

Surface Modification of Ready-to-Use Hollow Fiber Ultrafiltration Modules for Oil/Water Separation

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Reusing wastewater from oil-related industries is becoming increasingly important, especially in water-stressed oil-producing countries. Before oily wastewater can be discharged or reused, it must be properly treated, e.g., by membrane-based processes like ultrafiltration. A major issue of the applied membranes is their high fouling propensity. This paper reports on mitigating fouling inside ready-to-use ultrafiltration hollow-fiber modules used in a polishing step in oil/water separation. For this purpose, in-situ polyzwitterionic hydrogel coating was applied. The membrane performance was tested with oil nano-emulsions using a mini-plant system. The main factors influencing fouling were systematically investigated using statistical design of experiments.

Keywords: Design of experiment, Membrane fouling, Oil/water separation, Surface modification, Ultrafiltration

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1 Introduction

Tremendous amounts of oily wastewater, also known as produced water (PW), are created daily by oil-related industries that must be properly treated before discharging or reusing [1]. Oil-contaminated water is generally produced either naturally, i.e., water existing within the geological structure of wells, or because of water injection, so-called flowback water. In principle, composition and characteristics of PW differ depending on the geographical location of the well [2]. Oily wastewater may contain dissolved and/or dispersed oil, minerals, production chemicals (e.g., corrosion and scale inhibitors, surfactants and co-surfactants),

produced solids (e.g., clays and waxes) as well as dissolved gases (e.g., CO₂, O₂, H₂S) [3, 4]. Organic compounds in oily wastewater may contain aliphatic hydrocarbons, phenols, carboxylic acids, and polycyclic aromatic hydrocarbons [5, 6]. PW is slightly acidic, with an oil content in the range of 2–2000 mg L⁻¹, total suspended solids of 1–1000 mg L⁻¹, and total dissolved solids of 1000–400 000 mg L⁻¹ [7, 8]. Recent reports reveal that global production of PW is expected to increase significantly; the oil/water ratio may reach 1:12 by 2025, compared to 1:3 in 2007 [4]. There are more stringent regulations for oily wastewater discharge; the discharge limit for oil and grease was set to 42 and 10 mg L⁻¹ in USA and China, respectively [3, 7].

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The potential of PW reusing is gaining more attention, in particular in water-stressed oil-producing countries; therefore, efficient treatment methods are required [9]. Several reviews have critically concluded that pressure-driven membrane-based separation processes, e.g., microfiltration (MF) and ultrafiltration (UF), are promising due to high water recovery, simplicity, small footprint, and ease to be integrated into currently established treatment plants [3, 4, 7, 8, 10]. Today, more than 3000, standalone and/or hybrid, treatment plants based on polymeric UF/MF membranes and more than 75 treatment plants based on inorganic/ceramic membranes have been installed worldwide [11]. Nevertheless, high fouling propensity of polymeric UF membranes is still one of the major issues. Moreover, membrane performance and fouling behavior are substantially influenced by the operating conditions. The ultimate objective of the joint research project "UFO" was to optimize hollow fiber UF membranes for their use in a polishing step in treatment of oil-containing wastewaters.

Here, a facile approach for promoting antifouling propensity of polyethersulfone (PES) hollow fiber membranes is introduced. Surface modification of capillaries lumen in ready-to-use modules was realized via macro-initiator-mediated reactive coating of zwitterionic hydrogel layer using the method developed by Quilitzsch et al. [12]. The antifouling properties and stability under cleaning conditions of such hydrogel coating had also been investigated by Le et al. [13]. Performance of surface-modified vs standard pristine modules was investigated in multiple filtration cycles tests using a mini-plant testing unit. Oil nano-emulsions exhibiting a crude oil content < 5 ppm and an average oil droplet size < 0.5 μm were employed as model feed water. The influences of different operating conditions, i.e., concentrations of oil, surfactant/co-surfactant, and salt, as well as chemical cleaning backwashing (CEB) frequency on membrane performance were studied using design of experiment (DOE) approach.

