CERAMIC HOLLOW FIBER MEMBRANES AS NEW FILTER MEDIA AND THEIR APPLICATION IN OIL/WATER SEPARATION PROCESSES

Steffen Schütz, Frank Ehlen, Ina Unger, Sreenath Kariveti, Can Wang
MANN+HUMMEL GmbH, Grönerstraße 45, D-71636 Ludwigsburg, Germany

Mehrdad Ebrahimi, Steffen Kerker, Peter Czermak
Institute of Bioprocess Engineering and Pharmaceutical Technology, University of Applied Sciences Mittelhessen THM, Gutfleischstraße 3, D-35390 Gießen, Germany

ABSTRACT

Ceramic membranes become continuously attractive for separation applications with fluids at increased temperatures, at high or low pH levels and in contact with critical chemical species as solvents or other organic components when polymeric membranes often fail due to high fouling or material instability.

A ceramic hollow fiber membrane was developed at MANN+HUMMEL, see Figure 1. This ceramic hollow fiber membrane shows the advantages of a high volumetric filtration area and low material volumes compared to ceramic membranes with other geometries. The specific design of this membrane comprises a microfiltration ceramic support layer and an ultrafiltration ceramic functional separation layer with a pore size $d_{90} = 40$ nm. This two layer structure leads to high membrane fluxes and low pressure drop during operation. The membrane operation in cross flow mode allows the control of fouling layers due to the applied cross flow velocity.

![Figure 1: Cross-section of a ceramic hollow fiber membrane (MANN+HUMMEL).](image)

The operation behavior of this ceramic hollow fiber membrane was investigated for oil/water separation applications in close cooperation with a research partner and in application tests with customers. It was shown that the membrane can be operated with high oil loads up to 5000 ppm in the waste water without requiring a pre-treatment. The oil contents in the permeate water were reduced to 1 ppm. Pure mechanical backflushing with permeate water was sufficient to clean the membrane in place and to reach nearly the initial flux values of the new membrane during operation. The robustness of the membrane operation in industrial applications was shown by running the membranes for several weeks in water treatment processes with industrial waste water. The waste water treatment was also promising when additional high solid loads contaminated oily waste water to be cleaned.

KEYWORDS
Ceramic Membrane, Hollow Fiber Membrane, Oil Content, Produced Water
1. Introduction

The exploitation of raw oil and natural gas resources is increasingly performed by pumping water into the reservoirs and washing out the raw oil or natural gas reservoirs. The backflush water to be reused or to be disposed in the environment is the so-called “produced water”. The composition of produced water is very complex. Its characteristics and physical properties usually vary significantly depending on the geographic location of the exploitation field and the type of hydrocarbon product being produced [1]. It often contains different amounts of dispersed oil, dissolved organic compounds, production chemicals, corrosion products, heavy metals, large amounts of organic material, inorganic salts and natural radioactive minerals.

Considering water-based raw oil exploitation, three barrels of produced water are generated in average with a new oil well for each corresponding barrel of oil produced [2, 3]. This ratio increases as oil wells mature and may reach as many as seven to ten barrels of produced water per oil barrel, especially in mature oilfields [4]. The authors in [5] estimated that given the oil production in 2011 (around 72,000,000 barrel/day), and the minimum ratio of three barrels of produced water for each barrel of oil produced, a minimum of around 216,000,000 barrel/day of produced water was generated in 2011 alone by raw oil exploitation.

Considering the increasing importance of water based oil and natural gas exploitation, a significant amount of research has been conducted in the field of produced water treatment using microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), membrane distillation (MD) and their combined processes using different types of membranes [5, 6, 7]. The authors in [8] give an overview on different facets of membrane technology used for produced water treatment.

The removal of oil out of water is also relevant for various industrial applications e.g. in metal working processes. Cooling water to be reused is often contaminated with high oil loads, solid particles and organic components at high concentrations. The reuse of this waste water is crucial to reduce operating and water disposal costs.

