Investigations on the Use of Different Ceramic Membranes For Efficient Oil-Field Produced Water Treatment

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Abstract
Efficient performance of the combination of treatment processes for oilfield produced water generated from oil tank dewatering was investigated in the study presented below. By-produced wastewater is generated in significant quantity during exploitation of crude oil and gas from onshore and offshore production operations. This wastewater, commonly referred to as “produced water”, has distinctive characteristics, due to their organic and inorganic compounds. However, these characteristics change from well to well. The treatment process investigated here consists of a pre-treatment step utilizing microfiltration (0.1 and 0.2µm pore size filters) and/or a simulated batch dissolved air flotation (DAF), and a multistage post-treatment step utilizing cross-flow ultra- (0.05µm pore size and 20kDa molecular weight cut-off filters), and nanofiltration (1 and 0.75kDa MWCO filters). Filters used were ceramic membranes. To determine the separation capability of the processes described, various parameters, such as trans-membrane pressure varying from 0.5 to 2 bar, cross-flow velocity in the range of 0.6 to 1.3m/s, influent oil concentration ranging from 32 to 5420 parts per million (ppm) and different membrane cleaning methods used were investigated. The average permeate flux varied from 3.4 to 3300 l/h*m²*bar, total oil removal was up to 99.5% and total organic carbon removal reached 49%.

1. Introduction

The onshore and offshore conveyance of crude oil and natural gas is associated with the co-production of significant quantities of wastewater, referred to as “produced water”. Produced water is considered the largest volume waste stream in the exploration and production process of oil and gas [1]. Oilfield produced water has distinctive characteristics due to organic and inorganic matter. Mainly, it includes salts and oil hydrocarbons, which may be toxic to the environment. However, its characteristics and volume vary greatly from well to well and depend on the lifetime of a reservoir [4]. Over time, the percentage of water increases and the percentage of product decline. Hence, produced water is difficult to treat. Disposal, re-injection and reuse are the available handling options of produced water [2, 3]. Disposal of produced water requires imperative environmental regulations and produced water re-injection (PWRI) requires skilful planning and treatment to meet the quality needed for re-injection water to avoid formation damage.

In general produced water treatment is approached through de-oiling and de-mineralizing before its disposal or utilization. Various technologies and methods exist for treatment of oil field produced water. Successful treatment generally requires a series of pre-, and post-treatment operations to remove various contaminants. Traditional technologies such as clarifiers, dissolved air flotation, hydrocyclones and disposable filters and absorbers respectively [*e.g.*, 5] do not achieve the separation efficiency required for beneficial use of produced water by meeting potable and irrigation water quality standards [6]. The practicality of using treated produced water for beneficial purposes depends on a number of factors, including the volume of water available, the existence of a local need for water, and the amount of treatment required to meet government or industry-use standards [7].

Membrane technology is used in industrial processes, in industrial wastewater treatment, and is utilized currently for oil field produced water treatment [4, 8, 9]. Ceramic (or inorganic) membranes have attracted interest due to their superior mechanical, thermal, and chemical stability. The primary advantage of using ceramic membranes is the ability to accomplish the current and pending regulatory treatment objectives with no chemical pre-treatment. The study presented here focuses on the efficient development of single and combined treatment processes for oilfield produced water and different prepared feed solutions. The process consists of a pre-treatment step utilizing cross-flow microfiltration (MF) (0.1 and 0.2µm pore size filters) and/or a simulated batch dissolved air flotation (DAF), and a multistage post-treatment step utilizing cross-flow ultra- (UF) (0.05µm pore size and 20kDa molecular weight cut-off filters), and nanofiltration (NF) (1 and 0.75kDa molecular weight cut-off filters). Filters used were ceramic membranes. Various parameters potentially affecting the permeation and separation behaviour of the purification process such as trans-membrane pressure (TMP), cross-flow velocity (CFV), oil concentration in the feed and different membrane cleaning methods used were investigated through the measurement of the average permeate flux, the oil removal efficiency and the total concentration of organic compounds (measured as TOC).

2. Materials and Methods

Ceramic Membranes

Ceramic membranes used are tubular and consist of a porous support material (generally α-alumina), a minimum of one layer of decreasing pore diameter and a separating layer (α-alumina, zirconia, etc.) covering the internal surface of the tube [5]. Asymmetric multilayer Al_2O_3 and TiO_2 ceramic MF, UF and NF membranes in different stainless steel housing (Tab. 1 and Fig. 1) were used.