2 Materials and Methods

2.1 Chemicals and Membranes

Light crude oil (AR-2048, 2.01 wt % sulfur, Alpha Resources LLC, USA) was used to prepare model feed water. Sodium dodecyl sulfate (SDS, Merck, Germany) and 2-pentanol (Merck, Germany) were used as surfactant and co-surfactant, respectively. Sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) for membrane cleaning were purchased from VWR International, Belgium. Sodium metabisulfite for membrane storing was purchased from Carl Roth, Germany. Artificial seawater salt was purchased from Aqua Medic GmbH, Germany. Pure water of reverse osmosis permeate quality (conductivity: $\sim 35 \mu\text{S cm}^{-1}$, total organic carbon < 0.2 ppm) obtained by the system Osmose 190 (Denerle, Germany) was used.

For surface modification, zwitterionic monomer *N*-(3-methacryloylimino)propyl-*N,N*-dimethylammoniumpropanesulfonate (SPP) was synthesized from 1,3-propane sulfone and *N*-[3-(dimethylamino)propyl]methacrylamide (Sigma-Aldrich, Germany) [12]. The macromolecular redox co-initiator, poly((2-dimethylamino)-ethyl methacrylate-co-butyl methacrylate) (PBD, molecular weight 300 kDa) was prepared as reported in [12] from the monomers 2-(dimethylamino)ethyl methacrylate (98 %) and butyl methacrylate (99 %) and using the initiator 2,2'-azobis(2-methylpropionitrile) (98 %); all from Sigma-Aldrich, Germany. The crosslinker *N,N'*-methylene-bis-acrylamide (MBAA, ACROS Organics, UK), the initiator ammonium persulfate (APS, ACROS Organics, Spain), and iso-propanol (Fisher Scientific, AR., Germany) were also used for membrane modification.

PES hollow fiber UF membrane modules were supplied by inge[®] GmbH, Germany. Each module is 30 cm long and comprises 10 capillary fibers with 70 bores of 0.9 mm in diameter and a total membrane active area of 0.051 m². Two types of hollow fiber membranes were employed in this study, i.e., standard, and "open" membranes. Standard membranes (SM) are analogs to commercial UF membranes in the market, they have an average pore diameter of 20 nm and molecular weight cut-off (MWCO) of 75 kDa. Open membranes (OM) were specifically fabricated for this project; they had less dense membrane structure, bigger average pore diameter, and an MWCO of 120 kDa. OM were designed to maintain water permeability after surface modification comparable to SM.

2.2 Surface Modification of Ready-to-Use Membranes

Surface modification of capillaries lumen inside OM module was carried out via surface-initiated zwitterionic hydrogel grafting [12]. The received OM were rinsed alternately in NaOCl (50 ppm) at pH 12 and RO-quality water to remove residues of manufacturing and storage chemicals until a stable pure water permeability (*PWP*) of 1800–2000 L m⁻² bar⁻¹ h⁻¹ was maintained. Prior to surface modification, the OM module was equilibrated by circulating Milli-Q water followed by 20 % isopropanol in Milli-Q water, each for 30 min at constant flow rate of 80 mL min⁻¹.

The surface modification approach is illustrated in Fig. 1. The first step was the immobilization of the tailor-made macromolecular co-initiator PBD on the barrier layer surface inside the lumen of the membrane. It contains hydrophobic butyl methacrylate segments for anchoring to the hydrophobic membrane, and a tertiary amine moiety serves as co-initiator for accelerating initiator (APS) decomposition and triggering formation of crosslinked hydrogel. The macroinitiator solution was prepared by dissolving 0.25 g of PBD in 50 mL isopropanol and 2.5 mL of 1 M HCl, then Milli-Q water was added to prepare 250 mL solution.

