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ABSTRACT

In oilfield produced water treatment with ceramic membranes, process efficiency is characterized by the specific permeate flux and by the oil separation performance. Apart from the membrane properties, the permeate flux during filtration of oily wastewaters is known to be strongly dependent on the constituents of the feed solution, as well as on process conditions, e.g. trans-membrane pressure (TMP) and cross-flow velocity (CFV). In the current investigation tubular ceramic ultrafiltration membranes with a nominal molecular weight cut-off of 20 kD were evaluated for oilfield produced water treatment. The oil separation performance of the ceramic membrane was monitored online with an innovative oil-in-water monitor developed by DECKMA HAMBURG GmbH. The oil contamination in the feed and permeate stream could be measured continuously and recorded in the range from 0 to 200 ppm with a resolution of 1 ppm. With the ceramic membranes an oil removal up to 99 % could be achieved with permeate qualities of less than 1 ppm residual oil, meeting the regulations for discharge in most areas. Under certain process conditions, (high CFV, low TMP) permeate fluxes of 195 $l*m^{-2}*h^{-1}$ with virtually no flux decline over 12 h could be reached, promising long time operation with reduced number of cleaning cycles.

KEYWORDS

Ceramic Membrane, Produced Water Treatment, Oil Content, Online Monitoring

Introduction

Large amounts of effluents contaminated with oily emulsion are produced daily in different industrial areas. By far the largest amount is produced during oil and gas exploration where up to 9 barrels of contaminated water, so called produced water, are generated per barrel of crude oil and have to be treated before their disposal [1]. Another field where oil contaminated effluents are produced is shipping, where the wastewater that arises on deck and in the engine room of the ships is collected in the bilge tank. This so called bilge water is commonly contaminated with marine residual fuel oil alongside with surfactants used in the engine cleaning and other particulate contaminants, for example iron oxide. This bilge water has to be disposed on sea as it arises continuously and the capacities for storage on a ship are limited. There are different regulations limiting the maximum concentration in oily wastewaters for disposal. In most areas of the world the limit is 5 ppm residual oil for effluent disposal on sea. To meet these stringent demands, effective oil water separation techniques are necessary. The conventional oily wastewater treatment processes are based on the difference in specific gravity between the oil droplets and the water [2]. For the treatment of Industrial effluents API oil water separators are commonly employed, which are designed based on guidelines of the American Petroleum Institute (API). For bilge water applications oil water separators according to the classes quoted in the International Maritime Organization resolutions are used [3]. These techniques have some limitations in common. Heavy oils have only a small difference in specific gravity compared to water, extending the rise time of the oil droplets in the separator and thereby reducing its effectiveness. Additionally the droplet size distribution of the oil phase can be shifted to smaller droplets through surfactants that stabilize the oil emulsion leading to the same effect. Treatment processes based on cross-flow filtration are believed to be able to overcome these limitations, as they are not dependent on theses mechanisms. The membrane acts as a barrier to all contaminants that are bigger than the pores of the membrane and lets smaller constitutes pass through the pores, regardless of their specific gravity. In the current study a treatment process for oily waste waters or produced waters based on cross-flow filtration with tubular ceramic membranes is investigated. In order to evaluate the process performance regarding the oil water separation of the membrane an online oil in water monitor is integrated into the filtration process.

Materials and Methods

Online Oil Monitoring

The device to be integrated into the filtration process is a development out of a modified 15 ppm bilge alarm with a measurement principle based on light scattering. The OMD 2008 (DECKMA HAMBURG GmbH, Germany) is a 15 ppm bilge monitor meeting International Maritime Organization Resolution MEPC.107(49) for 15 ppm bilge Alarms. The reference method for the device is the International Standard ISO

9377-2:2000 “Water quality - Determination of hydrocarbon oil index –Part 2: Method using solvent extraction and gas chromatography” also known as H53 method. The prototype OMD 32 (Figure 1) with an increased measuring range of 0 – 200 ppm and increased temperature range (up to 60 °C) was developed for industrial applications like produced water treatment. Both monitor types produce a linearized output signal over the entire measuring range (current loop, 4 – 20 mA) and can be connected to the supervisory control and data acquisition system (SCADA) for process control.

