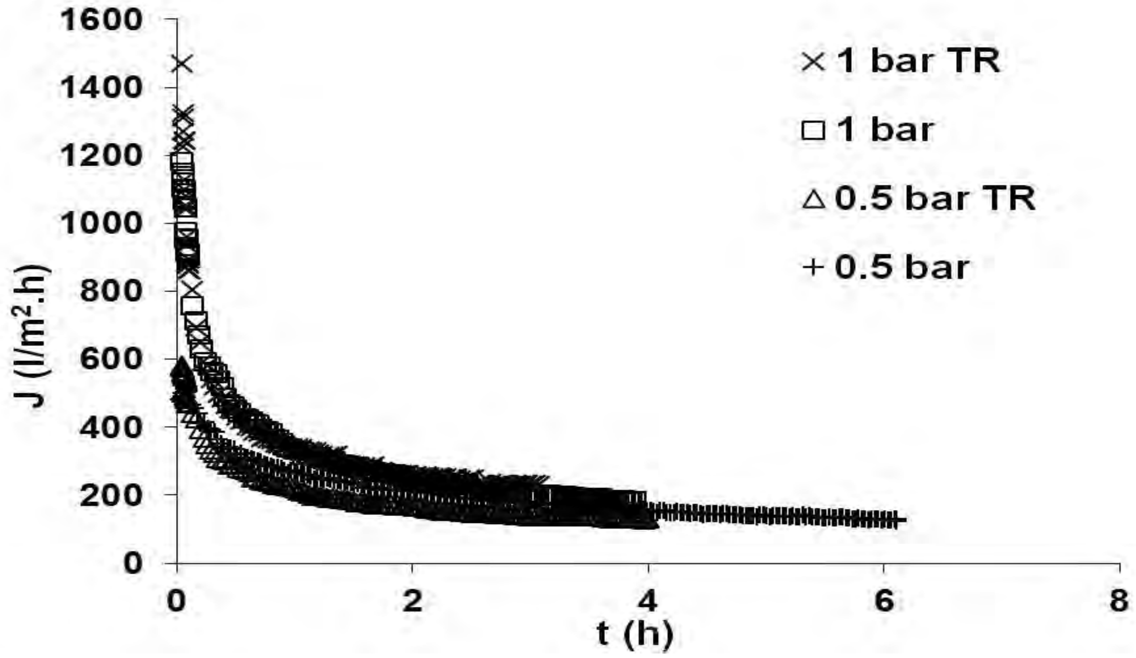

Fig. 4 Time-dependent fluxes of MV020 membrane during separation of real wastewater from carwash

Table V Characterization of real wastewater before (feed) and after (permeate) MF separation

ΔP, bar	FEED			PERMEATE		
	TSS, mg l^{-1}	Light fuel oil, mg l^{-1}		TSS, mg l^{-1}	Light fuel oil, mg l^{-1}	
		<1h	3 h		< 1h	3 h
1-TR	52.1	3.2	2.2	0	1.2	0.6
0.5-TR	48.9	3.0	2.1	0	1.8	1.7
1	51.3	1.7	4.8	0	1.2	1.3
0.5	36.7	1.8	3	0	1.5	1.8

meate flux the during experiments with waste water. The obtained values of resistances are given in Table VI.

It is clearly shown that the external fouling (EF) causes the highest resistance. This layer mainly consists of cake layer (1.438×10^{12} m^{-1}). Internal fouling (IF), which is mainly due to the plugging of pores, reached the smallest value 1.384×10^{11} m^{-1} and, only membrane had very small 1.738×10^{11} m^{-1}. EF can be influenced, for example, by process parameters, mainly cross flow velocity, the applied pressure difference and concentration [12]. For IF, we assume a small influence of the concentration because only a part of particles smaller than the diameter of pores can be inside the pores. For this reason, the distribution of particle size in wastewater is more important. We want to find out how it will

Table VI Resistances of different layers in separation of real wastewater

Type of resistance	$J^{1)}$, l m^{-2} h^{-1}	R, m^{-1}
Membrane	2301.3	1.738×10^{11}
Membrane+IF	1281.0	3.123×10^{11}
Membrane+IF2	1233.2	3.244×10^{11}
Total	228.6	1.751×10^{12}
IF		1.384×10^{11}
IF2		1.505×10^{11}
EF		1.438×10^{12}

Note: [1)] flux at 1 bar (permeability); IF2 means after second separation experiment and second cleaning

