FEASIBILITY OF USING CERAMIC MICRO-, ULTRA- AND NANOFILTRATION MEMBRANES FOR EFFICIENT TREATMENT OF PRODUCED WATER

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ABSTRACT

Generally, the production of crude oil and natural gas brings to the surface fossil water, termed "produced water." By far the largest by-product or waste stream by volume associated with oil and gas extraction, this water is always cleaned to some extent and the level of cleaning is determined by the intended use and/or current discharge regulations. Existing technologies are not usually capable of reaching the new levels of cleanliness demanded. This investigation focuses on the characterization of permeate flux using newly developed ceramic microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) membranes for efficient treatment of oilfield produced water. Results for average flux rates and flux degradation are shown.

KEYWORDS

Ceramic Membrane, Water Treatment, Crude Oil, Microfiltration, Ultrafiltration, Nanofiltration, Membrane Fouling, Permeate Flux

1. Introduction

Every oilfield is characterized by a concomitant presence of fossil water and gas that come to the surface together during oil extraction. The separated water, called *"produced water"* in the scientific literature, accounts for the majority of the waste derived from the production of crude oil [1]. The quantity of water produced per unit volume of hydrocarbons varies greatly, but typically increases with the age of the producing field. As well as free and emulsified hydrocarbons, this water may contain a wide variety of salts, fine silts of both silicon and clay compositions and in some cases, active biological materials.

Produced water is always cleaned to some extent with the level of cleaning dependent upon the intended use and/or current discharge regulations. Current technologies used to treat produced water consist of clarifiers, dissolved air flotation, hydrocyclones, and disposable filters/absorbers [2]. Typically, these technologies are not capable of achieving the new standards of cleanliness demanded by regulations without using additional expensive chemicals for coagulation, settling and the like. As a result, operating expenses increase and greater volumes of hazardous wastes are produced. After a primary process of separation from the oil, the water still contains drops of oil in emulsion in concentrations as high as 2000 mg/l, necessitating further treatment before it can be discharged. The international standards require more efficient separation systems.

To meet the challenges posed by more stringent regulations, operators have turned to membrane filtration schemes for their potential to minimize additional costs and disposal issues associated with current technologies. Both polymeric and ceramic membranes have been tried under many field conditions. While these membranes are effective in separating the oils, emulsions, and silts, they are prone to fouling by waxes and asphaltenes. The issues that need to be addressed are modification of the waxes and asphaltenes to prevent their fouling of the membranes during operation and the provision of an expedient, cost effective, and non-hazardous means of cleaning the membranes when they become fouled. The key technical obstacles for the integration of MF/UF/NF membrane filtration into the oilfield water treatment process are reviewed [4, 5]. However, membrane fouling constitutes a major obstacle to the application of membrane-based processes for the treatment of produced water for beneficial uses.

This investigation focuses on the characterization of permeate flux using newly developed ceramic micro-, ultra-, and nanofiltration membranes. Results for average flux rates, flux degradation, total organic carbon (TOC) removal and oil removal efficiency are shown.

2. Materials and Methods

Chemicals

All chemicals were obtained from VWR international GmbH (Darmstadt/Germany).

Membranes

Different types of commercial tubular ceramic membranes for micro-, ultra- and nanofiltration were investigated. Table 1 lists the properties of the ceramic membranes used in this investigation.

Table 1: Material and properties of the ceramic membranes

Membrane	**MF- Al_2O_3**	**MF- Al_2O_3**	**UF- TiO_2**	**NF- TiO_2**
Membrane material	Al_2O_3	Al_2O_3	TiO_2 / Al_2O_3	TiO_2 / TiO_2
cut-off	0.1 µm[1]	0.2 µm[1]	20 kD[1]	1 kD[1]
pH range	0 - 14	0 - 14	0 - 14	0 - 14
temp. Max. [°C]	121	121	121	150

[1] as indicated by the manufacturer

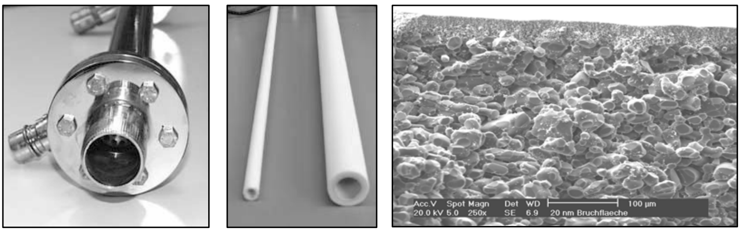

Figure 2: Module and ceramic membranes (SEM-micrograph).