Fouled membranes and cleaning methods

Fouling through suspended oil and grease, particles and colloids, salts and various other trace metals is one of the most common problems and a major operational factor encountered in produced water treatment applications of membranes [10]. To reduce membrane fouling, the effect of chemical cleaning and back flushing on ceramic membranes was investigated.
Chemical cleaning. Chemicals used for membrane cleaning were lye solutions (1 % (w/w) NaOH solution, Ultrasil P3-14, Ultrasil P3-10 for 30 to 60 min), dissolved in distilled water. Cleaning efficiency was evaluated determining the water flux after cleaning relative to the initial water flux.

Back flushing. Back flushing is a method applied commonly to remove a layer of retained material [11]. Here, the flow was reversed to flush the membrane pores from the permeate and, thus, to release material retained in the membrane pores.

Preparation of model solution

Three different model oily wastewaters (model solutions a-c) were prepared in a heated stirred tank through mixing waste oil (5%, 10%, 20% (w/w)) with distilled water for 30 min at 60°C (Tab. 2). To simulate a primary process of separation from the oil, the mixture was left for 30 min to clarify. The free oil was recovered and pumped back to the waste oil tank. The model oily wastewater showed a uniform yellowish colour.

Oilfield produced water characterization

Characteristics of produced water from oil and gas fields, mainly containing salts and oil hydrocarbons, vary and may differ significantly from well to well [12]. Samples of produced water from tank dewatering were obtained from German BP AG, Oil Refinery Emsland, Lingen. The concentration range of components in tank dewatering produced water (Tab. 2) used in this study are given.

Membrane-assisted continuous reactor

The cross-flow membrane filtration equipment (MF, UF, NF) was conducted using a continuous stirred tank reactor (CSTR) with a membrane module (Fig. 1). The unit had a maximum operating pressure and temperature of 3 bar and 90ºC respectively. It consists of a 5l feed vessel, a permeate vessel, a centrifugal pump and various self-made membrane modules and was equipped with tubing ensuring back flushing. At regular time intervals, back flushing was executed pumping a mixture of permeate and air reversely. The mean pressure at the membrane was determined measuring the pressure before (P_1) and after the membrane pressure (P_2) and averaging these values; this pressure is reported as the trans-membrane pressure (TMP). All filtration experiments were carried out at 60°C.

Application of simulated batch dissolved air floatation (DAF)

Flotation is a solid–liquid separation technique separating particles through a decreased density relative to the density of the ambient liquid [13]. Alternatively, DAF may be considered in treatment of oil refinery wastewater [*e.g.*, 14] or during the removal of oil in emulsions from refinery produced water [*e.g.*, 15]. During flotation, small bubbles of dispersed air are released into the effluent to attach to solids or droplets. Thus, due to a decreased density, contaminant-air-particles rise to the surface and the oil layer building up can be removed easily. In this study the integration of a simulated batch DAF (Fig. 2) as a pre-treatment step for produced water was investigated. At regular time intervals, samples were withdrawn from the bottom of the flotation cell using a pump.

Water quality analysis

Oil in water determination. To measure the average oil concentration in feed solutions and in the permeate, n-Hexane ($\geq$ 95 % grade purity) was used as an extraction solvent. The analysis of oil in water was executed using a oil-in-water analyzer based on UV fluorescence (TD-500D, Nordatec GmbH, Bremerhaven/Germany).

TOC determination. TOC concentrations were determined using the TOC cell test (measuring ranges: 5 to 80 mg/l TOC and 50 to 800 mg/l TOC) and a photometer (Photolab S6, WTW, Weilheim/Germany).

Conductivity. Using a multi-range conductivity meter (HI 9033, Hanna Instruments, Kehl am Rhein, Germany), salt concentrations in the feed and permeate were determined measuring the electrical conductivity, as an indicator of the amount of dissolved materials in the solution.