Figure 1: The online oil in water monitor OMD 32 (DECKMA HAMBURG GmbH, Germany)

Oily model Solutions

In order to get standardized conditions for the filtration experiments a synthetic produced water is necessary that is characterized by the defined dispersed oil content and droplet size distribution of the dispersed oil phase. For this purpose oily model solutions (OMS) were prepared by preemulsification of a crude oil (oilfield Bramberge, Germany) with a rotor stator homogenizer and subsequent processing with a Emulsiflex C5 high pressure homogenizer (Avestin, Germany) at 450 bar in single pass. The final concentration of dispersed oil was adjusted to 35 ppm by dilution with demineralized water while circulating the oily model solution through the OMD 32 oil monitoring device. The droplet size distribution of the model was measured with a Mastersizer (Malvern, Germany) based on laser scattering. The volume based mean droplet size of the resulting synthetic produced water is $d_{v0.5}$ =1.82 µm hence representing a fraction that cannot be effectively removed with methods based on the specific gravity difference between the water and the oil droplets like oil water separators.

Filtration process

The filtration experiments were carried out in cross-flow mode with a tubular ceramic ultrafiltration membrane having a nominal molecular weight cut-off (MWCO) of 20 kD (atech innovations, Germany). The data of the membrane are summarized in Table 1. The process temperature was 50 °C for all experiments and the initial oil concentration in the oily model feed was 35 ppm,. The cross-flow velocity and the trans-membrane pressure were varied, while the other parameters were kept constant. The filtrations were conducted in fed batch mode and the volume in the retentate tank was kept constant. In order to monitor the residual oil content in the retetate stream an OMD 32 oil monitoring device (DECKMA HAMBURG GmbH, Germany) was installed in a bypass. The permeate stream was completely lead through an OMD 2008 oil monitoring device, allowing to measure the oil concentration of the total collected permeate. The signal outputs of the two oil monitoring devices were connected to the SCADA system (Labbox, Hitec Zang, Germany) so that the oil contamination could be recorded continuously with a time resolution of one second. The permeate flow was measured with an electronic balance (DS 36K0.2, Kern, Germany) connected to the SCADA-system. The membrane was chemically cleaned after each filtration experiment. For this purpose the equipment was filled with a 1 % cleaning solution (P3 Ultrasil-14, Henkel). The cleaning solution was circulated in the equipment for 2 hours at 60 °C. The equipment was emptied and the membrane rinsed with demineralized water. After the cleaning process the permeability of the membrane was measured and the cleaning process was repeated until the initial permeability of the membrane was regained.

Table 1: Properties of the tubular ceramic ultrafiltration membrane used in the filtration of synthetic produced waters

nominal MWCO:	20 kD
material support:	α-Al_2O_3
material membrane:	TiO_2
design:	monochannel
length:	450 mm
diameter:	25 mm
channel diameter:	26 mm
manufacturer:	atech innovations, Germany

Results and discussion

OMD signal response and linearity

The signal response and the linearity of the output signal of the oil monitoring devices were tested with the oily model solutions. For this purpose an oily model stock solution with a defined droplet size was prepared and different volumes of the stock

solutions were diluted with demineralized water resulting in equally spaced concentration over the entire measurement range of each device. The different concentrations were subsequently measured with intermittent flushing of the measuring cell with clean water. Each concentration was measured for 30 seconds and the values were averaged. A linear regression was made with the data and the standard error and the coefficients of determination were established. The results for the OMD 2008 are presented in Diagram 1. There is a strong linear correlation between the output signal of the OMD 2008 and the concentration of dispersed oil in water. The coefficient of determination is R^2 = 0.997 meaning that 99.7 % of the signal response is a result of the oil concentration in the oily model solution. The standard error was estimated with 0.6 ppm for the OMD 32, which is far better than the 5 ppm criteria given by the IMO regulations for 15 ppm bilge alarms.