Ceramic membranes have been developed and used in a variety of different applications, especially where harsh process conditions (e.g. critical physical and chemical properties of the feed solution or high temperature and pressure operation) preclude the current practice of using polymeric membranes. In this context, the application of tubular and rotating ceramic membranes has been proposed as a promising technology for treatment of oil contaminated water. Ceramic hollow fiber membranes (CHFM) represent a new generation in the development of inorganic membranes by offering the advantages of one membrane consisting of both inorganic material and hollow fiber geometry. CHFM, as they are used in this study, show some advantages and characteristic properties compared to other types of hollow fiber membranes.
2. Ceramic Hollow Fiber Membranes (CHFM)

The ceramic hollow fiber membranes which are used for the subsequently described investigations in oil/water separation are produced starting with the raw materials of ceramic and polymeric granular powder, an adequate solvent system and some additive ingredients. These components are mixed homogeneously, and the viscosity of the resulting liquid single-phase spinning dope is a significant quality parameter that gives an indication of the properties of the subsequently produced hollow fiber membranes. The spinning dope is pressed through a two-component nozzle into an aqueous precipitation bath ("spinning process") where the solid structure of the hollow fiber membrane is developed from the liquid spinning dope by phase inversion. In detail, the solvent is washed out from the spinning dope by the water within the precipitation bath. As the polymeric component is not soluble in water, it becomes a solid structure, which then generates the hollow fiber membrane.

This so-called green fiber shows polymeric characteristics and it comprises singular embedded ceramic particles. The green fiber is further washed and then sintered at high temperatures. During the sintering process, the polymeric component is burned completely and the ceramic particles combine with each other forming sinter necks between the single particles. In the end, a pure ceramic hollow fiber membrane is generated. This ceramic hollow fiber membrane has smaller dimensions in comparison to the green fiber due to thermal shrinkage.

The applied ceramic hollow fiber membranes consist of a two-layer structure. The ceramic microfiltration support layer with open pores and low pressure drop results from the previously described spinning (precipitation) process and gives the mechanical stability to the membrane. After sintering, this support layer is covered by a functional ultrafiltration ceramic coating layer (active layer) on the feed side of the membrane. As the membranes are operated in an in/out filtration mode, the coating is applied on the inner lumen surface of the hollow fiber membrane. For this coating process, the hollow fiber channel is flushed with a ceramic suspension, which adheres as a thin layer to the support layer. After flushing, the ceramic hollow fiber membrane is sintered a second time to achieve a stable bond between the ceramic coating and the support layer.

As the membrane surface resulting from the spinning process is very smooth a single coating step is sufficient to apply the functional ultrafiltration coating layer.

With this membrane design, the active coating layer has a thickness of only a few micrometers. This membrane design leads to a low trans membrane pressure in operation and to a high permeate flux meaning the pressure drop of the open-structured support layer can almost be neglected.

In Figure 2, this specific membrane structure is shown within an SEM photo with the active coating layer and the support layer.
3. Experimental Procedure in Produced Water Treatment

The filtration experiments in produced water treatment were carried out in cross flow mode with ceramic hollow fiber ultrafiltration membranes (MANN+HUMMEL GmbH, Ludwigsburg, Germany) with in/out filtration direction. For the most part of the experiments performed the hollow fiber support as well as the active layer consist of an $\text{Al}_2\text{O}_3$ ceramic material ($\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ membrane). These membranes have a $d_{90}$ pore diameter of 40 nm in the filtration active layer. The inner diameter of each single hollow fiber membrane is 1.8 mm, the outer diameter is 3 mm. Two kinds of modules were used with 30 and 100 hollow fibers at module lengths of 26 cm and 45 cm and with filtration areas of $0.037 \text{ m}^2$ and $0.25 \text{ m}^2$.

To investigate the influence of the membrane material of the active layer on the filtration behaviour a further hollow fiber module was used consisting of the $\text{Al}_2\text{O}_3$ hollow fiber support with the same geometry as mentioned before combined with an active SiC membrane layer ($\text{SiC}/\text{Al}_2\text{O}_3$ membrane). The $d_{90}$ pore diameter of the SiC active layer used is 100 nm.