3. Results and discussion

MF as a Pre-treatment step. Flux decline is a major problem in membrane filtration including the treatment of oilfield produced water [4-5, 8-10]. The permeate volume was detected during the continuous MF process utilizing ceramic membranes (0,1 and 0,2µm), tank dewatering produced water and model solution (a). Concerning both MF-membranes and when a model solution was used, a decrease in the permeate flux occurred during filtration at a constant TMP of 1bar and a temperature of 60°C (Fig. 3). Regarding the 0,2µm MF membrane and using tank dewatering produced water, a change of conductivity in the permeate and a decrease in the permeate flux from initially 126 to 27 l/h*m²*bar after a running time of 120min were observed (Fig. 4). The 0,2µm MF membrane is able to remove a percentage of total oil from 93% after 90min and of 74% after 120min of running time. Similar results were presented previously [*e.g.*, 9].

Pre-treatment with simulated batch DAF. Combinations of varied experimental parameters were tested. The airflow rate varied from 0 to 0,8 Nl/sec, the reaction time varied from 30 to 90 min, temperature was 60°C and stirring speed was 500 rpm. Data indicate that the application of a simulated batch DAF for the treatment of model solution (b) may provide a maximum removal percentage of total oil of up to 90% after 90min (Tab. 3).

Treatment with UF and/or NF membranes without pre-treatment step. The degree of efficiency of the UF and NF process was assessed in terms of the average flux rate, fouling characteristics, and the degree of oil removed. Using the 20kDa UF membrane and model solution (a), the trans-membrane flux decreased from 450 to 171 l/h*m²*bar (1 bar TMP, 120min process time) (Fig. 3). Using a 0.05µm UF membrane and tank dewatering produced water, the trans-membrane flux increased with the TMP increased from 0.5 to 2bar (Fig. 5 and 6). Oil removal up to 99% and the change in conductivity are shown (Fig. 5). With regard to the use of NF membranes and tank dewatering produced water, the initial flux across the 0.75kDa membrane is increased compared to the flux across the 1kDa membrane (Fig. 9). Data is evidence for a performance of oil removal after 45min using the 0.75kDa membranes slightly better compared to the performance using the 1kDa membrane for 60min.

Pre-, and final-treatment membrane processes in series. The multistage treatment performance utilizing 0.1µm MF and 0.05µm UF in series to process model solution (c) was compared to the multistage performance utilizing 0.05µm UF and 1kDa NF in series to process tank dewatering produced water (Fig. 7, Tab. 4 and 5). Combining MF and UF to process model solution (c), a total oil removal percentage up to 78% was obtained (experiment time of 600min, TMP of 1bar, temperature of the feed water of 60°C) (Tab. 4). The TOC removal after MF was about 38%. Combining UF and NF to process tank dewatering produced water, total oil removal was 99.5% and TOC removal was about 49% (Tab. 5). However, depending on feed characteristics and on the size and design of the membrane used, permeate flux of the membranes investigated varied from 3.4 to 3300 l/h*m²*bar (TMP of 1bar, temperature of the feed water of 60°C).

Membrane cleaning. One of the most common problems encountered in water treatment applications of membranes is fouling [16]. During membrane-based filtration of oily waste water, the oil particles may coalesce on the inner surface of the ceramic membrane, forming a layer of oil which migrates through the pores of the membrane due to the transmembrane pressure and forms an oil layer on the surface of the membrane. To maximize flux recovery of fouled membranes, chemical cleaning and back flushing were investigated as cleaning strategies. The efficiency of chemical cleaning of MF and NF membranes was in the range of 33 to 61 % using various lye solutions (Tab. 6). Utilizing a 0.2µm UF membrane, the trans-membrane flux versus operation time is shown for continuous and back flushed operation (Fig. 8). Back flushing was carried out for periods of 120sec at every 20min by pumping a mixture of permeate and air at a TMP of 2bar. When no back flushing was used the trans-membrane flux declined continuously from initially 236 to 57 l/h*m²*bar after 10 min.

4. Conclusions

In this study, efficient performance of the combination of treatment processes for oilfield produced water generated from oil tank dewatering and prepared model oily wastewaters was investigated. The influence of different pore sizes of the ceramic membranes and characteristics of feed water used on the separation behaviour were investigated determining permeate flux, TOC and oil removal efficiency. Data obtained in this study indicate that the single and combined treatment processes presented as pre-, and post-treatment steps, which consists of micro-, ultra-, and nanofiltartion systems using different ceramic membranes, were feasible to remove oil from oilfield produced water and various prepared model solutions. Total removal percentage of oil content up to 93% with MF as pre-treatment step and up to 99.5% with UF followed by NF as final treatment was shown. The oil removal efficiency results obtained from experiments show good agreement with those available in the literature [e.g., 17-21]. Mueller et al. [17] studied two ceramic membranes (0.2 and 0.8µm pore sizes) for the treatment of oily water Hueneme field in California. The oil removal efficiencies were about 98% to 99%. Zhong et al. [20] studied the performance of MF using 0.2µm ZrO_2 ceramic membrane combined with traditional chemical method-flocculation as pretreatment. Tompkins et al. [21] report that the U.S. Navy has successfully developed a system capable of meeting oily wastewater discharge regulations. This system uses dense-pack ceramic ultrafiltration membranes. The permeate quality averaging less than 5 ppm and below 15 ppm has been achieved aboard ship 95% of the time.