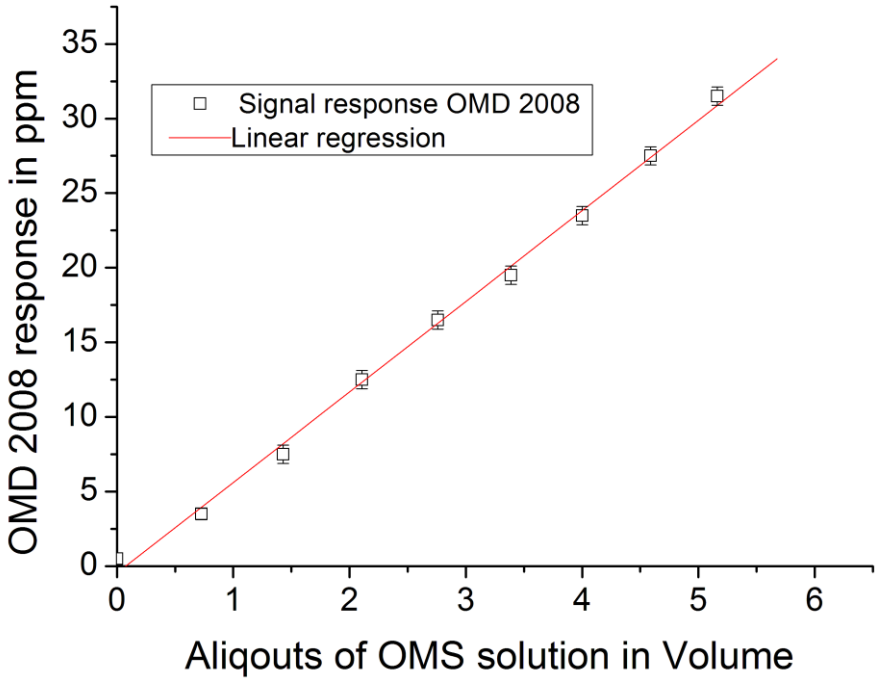

Diagram 1: Signal response of the OMD 2008 for different oil concentrations in the synthetic produced water

In Diagram 2 the results for the OMD 32 with the extended measurement range are schown. Again a strong linear correlation between the oil concentration and the OMD 32 signal output could be observed. The coefficient of determination was with R^2 = 0.999 even better than the one determined for the OMD 2008. The standard error was determined with 1.9 ppm promising the employment of this device for the accurate determination of residual oil contamination in industrial applications in a range from 0 – 200 ppm.

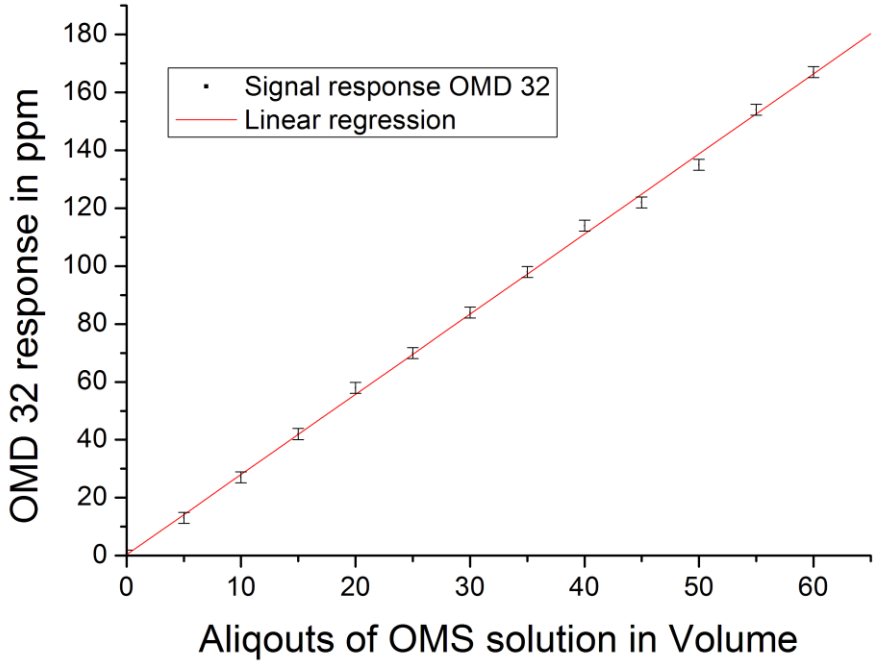

Diagram 2: Signal response of the OMD 32 for different oil concentrations in the synthetic produced water