Membrane-assisted continuous reactor

Cross-flow filtration processes (MF, UF, NF) were studied in a continuous stirred tank reactor (max. volume 3 l) with a membrane module as shown in Figure 1. The influence of different pore sizes of the ceramic membranes used on the separation behaviors were investigated by the measurement of permeate flux, total organic carbon (TOC) and oil removal efficiency, respectively. The pressure readings of P_1 and P_2 remained approximately equal; this pressure is reported as the trans-membrane pressure (TMP). All filtration experiments were carried out at 60°C.

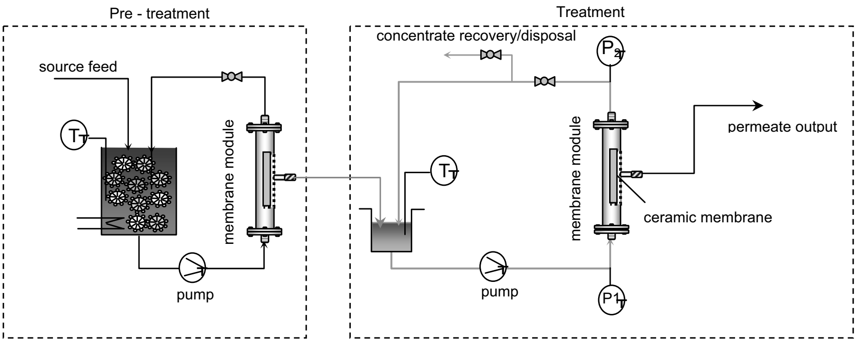

Figure 1: Schematic diagram of the laboratory scale cross-flow filtration system with liquid circulation.

Preparation of model solution

The oily wastewater (model solution) was prepared in a heated stirred tank by mixing waste oil (5%) with distilled water for 30 min at 70°C. As a simulated primary process of separation from the oil, the mixture was left for 30 min for clarification. The free oil is recovered and pumped back to the waste oil tank. The mixture showed a uniform yellowish color.

Oil in water determination

n-Hexane (≥ 95 % grade purity) was used as an extraction solvent for measuring average oil concentration in feed solution and in permeate. The samples were analyzed by the TD-500D handheld fluorometer (Nordatec GmbH, Bremerhaven/Germany). The standard solution was prepared by dissolving a known amount of oil in 100 ml of n-Hexane. 100 ml of feed or permeate sample was collected in a suitable glass container. 6N HCL was added until the pH of the water sample was <2. Extraction solvent (10 ml) was added and the container was securely capped. The container was shaken vigorously for 2 minutes to extract the oil from the water. After 1 minute, 1 ml of the solvent extract was removed from the top of the water and analyzed by the fluorometer on channel A.

Total organic hydrocarbon (TOC) determination

The total organic hydrocarbon concentrations were determined with the TOC cell test (measuring range: 5.0 – 80.0 mg/L TOC) in the photometer Photolab S6 (WTW, Weilheim/Germany).

3. Results

The MF, UF and NF processes ran for 2 h continuously. Figure 3 shows the change in membrane fluxes and flux degradation for different ceramic membranes with filtration time. At the beginning, permeation fluxes declined gradually until an invariable flux value was obtained. The results here indicate that membrane fouling of different membranes used and different operation modes produce completely different fouling situations, as reported previously [3].