However, removal of TOC from tank dewatering produced water and prepared model solution using various membranes was in summary below 49% and thus unsatisfactory. Consequently, to optimize the treatment process and TOC removal from oilfield produced water, the effect of process parameters such as initial feed concentration, various TMP and cross-flow velocities, different properties of membranes used and statistical combination of these parameters have to be investigated.

Simulated batch dissolved air floatation (DAF) was used as a pre-treatment step to simulate produced water treatment and to identify relevant process parameters such as reaction time and airflow requirement in a small scale. Simulated batch DAF has limitations due to differences between batch and continuous flow processes. Though, it was used here as a useful, *i.e.*, simple and rapid process to assess the performance of DAF used for pre-purification.

To clean ceramic membranes fouled by oilfield produced water, using the experimental conditions reported here, back flushing was assessed (in terms of flux recovery) as more effective than chemical cleaning using various lye solutions.

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Table 1 Material and properties of the ceramic membranes used in this investigation

Membrane	MF - Al_2O_3	MF - Al_2O_3	UF - TiO_2	NF - TiO_2	NF - TiO_2
Membrane material	Al_2O_3	Al_2O_3	TiO_2 / Al_2O_3	TiO_2 / TiO_2	TiO_2 / Al_2O_3
Cut-off	0.1µm[1]	0.2µm[1]	0.05µm[1] and 20 kDa[1]	1000Da[1]	750D[1]
External diameter	25.4mm	25.4mm	25.4mm	10mm	10mm
Internal diameter	10mm	10mm	10mm	6mm	6mm
length	450mm	450mm/70mm	450mm/70mm	250mm	250mm
pH	0-14	0-14	0-14	0-14	0-14
Temp. Max. [°C]	121	121	121	150	120

[1] as indicated by the manufacturer

Table 2 Characteristics of the model solutions (a-c) and tank dewatering produced water used

Parameter	Model solution (a)	Model solution (b)	Model solution (c)	Variation range Tank dewatering produced water
Dispersed oil	113 mg/l	5420 mg/l	148.6 mg/l	200-1000 mg/l
pH value	7,5	6	7,3	6.0-8.0
Conductivity	213 µS/cm	162 µS/cm	168 µS/cm	20000-80000 µS/cm
TOC	94 mg/l	41,1 mg/l	23 mg/l	200-2000 mg/l
wt%	5	20	10	--
Waste oil type-nr.	1	2	3	1

Table 3 Summary of the results derived from simulated DAF for pre-treatment step of model solution (b) versus different times and air flow rates, temperature 60°C, 500 rpm

Feed	Reaction time [Min]	Airflow rate [Nl/sec]	C_{oil} [ppm]	Oil removal Total [%]
Model solution (b)	--	--	5420	--
	30	0	4690	13.5
	60	0.16	1250	76.9
	90	0.8	530	90.1
	120	0	1270	76.5
	240	0.16	590	89
	360	0.8	570	89.4

Table 4 Summary of the results derived from 0.1 and 0.05µm ceramic membranes MF followed by UF using model solution (c) after filtration across the membranes; N.A.: not available.