Residual oil in permeate and retentate

The permeate quality regarding residual oil contamination seemed not to be affected by the varying operation parameters cross-flow velocity and trans-membrane pressure within the investigated range of TMP = 0.5 – 1.5 bar and CFV = 3.3 – 5.8 $m*s^{-1}$ (Table 2). Also the increasing oil concentration in the retentate stream had no influence on the oil content in the permeate, so that the 5 ppm alarm threshold of the OMD 2008 was never reached. Diagram shows the typical course of the permeate quality and the dispersed oil concentration in the retentate stream facing the membrane. In all experiments with the ceramic 20 kD ultrafiltration membrane the permeates produced had residual oil contamination of below 1 ppm as monitored with the OMD 2008. The oil concentration in the retentate stream increased with increasing volume concentration factor and could be monitored up to 200 ppm with the OMD 32 online monitoring device.

Table 2: Filtration performance of a tubular ceramic membrane with a nominal MWCO of 20 kD at 50 °C and varying operational parameters (CFV, TMP)

CFV in $m*s^{-1}$	TMP in bar	initial flux in $l*m^{-2}*h^{-1}$	final flux in $l*m^{-2}*h^{-1}$	filtration time in min	flux decline in %	residual oil in permeate in ppm
5.8	1.5	600	415	600	31	< 1
5.8	1.0	405	360	640	11	< 1
5.8	0.5	205	195	720	5	< 1
4.6	0.5	200	80	700	60	< 1
3.3	0.5	220	50	700	77	< 1

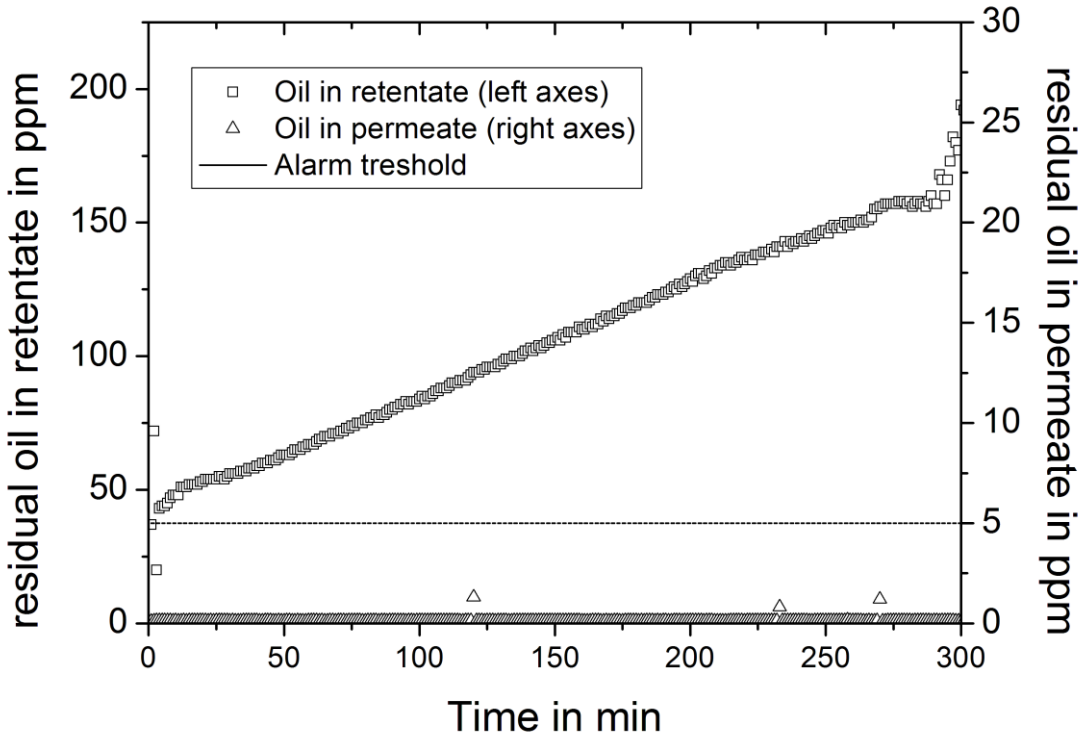

Diagram 3: Concentration of dispersed oil in the permeate and in the retentate stream during a filtration of synthetic produced water with a tubular ceramic UF-membrane