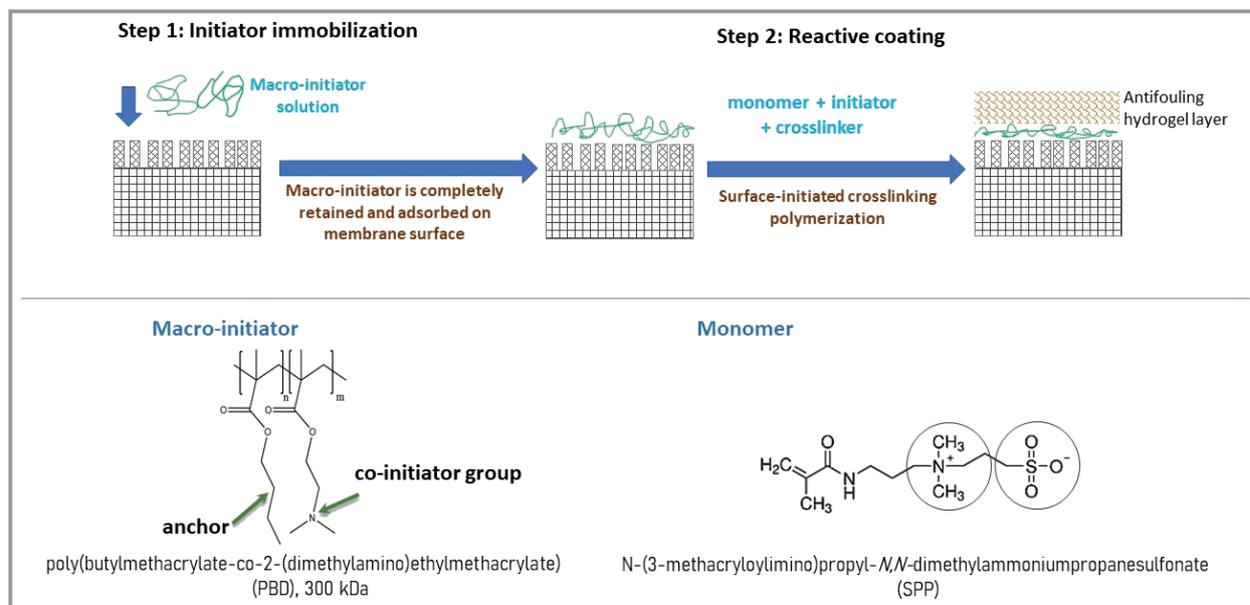


Figure 1. Surface modification approach for ready-to-use membrane modules.

Pre-modification of OM was performed by circulating macroinitiator solution at 80 mL min^{-1} for 60 min. Then, it was washed by circulating Milli-Q water for 30 min. The second step was reactive coating, SPP and MBAA were used as monomer and cross-linker, respectively. The pre-modified OM membrane was washed with argon-saturated Milli-Q water for 30 min. Monomer solution was prepared by dissolving 2.2 g SPP and 146 mg MBAA in 30 mL Milli-Q water at continuous stirring. The monomer solution was degassed by argon purging for 20 min. Then, 300 μL of 0.5 M APS were added 5 min before the end of degassing. Thereafter, OM was rinsed with the reaction mixture (or hydrogel-forming solution) for 120 min. During modification, the permeate opening was sealed and the membrane module was kept vertical to avoid air bubbles. After modification, the modified module (MM) was washed thoroughly using 2 L Milli-Q water at 80 mL min^{-1} .

2.3 Preparation of Oil-in-Water Nano-emulsions

Oil stock emulsions were prepared by mixing crude oil and pure water at a volumetric ratio of 1:250; the mixture was intermittently premixed by a high-speed stator rotor mixer (Ultra-Turrax[®] T 25, IKA, Germany) at maximum speed of 24 000 rpm for a total mixing time of 1 min. Then, it was passed through a high-pressure homogenizer (HPH 2000/4-SH5, IKA, Germany) at 1000 bar for two passes. Oil stock emulsions were then filtered through filter paper (N310, VWR, Germany) for removing oil droplets bigger than 10–20 μm , to simulate PW water after conventional treatment steps in water treatment plants. Trial experiments using real PW samples showed that oil concentration remaining in treated PW is generally in the range of 1–10 mg L^{-1} .

Accordingly, oily feed water in this study was prepared at analogous concentration from oil stock emulsions by dilution with RO-quality water as specifically described in respective experiments. Total organic carbon (TOC) was employed as representative parameter for expressing oil content in the oily feed water. TOC was measured by TOC-L (Shimadzu, Japan). Oil droplet size distribution was measured by a laser size analyzer (Model: LS 13 320, Beckman Coulter, USA). Preparation of oil-in-water nano-emulsions was reproducible to very good extend; oil droplet size distributions for five oil stock emulsions are shown in Fig. 2.