Membrane Cut-off	Feed water / Permeate	$C_{oil,}$ [ppm]	Oil Removal Total [%]	$C_{TOC,}$ [mg/l]	TOC Removal Total [%]	Temperature [°C]
--	Model Solution (c)	148.6	-	23	-	60
MF (0.1µm)	Permeate after MF	57.4	61.4	14	38.6	60
UF (0.05 µm)	Feed: Permeate from MF	32.3	78.2	N.A.	N.A.	60

Table 5 Summary of the results derived from 0.05µm and 1000Da ceramic membranes UF followed by NF using tank dewatering produced water after filtration across the membranes. TMP 1 bar, temperature 60°C

Membrane Cut-off	Feed water / Permeate	$C_{oil,}$ [ppm]	Oil Removal Total [%]	$C_{TOC,}$ [mg/l]	TOC Removal Total [%]	Conductivity [µS/cm]
--	Tank dewatering PW	565	-	582	-	39600
UF (0,05µm)	Permeate after UF	5.8	99.15	503	13.6	27400
NF (1000Da)	Feed: Permeate from UF	2.6	99.53	292	49.8	26000

Table 6 Chemical cleaning efficiency using lye solutions

Membrane Cut-off	$C_{oil, feed}$ [%]	Initial flux [l/h.m².bar]	Final flux [l/h.m².bar]	Flux after chem. cleaning [l/h.m².bar]	Cleaning efficiency [%]
0.2µm	5	2657	771	878	33
0.1µm	5	715	319	446	61
1000Da	10	123	64	80	41

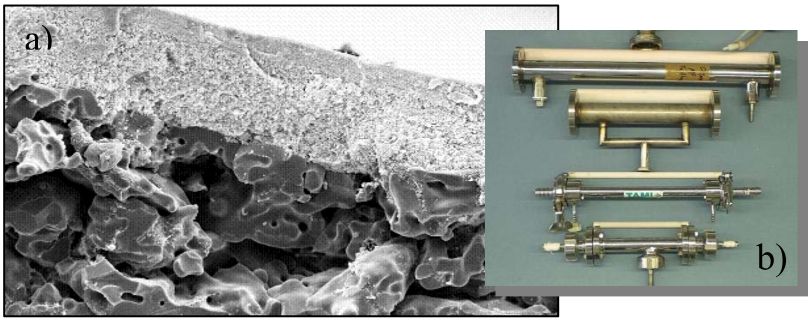

Fig. 1. a) SEM-micrograph of a ceramic UF-membrane, b) Different ceramic membranes and housing

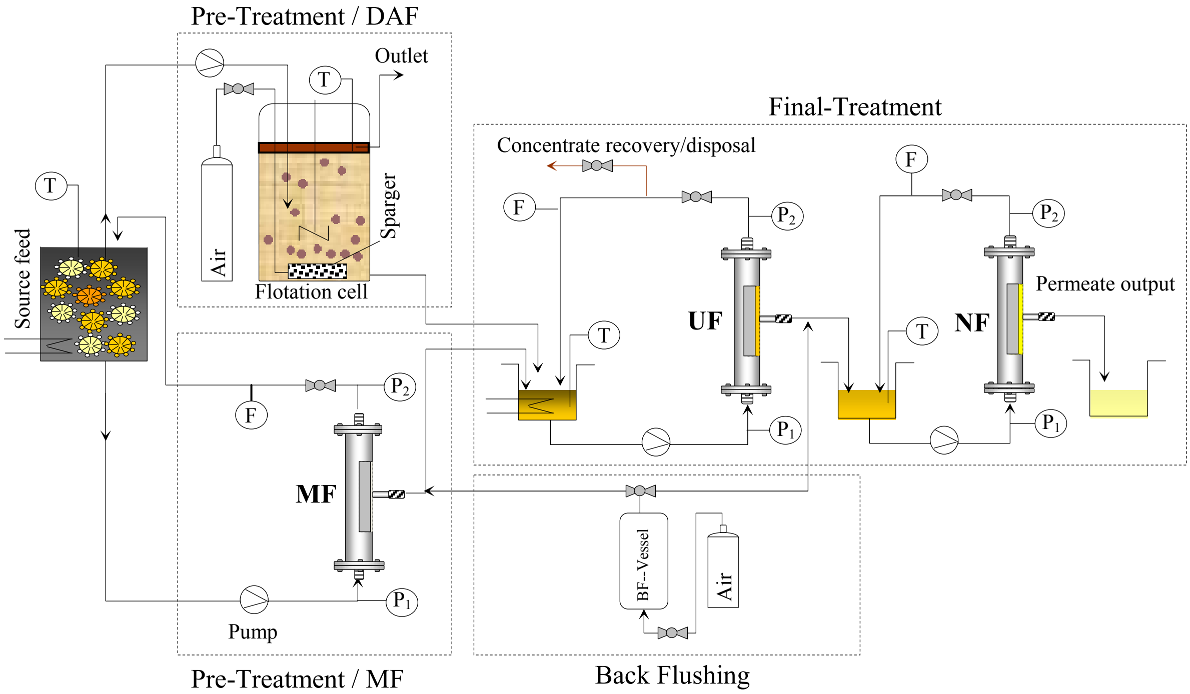

Fig.2. Schematic diagram of the laboratory scale cross-flow filtration system (with simulated DAF/ MF as pre-treatment process and/or final-treatment) and liquid circulation