The filtration experiments were conducted optionally in fed-batch and total recycle mode, respectively. As needed, back-flushing was executed by pumping permeate water at regular time intervals, in the reverse out/in direction. During the experiments the feed, permeate and retentate fluxes as well as the trans membrane pressure TMP were recorded. The oil and organic contents were measured in online and offline mode. The experimental set-up is described in [9].
4. Results in Produced Water Treatment with the Al$_2$O$_3$/Al$_2$O$_3$ Membrane

In this and in the following sections the results considering the membrane flux, the separation efficiency and the cleaning efficiency are presented. The experiments were performed by variation of the cross flow velocity and the oil concentration in the feed flow as well as the operational parameters in the cleaning mode.

Within all experiments the cross flow velocity was varied between 1.5 m/s and 2.5 m/s which results in Reynolds numbers within the membrane lumen between 2,900 and 4,800 indicating a moderately turbulent flow regime.

In the subsequent diagrams the normalized membrane flux is indicated dependent on the operation time. The normalized membrane flux is defined as the membrane flux at time $t$ related to the membrane flux at the beginning of the respective experiment. At $t=0$, the normalized membrane flux is one with this definition. The flux decay with the operating time is an indication for the degree of membrane fouling.

4.1 Influence of Oil Concentration in the Feed Flow on the Permeate Flux

In Figure 3, the time dependent membrane flux is shown for the filtration of two oil/water systems, the oily model system with an oil concentration of 35 ppm and the field oily waste water (tank dewatering produced water TDPW) with an oil concentration of 1000 ppm. The cross flow velocity was 2.5 m/s, the operation was performed without mechanical backflushing or chemical cleaning during operation.

![Normalized permeate flux dependent on testing time during filtration of TDPW (tank dewatering produced water) with a feed oil concentration of 1,000 ppm and OMS (oily model system) with a feed oil concentration of 35 ppm, cross flow velocity 2.5 m/s.](image)

**Figure 3:** Normalized permeate flux dependent on testing time during filtration of TDPW (tank dewatering produced water) with a feed oil concentration of 1,000 ppm and OMS (oily model system) with a feed oil concentration of 35 ppm, cross flow velocity 2.5 m/s.
Three sections can be identified within the operation behaviour for the time dependent membrane flux. Within the first section (I) a clear decay of the membrane flux is observed, dependent on the fouling potential of the feed, the process parameters and the surface properties of the membrane. The time period for the second (II) section with lower flux decay depends on the feed characteristics. Within the third section (III) approximately steady-state conditions are reached.

The results of Figure 3 show that the decay of the normalized permeate flux with time is stronger during the filtration of the OMS compared to the filtration of TDPW with a much higher oil concentration in the feed flow. This is due to the higher absolute permeate flux with the OMS system at the beginning of the experiment compared to the absolute flux of the TDPW system at t=0.

Due to the higher fouling potential of the TDPW system the steady state is reached earlier compared to the filtration of the OMS.

4.2 Influence of Cross Flow Velocity on the Permeate Flux

In Figure 4, the time dependent membrane flux is shown for the filtration of the OMS system with an oil concentration of 35 ppm with two different cross flow velocities (1.6 m/s and 2.5 m/s).

![Normalized permeate flux dependent on testing time during filtration of OMS (oily model system) with a feed oil concentration of 35 ppm, cross flow velocities 1.6 m/s and 2.5 m/s.](image.png)

**Figure 4:** Normalized permeate flux dependent on testing time during filtration of OMS (oily model system) with a feed oil concentration of 35 ppm, cross flow velocities 1.6 m/s and 2.5 m/s.

According to Figure 3, the three different flux regimes (I, II and III) are indicated in Figure 4. The experimental results show clearly the influence of a reduced cross flow
velocity with 1.6 m/s on the membrane performance and on the location of the regions (II) and (III) which are shifted compared to the operation conditions at the cross flow velocity of 2.5 m/s. The steady state (III) is reached later with the reduced cross flow velocity at a clearly lower level of the membrane flux. The membrane fouling is more distinct with the lower cross flow velocity as the shear forces at the membrane surface limiting the fouling layer thickness are reduced.

4.3 Filtration of Tank Dewatering Produced Water with Increased Testing Times

Filtration experiments with real tank dewatering produced water (TDPW) were performed over testing times of 30 hours. These experiments were performed in the total recycle mode and in the fed batch mode with and without backflushing. The cross flow velocity was adjusted to 2.0 m/s, the trans membrane pressure to 0.5 bar. In Figure 5, the time dependent permeate flux is given for two different oil concentrations (TDPW1 with 5,200 ppm, TDPW2 with 2,100 ppm).