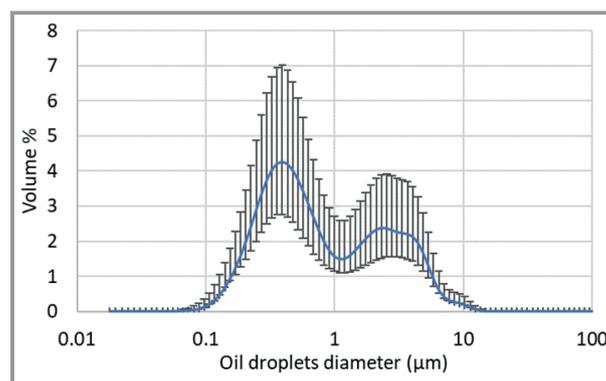


Figure 2. Oil droplet size distribution of oil stock nano-emulsions prepared from crude oil volume ratio of 1:250 (oil in water) without addition of dispersing agents. Results are the average of five samples.

2.4 Mini-plant Oil Filtration Experiments

Filtration experiments were performed employing two custom-designed fully automated mini-plant testing units, designed and assembled by Convergence Industry B.V., The Netherlands, “Poseidon” and “Neptunus”. Both were programmed to perform challenging dead-end oil filtration tests at conditions close to full-scale application. Mini-plant testing units were revealed to be able to investigate hollow fiber membrane performance at conditions comparable to industrial application in the lab without the need for complicated/expensive pilot-scale systems [14]. The Poseidon system was used for the initial challenging oil filtration tests to evaluate the impact of surface modification on fouling propensity. The Neptunus system was used for DOE experiments to investigate the influence of various operating conditions (cf. Sect. 2.5); it can run two filtration tests simultaneously for two membrane modules using the same feed water.

Prior to filtration experiments, SM modules were rinsed alternately in NaOCl (50 ppm) at pH 12 and RO-quality water to remove residues of production and/or preserving chemicals, and then, they were stored in sodium metabisulfite solution (7.5 g L⁻¹) at pH 3–4 ready for testing. MM modules were used directly after hydrogel coating and subsequent washing, i.e., without further post-treatment. PWP values for SM and OM modules were measured by filtering RO-quality water at constant flux of 100 L m⁻²h⁻¹ for 3–5 h until stable PWP values were maintained for at least 1 h. The general membrane testing procedures, using Poseidon and Neptunus, are described in Fig. 3.

Oil filtration tests started by filtering pure water for 15 min to determine the initial PWP. Then, model feed water was filtered for several filtration cycles (normally 9 cycles unless another number is mentioned, or the filtration stopped when the pressure inside the system exceeded 4 bar because of strong membrane fouling). Each filtration cycle was performed for 45 min at a constant flux of 100 L m⁻²h⁻¹ and followed by mechanical backwashing at a flux of 230 L m⁻²h⁻¹ for 60 s (30 s from feed side and 30 s

from dead-end side). After the last filtration cycle, PWP was measured and mechanically backwashed; the latter steps were repeated three times as shown in Fig. 3. At the end, intensive chemical cleaning in place was performed using SDS (1.2 g L⁻¹) and NaOCl solution (200 ppm as free chlorine) at pH 12. The model feed water was different based on the phase of the experiment. Oily feed water of 1 mg L⁻¹ TOC and with an average oil droplet Sauter mean diameter of 500 ± 50 nm, without adding dispersing agents and salt, was used for challenging oil filtration tests using Poseidon, while compositions of model feed waters employed for DOE experiments are listed in Tab. 1.

Membrane filtration performance was assessed by collecting filtered volume rate (Q , L h⁻¹) and transmembrane pressure (TMP, bar) data over filtration time; subsequently, filtration flux (J , L m⁻²h⁻¹), membrane permeability ($Perm$, L m⁻²h⁻¹bar⁻¹), and normalized permeability were calculated as following:

$$J = \frac{Q}{A_m} \quad (1)$$

where A_m (m²) is the active surface area of the membrane.

$$Perm = \frac{J}{TMP} = \frac{J}{P_{feed} - P_{perm}} \quad (2)$$

where P_{feed} and P_{perm} are pressure values in bar at the feed and permeate side, respectively.

$$\text{Normalized permeability} = \frac{Perm}{PWP_0} \quad (3)$$

where PWP_0 is the initial pure water permeability, i.e., before the fouling experiments.