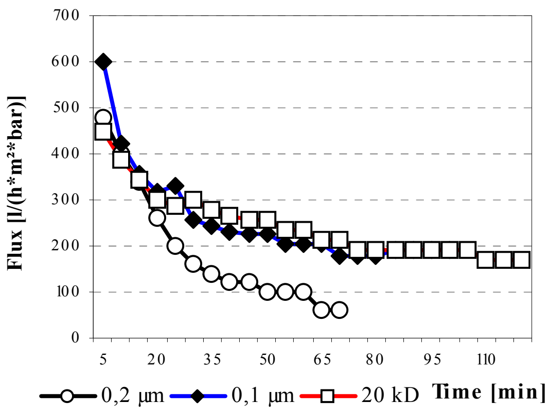

Fig. 3. Average flux rates for different ceramic membranes. Model solution (a) used, TMP 1 bar; temperature 60°C; running time, 70 min and 120 min respectively

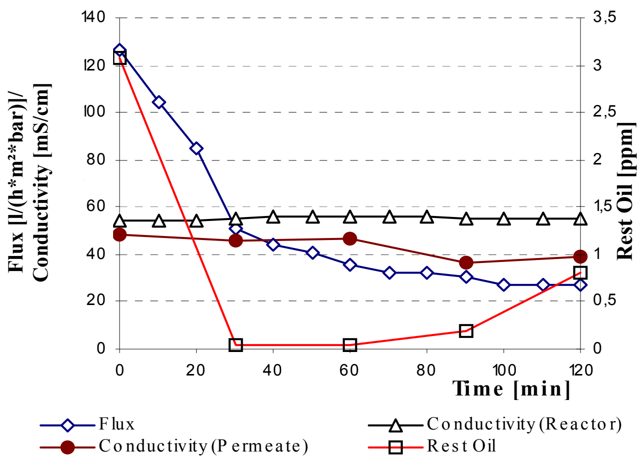

Fig. 4. Average flux rate, oil removal efficiency and conductivity for a 0.2µm membrane. Tank dewatering produced water used, TMP 1 bar, temperature 60°C.

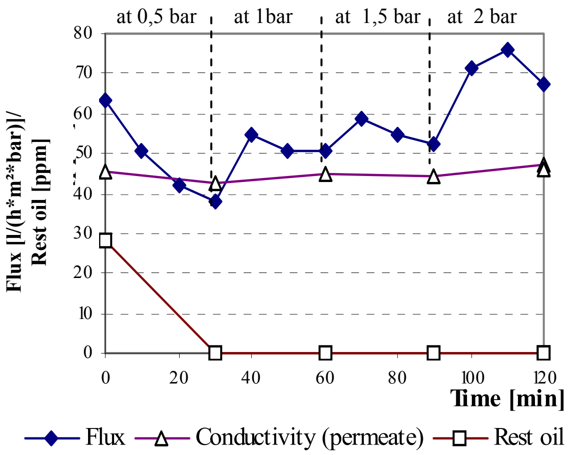

Fig. 5. Average flux rate, oil removal efficiency and conductivity at different TMP for a 0.05µm membrane and tank dewatering produced water

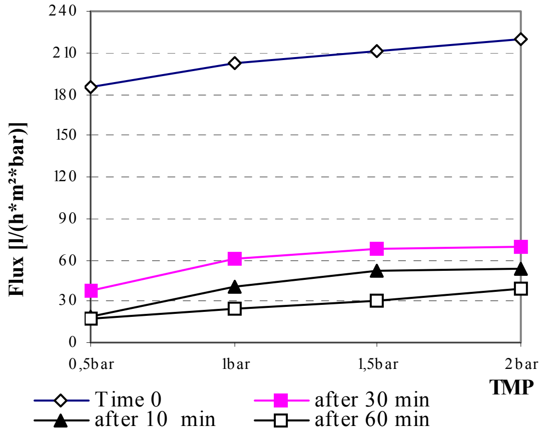

Fig. 6. Average flux rate at different TMP for a 0.05µm membrane. Tank dewatering produced water used, temperature 60°C.