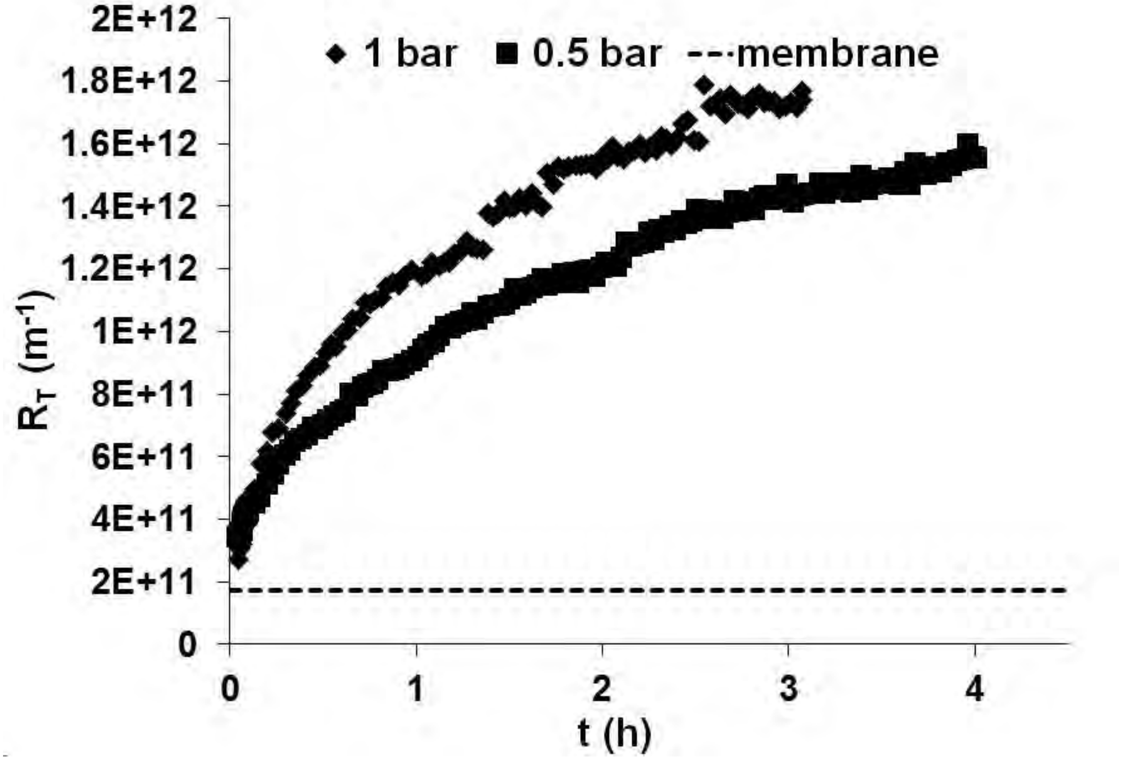

Fig. 5 Time-dependent total resistance during separation of real waste water (MV020, 1 a 0.5 bar)

change with increasing number of experiments. We repeated the experiment, cleaned the membrane and calculated it again. We obtained very similar values (1.384×10^{11} or 1.505×10^{11} m^{-1}). It means that this resistance after one experiment is stable and can be added it to membrane resistance. This value does not influence

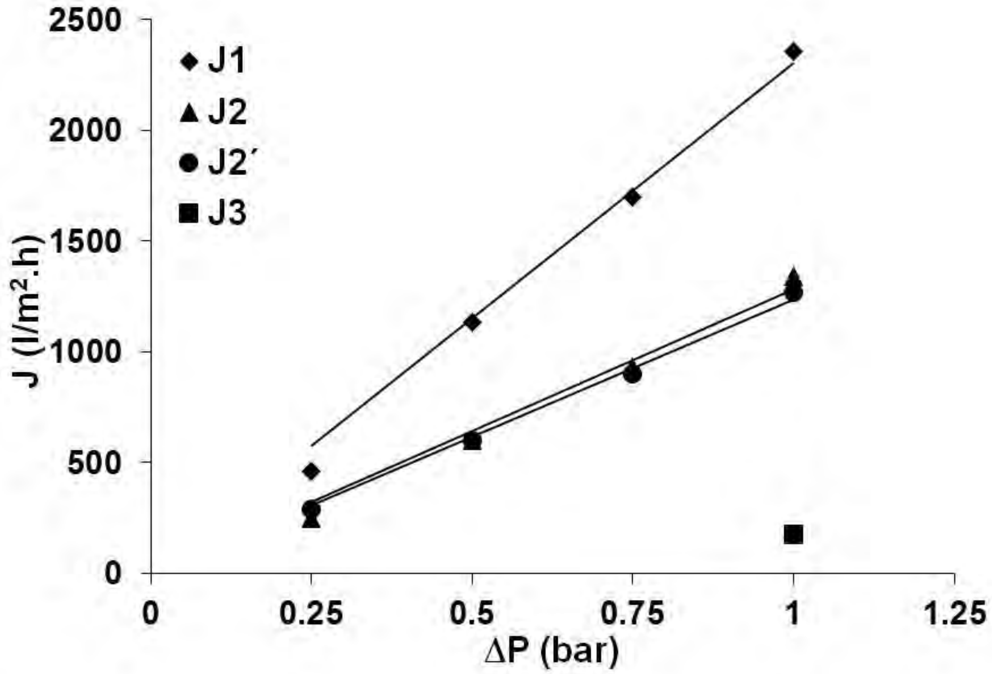

Fig. 6 Permeate flux as function applied pressure at different states of membrane (different resistances exist)

the total resistance in next experiments.

Figure 5 shows the influence of pressure and time on the evolution of the total resistance. The total resistances were 1.438×10^{12} m^{-1} and 1.557×10^{12} m^{-1} for 0.5 and 1 bar, respectively.

Figure 6 shows the permeate flux as a function of applied pressure at different states of membrane (J1 new membrane, J2 and J2′ after first cleaning and second cleaning, and J3 steady-state during separation).

Conclusion

It was clearly shown that UF have the ability of separating oil from water. The rejection obtained was higher than 95 %. More important is the fact that permeates have met the maximum allowable discharge limit (i.e., < 1 mg l^{-1}). However, considering the fact that the new Czech standards demand not more than 0.5 mg l^{-1} of oil in the wastewater, dense membranes must be used.

Membrane MV020 cannot be used directly for a decreasing oil concentration below discharge limit. However, it can be used as useful pretreatment for UF stage of the real separator. This membrane retains all TSS and, therefore, decreases the feed fouling potential.

UF membrane can be recommended for final separation of light fuel oil from wastewater. The best suitable membrane can be UH050 which has the smallest fouling potential.

Acknowledgement

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