Membrane fouling propensity along multiple filtration cycles was quantified in terms of relative total hydraulic irreversible fouling (F_{HI} , %/cycle):

$$F_{HI} = \frac{PWP_0 - PWP_f}{PWP_0 N_Z} \cdot 100\% \quad (4)$$

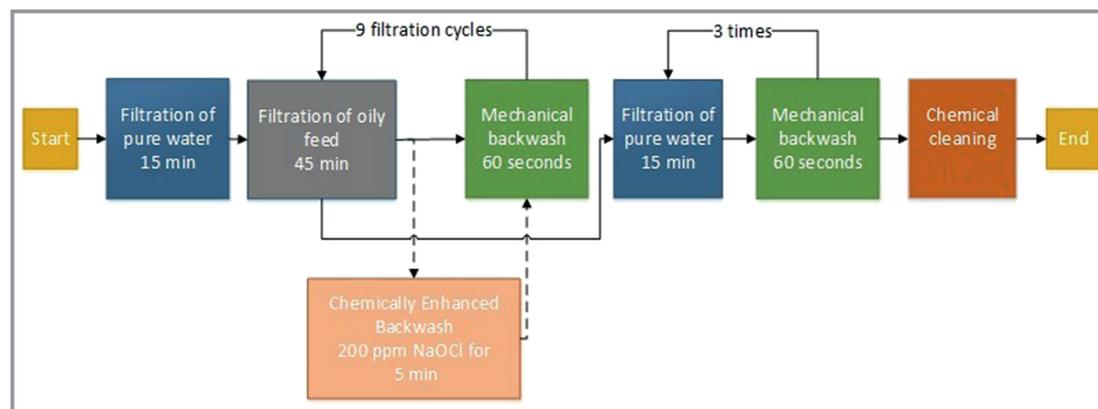


Figure 3. Membranes testing procedures for the mini-plant filtration tests.

Table 1. Testing conditions and relative total hydraulic irreversible fouling per cycle for DOE experiments.

Exp. no.	CEB frequency (number of filtration cycles before CEB) [-]	Oil concentration [mg L ⁻¹]	Salt concentration [mol L ⁻¹]	SDS concentration [g L ⁻¹]	F_{HI} [%/cycle]	
					SM	MM3
1	1	1	0.251	0.24	0.1	0.4
2	5	1	0.251	0.24	0.2	0.4
3	1	5	0.251	0.24	1.1	0.1
4	5	5	0.251	0.24	3.7	2.8
5	1	1	0.003	0.24	0	0
6	5	1	0.003	0.24	0.4	0.8
7	1	5	0.003	0.24	6.4	2.8
8	5	5	0.003	0.24	10.4	10.3
9	1	1	0.251	0.96	23.8	23.6
10	5	1	0.251	0.96	1.6	1.8
11	1	5	0.251	0.96	23.9	23.6
12	5	5	0.251	0.96	47.8	48.5
13	1	1	0.003	0.96	0.5	0.9
14	5	1	0.003	0.96	6.8	5.8
15	1	5	0.003	0.96	0	1.2
16	5	5	0.003	0.96	0.9	2.4
18	6.22	3	0.028	0.6	6.3	7.4
20	3	6.22	0.028	0.6	46.8	46.7
21	3	3	0.933	0.6	1.7	0.4
22	3	3	0.0008	0.6	7	8.3
23	3	3	0.028	0	4.3	0.9
24	3	3	0.028	1.2	4.1	3.1
25	3	3	0.028	0.6	6.6	5.6
26	3	3	0.028	0.6	2	5.6
27	3	3	0.028	0.6	7.6	3.8
28	3	3	0.028	0.6	3.1	5

where PWP_f is the pure water permeability measured at the end of the filtration test, and N_Z is the total number of performed filtration cycles.