Figure 5: Normalized permeate flux dependent on testing time during filtration of TDPW (tank dewatering produced water) with a feed oil concentration of 5,200 ppm (TDPW1) and 2,100 ppm (TDPW2), cross flow velocity 2.0 m/s. The test with TDPW1 was performed with mechanical backflushing after 17 hours.

The comparison of the results shows that there is a higher membrane flux over time with the lower initial oil concentration (2,100 ppm TDPW2) due to lower membrane fouling. With the lower oil concentration the flux remained on a sufficiently high level so that a backflushing or cleaning step of the membrane was not required. With the
oil concentration of 5,200 ppm (TDPW1) a mechanical backflushing was required after 17 hours as the flux reached a value of 30% of the initial flux.

The experiments show that a simple mechanical backflush with permeate water for a short time of 10 s with a backflush pressure of 3.5 bar is sufficient to reach again a quite high level of the membrane flux. The initial value of the membrane permeate flux at the beginning of the experiments was about 140 liter/m²/h.

Backflushing is the principal choice to increase membrane fluxes during operation and to control membrane fouling [10]. The process efficiency depends on the time, the water volumes and the energy required for backflushing. Within these investigations the high effectivity of a fast and simple mechanical backflush was shown for the ultrafiltration of oily produced water with ceramic hollow fiber membranes.

4.4 Influence of Membrane Material on Long Term Filtration Performance

In this section the results considering the influence of the membrane material on the long term filtration behaviour are illustrated. The experiments were performed with a standard Al₂O₃/Al₂O₃ as well as with a SiC/Al₂O₃ hollow fiber membrane module. Filtration experiments with real tank dewatering produced water (TDPW) were performed over testing times of nine days. The experiments were performed in the total recycle mode with backflushing. Within all experiments the cross flow velocity was adjusted to 2.0 m/s, the trans membrane pressure to 0.5 bar.

In Figure 6, the time dependent membrane flux of the Al₂O₃ and SiC coated membranes is shown for the filtration of the TDPW system with an oil concentration of 5,200 ppm.

The comparison of the results in Figure 6 shows that there is a clearly higher membrane flux over time with the SiC membrane. Even within the steady state the permeate flux of SiC membrane is almost two times higher than the flux of the Al₂O₃ membrane. For keeping the flux of the Al₂O₃ membrane on a constant level backflushing had to be carried out every three hours whereas no backflushing was necessary during the first seven days of the filtration experiment with the SiC hollow fiber membrane. After seven days three backflush cycles with different modes were performed to check the cleaning effectiveness of the SiC membrane.

Compared to Al₂O₃ membrane the mechanical backflushing of the SiC membrane caused an increase of the flux from 83 l/m²/h to 99 l/m²/h. For the Al₂O₃ membrane the cleaning effectiveness of backflushing is strongly decreasing over filtration time so that nearly no cleaning effect could be observed after an operation time of seven days. The oil retention capacity of both membrane types in this long term experiment was above 99.9% over the whole time of the experiment.

An explanation for the reduced fouling tendency and more effective backflushing behaviour of the SiC hollow fiber membrane compared to the Al₂O₃ hollow fiber
membrane can be found in the different surface charges of the materials (pH of isoelectric point for SiC 2.5-3.5 [11] and for Al₂O₃ 7.0-9.5 [12]). In the present study the hypothesis from literature is confirmed that the membrane with the highest negative charge or highest hydrophilicity fouls the least [11]. Even though other parameters like surface roughness, membrane structure (average pore size and porosity) and geometry may play a certain role as well, further experiments with varying pore size and porosity showed that for produced water treatment or in oil/water separation processes the surface charge respectively the surface chemistry of the active membrane layer are the dominant influencing factors on the fouling behavior.

Figure 6: Permeate flux dependent on testing time during filtration of TDPW with an oil concentration of 5,200 ppm (TDPW1), cross flow velocity 2.0 m/s. The test with the Al₂O₃ membrane was performed with mechanical backflushing every three hours. The SiC membrane was backflushed after seven days filtration time for the first time.