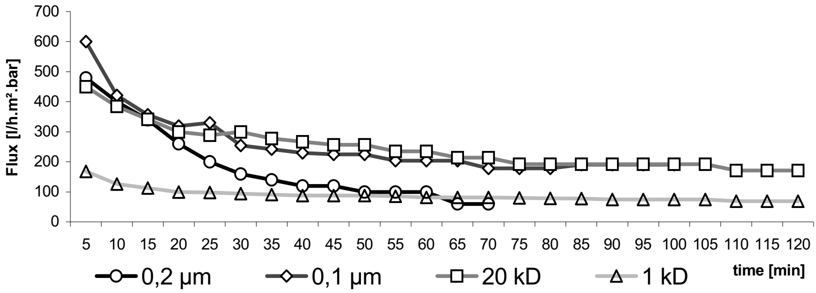

Figure 3. Average flux rates and flux degradation for different ceramic membranes. Model solution used (produced water from waste oil) in a membrane-assisted continuous reactor, experiments conditions were TMP: 1 bar, Temp.: 60°C, running time: 2 hours.

In order to investigate the water quality for each filtration process, feed and permeation water were analyzed, respectively. The percentages of removal for oil and TOC measured in steady state after 2 hours are shown in Table 2.

Table 2: Summary of the results derived from different ceramic membranes measured after 2 h filtration across the membranes. NA: not available.

Membranes cut-off	$C_{oil,}$ Feed [ppm]	Oil Removal [%]	$C_{TOC,}$ Feed [ppm]	TOC Removal [%]
0,2 µm	113	67	94	13
0,1 µm	113	NA	94	38
20 kD	113	84	94	27
1 kD	113	80	94	13

The microfiltration process ran for 32 h continually. Figure 4 shows the profile of flux degradation within the operation time.

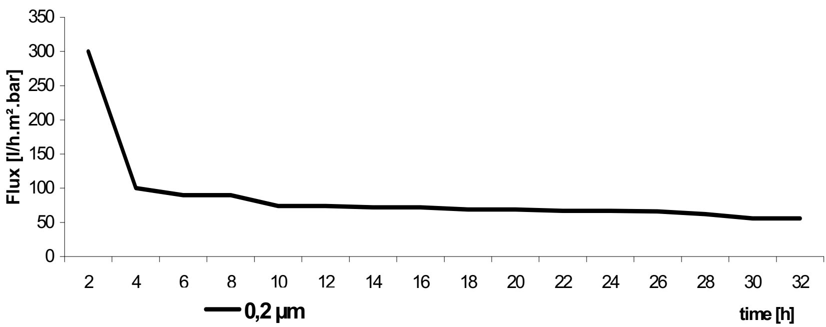

Figure 4. Average flux rates and flux degradation for the ceramic membrane with a 0.2 µm pore size, model solution (produced water from waste oil) was used in a membrane-assisted continuous reactor, experiments conditions were TMP:1 bar, Temp.: 60°C, running time 32 hours continuously.

The average percentages of feed concentrations and removal for microfiltrated oil and TOC measured in steady state after 32 hours are shown in Table 3.

Table 3: Results derived from ceramic membrane with a 0.2 µm pore size after 32 h filtration across the membranes..

Membranes cut-off	$C_{oil,}$ Feed [ppm]	Oil Removal [%]	$C_{TOC,}$ Feed [ppm]	TOC Removal [%]
0.2 µm	113	82	94	27

4. Conclusions

The investigated ceramic membrane systems under micro-, ultra-, and nanofiltration conditions have proven to be economically attractive for the removal of oil from produced water (model solution). The results indicate that the investigated membranes are not suitable to reach an acceptable level of removed TOC under present experiment conditions (Table 2, 3). Significantly, in the case of investigated nanofiltration ceramic membranes the average percentage of removed oil and TOC are lower in comparison to micro-, and ultrafiltration membranes. These results demonstrate that the effective molecular weight cut-off of the nanofiltration membrane is perhaps larger than their nominal 1.000 Da value, as indicated by the manufacturer. For this reason, further modified ceramic membranes under varying conditions (TMP, feed concentration, cross-flow velocity) and different cleaning methods need to be investigated.
The key obstacles for the integration of membrane filtration into produced water treatment are: high filtrate flux, low fouling properties, easy cleaning, chemical and thermal stability.

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