Filtration performance

The filtration performance of the ceramic membranes under varying process conditions (TMP, CFV) is expressed as permeate flux over the filtration time. The results for the filtrations with varation of the cross-flow velocity at a constant transmembrane pressure of 0.5 bar are given in Table 2. The flux decline over the filtration time decreases with increasing cross-flow velocity. The initial permeate flux was between 195 and 220 $l*m^{-2}*h^{-1}$ in all three experiments. In the filtration with a cross-flow velocity of 3.3 $m*s^{-1}$ the permeate flux dropped continuously from its initial value down to 50 $l*m^{-2}*h^{-1}$ within 700 minutes at which time the flux seemed to stabilize at this level. The filtration with a cross-flow velocity of 4.6 $m*s^{-1}$ showed a less pronounced decline in permeate flux during the filtration time. The flux decreased from its initial value of 200 $l*m^{-2}*h^{-1}$ down to 80 $l*h^{-2}*m^{-1}$. Unlike in the experiment with 3.3 $m*s^{-1}$ a stable flux was not achieved within 700 minutes of filtration. After a small drop within the first 5 minutes from 205 $l*m^{-2}*h^{-1}$ to 195 $l*m^{-2}*h^{-1}$ a nearly stable flux with virtually no decline over the filtration time of 720 minutes could be observed with the highest cross-flow velocity of 5.8 $m*s^{-1}$. Under such conditions not only a constant high filtration performance can be expected, but also the time between cleaning cycles can be extended, leading to reduced consumption of cleaning chemicals. In the filtration at 1.0 bar trans-membrane pressure the initial flux was 405 $l*m^{-2}*h^{-1}$. There was only a very small decline in the permeate flux down to 360 $l*m^{-2}*h^{-1}$ over the filtration time of 640 minutes. In the filtration experiment at 1.5 bar trans-membrane pressure the initial permeate flux was 600 $l*m^{-2}*s^{-1}$ and continuously decreased down to 415 $l*m^{-2}*h^{-1}$ after 600 minutes of filtration. The flux at this time was only slightly above the flux in the experiment with 1.0 bar TMP.

Summary and Outlook

A process for the treatment of produced water with tubular ceramic membranes in cross-flow mode was investigated. The operational parameters trans-membrane pressure and cross-flow velocity were varied and the process performance in terms of permeate flux and permeate quality was determined. A tubular ceramic ultrafiltration membrane with a nominal MWCO of 20 kD was tested for trans-membrane pressure from 0.5 - 1.5 bar and cross-flow velocities from 3.3 – 5.8 $m*s^{-1}$. The process yielded permeate with an oil content of below 1 ppm under all process conditions and for all retentate oil concentrations. Within the investigated range of operation parameters for the cross-flow filtration with the tubular ceramic ultrafiltration membrane the setting with TMP = 1.0 bar and CFV = 5.8 $m*s^{-1}$ was identified as most promising for long term operation with extended time intervals between chemical cleaning. For the online monitoring of the oil concentration in the permeate and retentate stream an oil monitoring device was employed in order to assess the process regarding its oil separation performance. The suitability of the online monitoring devices for the determination of the oil content in the synthetic produced

water was shown. The standard error for the output signal was 0.6 ppm for the OMD 2008 and 1.9 ppm for the OMD 32 with extended measurement range. For both devices the demands of the IMO regulations regarding accuracy are exceeded. The integration of the online of the OMD series monitors for the supervision and control of produced water treatment processes by cross-flow filtration could be successfully demonstrated. In further investigations the cleaning process of the membrane after filtration will be optimized with focus on reduced cleaning chemical expenditure. Furthermore the integrated cleaning of the measuring cell of the oil monitor needs to be realized.

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