4.5 Retention of Oil and Total Carbon

Besides the permeate flux, the retention efficiency for oil and total carbon components is an important membrane characteristic for produced water treatment applications. Within all experiments performed a high oil retention capacity above 99.5% was shown in the treatment of OMS as well as for the TDPW systems. The total carbon (TC) retention efficiency was in the range of 90-95% during the filtration of OMS and between 61% and 94% for different TDPW systems.
5. Industrial Waste Water Treatment I – Waste Water from Metal Working

A first example of an industrial waste water treatment application is described within this section. The waste water to be treated is resulting from a metal working company. It is contaminated with organic solid particles with high chemical oxygen demand (COD) and total suspended solids (TSS), see composition in Table 1.

### Table 1: Characteristic feed water composition of waste water from metal working

<table>
<thead>
<tr>
<th>pH</th>
<th>Conductivity [µS/cm]</th>
<th>COD [mg/L]</th>
<th>TOC [mg/L]</th>
<th>Oil content [mg/L]</th>
<th>Turbidity [NTU]</th>
<th>Particle size [nm]</th>
<th>TSS [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>850</td>
<td>13,000</td>
<td>176</td>
<td>265</td>
<td>5540</td>
<td>170-400</td>
<td>4900</td>
</tr>
</tbody>
</table>

5.1 Experimental Test Set-up and Procedure

A pilot test skid was manufactured to run the experiments in in-out cross flow mode with two membrane modules. Each membrane module includes an effective filtration area of 0.3 m². To maintain the constant cross flow velocity (CFV) in the system a manual valve is operated in the reject line to control the pressure. The applied trans membrane pressure (TMP) was in the range of 0.6 - 0.9 bar, and the CFV was in the range of 1.0 - 1.2 m/s The separation experiments were performed by using the standard ceramic hollow fiber membranes with Al₂O₃ ultrafiltration coating layer. The volume of the feed solution was 1 m³ for each batch. During the experiments two operational modes were chosen, the recirculation mode and the concentration mode. The recirculation mode was used to attain a stable filtration performance with the membrane for the feed water. The concentration mode was chosen to understand the membrane capability in separation of feed water contaminants and concentrating the feed water components to the maximum level. Also in this second mode a reduction in the volume of generated waste during the filtration process was observed which is a significant contribution in reducing operational costs of the water cleaning process. The two operation modes are shown schematically in Figure 7.

![Figure 7: Schematic process outline for recirculation mode and concentration mode operation.](image-url)
The feed and permeate samples collected were measured and then returned to the feed tank for recycling at regular time intervals. Figure 8 gives an idea of the feed and permeate quality.

![Image of feed and permeate samples]

**Figure 8:** Feed water and permeate water from industrial waste water cleaning process.

### 5.2 Analysis Procedure

During the experimental evaluation three water quality parameters were measured to evaluate the performance of the ceramic hollow fiber membrane in this application – total suspended solids, chemical oxygen demand, and turbidity.

- **Total Suspended Solid (TSS):** The total suspended solid concentration is a parameter to indicate the amount of solid inorganic and organic material suspended in water. The standard APHA 2540D has been followed to test TSS of feed and permeate water. The glass microfiber filters (Whatman TM 934-AHTM) with 1.5 µm particle retention have been used to prepare TSS samples.

- **Chemical Oxygen Demand (COD):** The chemical oxygen demand represents the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. The photometric test system (Merck Spectroquant®) with COD test cells (Merck, 25-1500 mg/L or 500-10,000 mg/L) has been used for COD tests.

- **Turbidity:** Turbidity is the cloudiness or haziness of a fluid caused by large numbers of individual particles that are generally invisible to the eye. The turbidity of feed and permeate samples have been measured by a turbidity meter (Merck Turbiquant® 1500 IR).

### 5.3 Results

#### 5.3.1 Flux Behaviour

The flux behaviour was observed at constant cross flow velocity (CFV) of 1 m/s during the filtration process in concentration mode. In Figure 9, the permeate flux and the trans membrane pressure (TMP) are shown dependent on the operating time. The permeate flux is given in a normalized quantity having the value one at the beginning of the filtration process. It is shown that a steady-state flux was reached after about 120 hours of operation while the TMP increased from 0.3 to 0.8 bar.
Figure 9: Normalized flux and trans membrane pressure dependent on operating time.