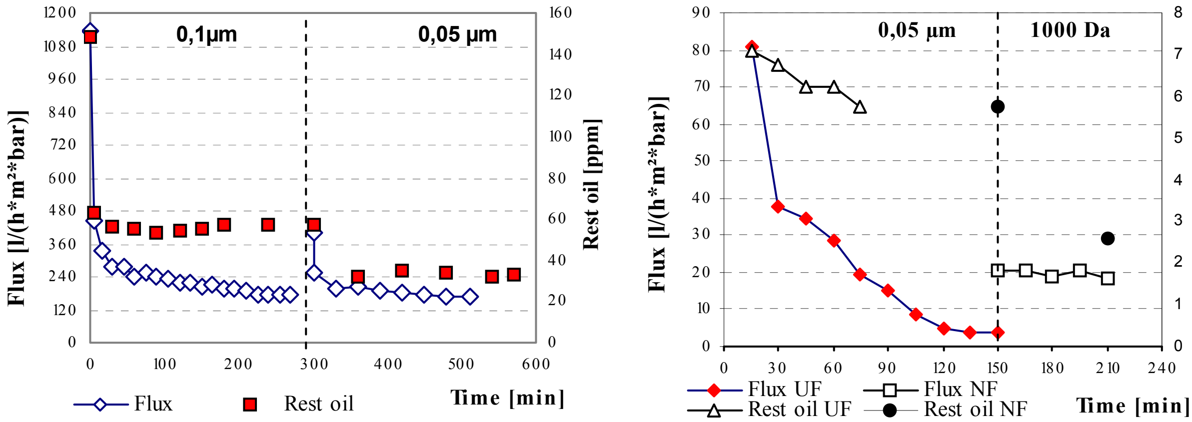

Fig. 7. Average flux rates and oil removal efficiency for different ceramic membranes UF (0.05µm) followed by NF (1000Da), tank dewatering produced water used (right), and MF (0.1µm) followed by UF (0.05µm) model solution (c) (initial C_{oil} 564 ppm) used (left). TMP 1 bar, temperature 60°C.

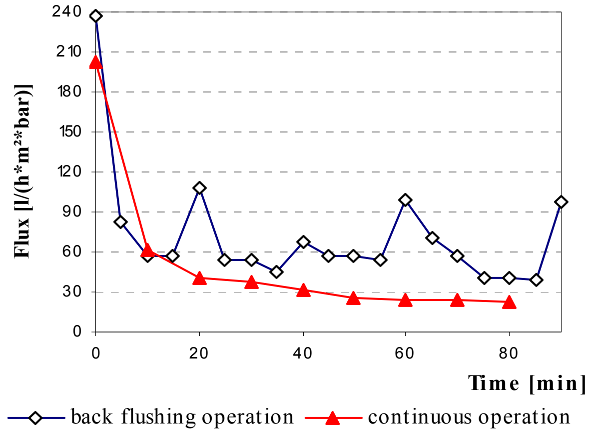

Fig. 8. Permeate flux rates as a function of operation time for continuous and back flushed operations for a 0.2µm membrane, tank dewatering produced water used.

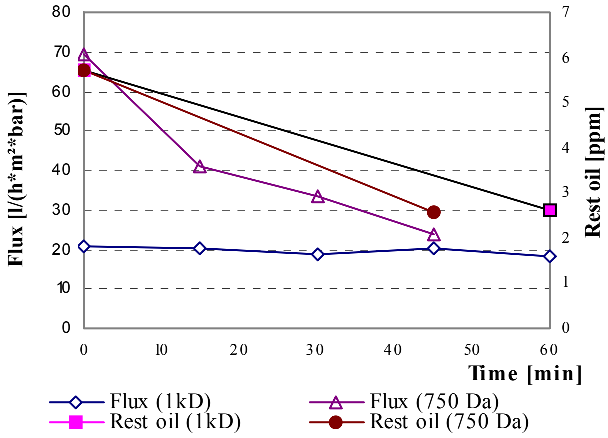

Fig. 9. Average flux rate and oil removal efficiency for different ceramic NF membranes (1000 and 750 Da), tank dewatering produced water used, TMP 1 bar, temperature 60°C.