5.3.2 Retention of Particulate Matter and COD:

As shown in Table 1, the industrial waste water has high organic solid particle load in the feed. From the filtration experiments it was shown that the separation efficiency of the ceramic hollow fiber membranes for the organic suspended solids from waste water is very high.

The water quality data measured during the experiments for the feed water and permeate water are given in Figure 10. The significant behaviour of the ceramic hollow fiber membrane shows that the waste water was concentrated up to 5% of the initial feed volume i.e. total 3 m$^3$ of waste water feed were reduced to 150 litres and the remarkable result from these experiments is that the total suspended solids (TSS) concentration in the waste is increased up to 17% from 0.5% in the original feed water.

From Figure 11, it is also observed that effective separation of suspended solids from the waste water consequently results in reduction of COD as well which meets the industrial discharge requirements. The COD in the concentrated feed water was increased up to 37,000 ppm.

The operating conditions underlying the results in Figures 10 and 11 are the same as for the results in Figure 9 – operation in concentration mode with a cross flow velocity of 1 m/s.
5.4 Long Term Operational Behaviour on Site

After the pilot trials for 5 m$^3$ of feed waste water, a full scale plant was designed and manufactured with 25 membrane modules. An in-out cross flow mode operating system was designed for a feed water capacity of 5 m$^3$ per day. The system was installed on site to perform the filtration of high organic solid loads from the feed water and the long term filtration performance of the ceramic hollow fiber membranes was observed.
Figure 12: Flux and TMP characteristics of the CHFM field installation during an operation time of one month.

The results in Figure 12 show that the permeate flux of the ceramic hollow fiber membranes is stable over one month of operation on site. The filtration capacity was fixed for the first few days to evaluate the effect of TMP on the permeate flux. After the first week the membranes were cleaned with chemicals (CIP-1) and afterwards the system was run continuously to operate at higher permeate capacity to manage the incoming feed water. It is observed that TMP was increased from 0.8 to 1.4 bar and the flux declined. Over 17 days of stable operation from the first cleaning the flux decline is high and chemical cleaning for two module lines (CIP-2) was performed to recover the flux. After this second chemical cleaning the membranes are recovered and they achieved a stable flux level.

Figure 13: Feed and permeate parameters during an operation time of one month.

In Figure 13, the two parameters TSS and COD are shown for the feed and permeate water. The feed water TSS is increased from 8000 ppm to 25,000 ppm concentration whereas the permeate water TSS is always < 5 ppm. This trend is
observed during the continuous operation for one month. It shows that the feed water is concentrating in few days and reducing the total waste volume to be further treated. Also the COD of the feed and permeate is shown for the period of one month. It is observed that a significant reduction of COD in the concentrated feed water from 8000 ppm to less than 600 ppm in the permeate water is reached consistently which meets the discharge requirements.

6. Industrial Waste Water Treatment II – Treatment of Floor Cleaning Water

A second water cleaning application is currently running with the ceramic hollow fiber membrane technology. This application is related to cleaning waste water from floor cleaning vehicles which operate in an industrial environment of plastic and metal processing. The floors are cleaned daily, and in some cases even several times a day. 16 different cleaning agents are applied, which are added to the water tanks, depending on the respective contamination.

The cleaning vehicles spray the mixture onto the floor under high pressure and then vacuum up the dirty water again. As a result, 200 litres of waste water are produced with standard cleaning and up to 5 m$^3$ by intensive cleaning within this production site. Over the course of a week, this adds up to around 6 m$^3$. Before the water enters the sewage system and makes its way to the public sewage treatment plant, it must first be cleaned to remove oil, grease, particulate matter and swarf to fulfill the legal requirements for disposal to the public waste water drain system.

Instead of using an evaporator system, the new membrane system was installed.

Currently the water cleaning takes place in several steps with a ceramic hollow fiber membrane at the end. Within the cleaning process, first, the cleaning vehicles discharge the waste water into a large sump pump. The water is then pumped into the storage tank via a submersible pump. This tank has a funnel-shaped floor so that coarse particles and swarf are deposited and can already be removed at the beginning of the cleaning process.

Oil floating on the surface is also pumped off at this point, and additional oil is also collected at the vanes of a light fluid separator. Smaller solids, particles and swarf are filtered off in a band filter. The used nonwoven material is subsequently wound up and disposed of together with the sludge. The subsequent ultra-filtration process removes even the tiniest particles thanks to a ceramic membrane.

Separation of the heavy metals then takes place by means of a downstream selective ion exchanger. The entire system operates almost fully automatically. The new plant not only achieves significantly higher cleaning efficiency, but also reduces energy consumption by 80 to 90 percent compared to the previous process [13].

The ceramic hollow fiber membrane used for the ultrafiltration step reduces the hydrocarbon concentration from approx. 1000 mg/l to 2 mg/l.

Table 2 gives an overview on the regulation requirements and the current clean water quality parameters after treatment.
Table 2: Comparison between regulation requirements and actual water quality parameters after water treatment process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>Hydrocarbon [ml/L]</th>
<th>Solids [mg/L]</th>
<th>Zinc [mg/L]</th>
<th>Nickel [mg/L]</th>
<th>Lead [mg/L]</th>
<th>Copper [mg/L]</th>
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<tr>
<td>Legislation limit</td>
<td>6.0 – 9.5</td>
<td>&lt; 20</td>
<td>&lt; 1</td>
<td>&lt; 2</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Current values permeate</td>
<td>8.2</td>
<td>2</td>
<td>&lt; 1</td>
<td>&lt; 2</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

7. Conclusions

The experiments have shown that ceramic hollow fiber membranes are a new and attractive filter medium to be applied for the effective and efficient separation of oil/water systems and of industrial waste water systems including high organic and solid loads. In the investigations of the authors a two-layer ceramic hollow fiber membrane was applied with an Al₂O₃ support structure and a functional ceramic ultrafiltration coating consisting of Al₂O₃ or SiC. The relevant pore diameter of the functional coating is d₉₀ = 40 nm for the Al₂O₃ coating, respectively 100 nm for the SiC membrane coating. The two-layer structure reduces the energy requirements due to the low trans membrane pressure to be applied.

It was demonstrated that a simple mechanical backflush with permeate water at a short time interval with a high pressure pulse is sufficient for an effective membrane cleaning during the filtration process. Further experiments have shown that the initial membrane flux can be nearly achieved when a chemically enhanced backflush is applied.

It is a promising result that stable membrane operation behaviour with economically attractive operating conditions was also achieved during the experiments with high feed oil concentrations of some thousand ppm. Usually produced water treatment is performed in multiple cleaning steps and the ultrafiltration step is performed at the end to fulfil the legal requirements for low oil concentrations before the water is disposed to the environment. In current produced water treatment technologies the oil concentration in the feed water for the ultrafiltration step is only low with about 100 ppm resulting from previous cleaning steps.

Very promising results concerning permeate flux, fouling tendency, backflushing effectivity and oil retention could be achieved with the SiC/Al₂O₃ hollow fiber membrane. Such a system with an active SiC membrane layer shows almost a doubling of the permeate flux in the steady state compared to the Al₂O₃/Al₂O₃ hollow fiber membrane and with which no cleaning procedure was necessary during the first seven days.
As the experiments have also shown, the applied ceramic hollow fiber membranes can treat very high feed oil and particle concentrations. This means in consequence that there is a potential to combine two or more process steps in the current produced water or industrial waste water treatment technology to one ultrafiltration step by application of ceramic hollow fiber membranes which can be operated with high contamination loads. Besides the technological simplification this would lead to reduced energy requirements and lower footprints in produced water treatment processes.

Considering the results from industrial field applications it was shown that the ceramic hollow fiber membranes keep high operational robustness over the observed operation times. These industrial waste water treatment applications show especially that the ceramic hollow fiber membranes operate robustly with changing feed water qualities including high solids and/or organic loads. The legal requirements for the permeate water quality to be discharged were met in the application examples. From the perspective of operational costs for industrial waste water treatment it was demonstrated that the water pollutants could be concentrated to a very high level so the waste water volume to be treated as special waste can be reduced significantly.

References