2.5 Studying the Influence of Testing Conditions via Design of Experiment

Four testing parameters were investigated, oil concentration in feed water, salt concentration, and surfactant concentration, in addition to frequency of chemical enhanced backwashing (CEB). These parameters were systematically varied to create the experimental matrix. A two-stage factorial design was used as described by Kleppmann [15]. Such

design contains center and star points. A center point is an additional measurement point in the middle of the testing area, whereas star points are located at the edges, slightly outside the frequent range for a certain parameter. The corresponding test was not performed if the calculated star point was negative. By defining respective distances between measuring points of the steps and the center/star points, an orthogonal experimental design was generated.

The ranges for testing parameters and the correspondent center and star points are listed in Tab. 1. The CEB frequency was represented by the number of filtration cycles before running a CEB. The lower and upper values for CEB frequency were set to 1 and 5 filtration cycles, respectively, which resulted in a center point of 3 and an upper star

point of 6.25, whereas the lower star point was negative. CEB was carried out using NaOCl solution at a concentration of 200 ppm free chlorine and pH 12. The limit oil concentration values were set to 1 and 5 mg L⁻¹ TOC, which produced center and upper star points of 3 and 6.25 mg L⁻¹ TOC, respectively, and negative lower star point. The limits for salt concentration were aimed at covering salinity ranges for seawater, brackish water, and freshwater. Therefore, limits were set to 0.003 and 0.251 mol L⁻¹ that led to a center point of 0.028 mol L⁻¹, besides lower and upper star points of 0.0008 and 0.933 mol L⁻¹, respectively. Moreover, the surfactant/co-surfactant (SDS/2-pentanol) ratio was set constant at 7:6 (w/w); SDS limits were 0 and 1.2 g L⁻¹ for the lower and upper star point, respectively. The critical micelle concentration (CMC) of SDS is 8.2 mMol L⁻¹ (~2.4 g L⁻¹). A total of 28 experiments were performed, 16 experiments for two-stage full factorial plan, eight experiments for star points, and four replicates of the central point to check reproducibility. Nano-emulsions that were implemented in this study were first prepared as described in Sect. 2.3, and then, SDS and 2-pentanol were dosed. Finally, oily feeds were filtered simultaneously through both SM and MM membranes utilizing the Neptunus mini-plant as described in Sect. 2.4.

Thereafter, the results were analyzed using MiniTab[®] statistical program and response surface methodology. A Box-Cox transformation was performed to find out the most appropriate quadratic model, in which the impacts of influencing parameters are investigated individually and in all possible quadratic products. The parameters CEB frequency, oil, salt, and surfactant concentrations were indicated as *A*, *B*, *C*, and *D*, respectively. The target variable was defined as F_{HI} (given as *Y*). Subsequently, the complete quadratic function (Eq. (5)) may include terms *A*, *B*, *C*, *D*, *A*², *B*², *C*², *D*², *AB*, *AC*, *AD*, *BC*, *BD*, and *CD*.

$$Y^\lambda = f(A, B, C, D) \quad (5)$$

where λ is the response power that was used to obtain the best fitting. To avoid less influencing and interfering terms, stepwise backward elimination based on null hypothesis testing was performed [16], and decision was made using a regression method. The evidence measure (probability *p*) for the credibility of null hypothesis was calculated for a significance level of 5% and the coefficient of determination (*R*²) was also determined. In addition, the MiniTab[®] prediction model was used to find out the optimal combinations of influencing variables to achieve a defined target variable at the highest overall model desirability (close to 1); here, oil concentration was set as target value.

3 Results and Discussions

3.1 Performance of Modified Membranes vs Standard Membranes

Both MM and SM modules were challenged in dead-end filtration experiments of oily feed water (1 mg L⁻¹ TOC) prepared without dispersing agents or salts. Hydraulic backwashing rate was altered within the experiment every three cycles in the sequence: 1400, 940, 700, and 240 L m⁻²h⁻¹. Performance curves for twelve filtration cycles are shown in Fig. 4. MM modules exhibited an improved antifouling propensity and lower normalized permeability decline (38%), compared to 73% permeability decline in case of SM modules. Moreover, chemically irreversible fouling for SM modules was doubled compared to that of MM modules.

Interestingly, no impact of backwashing fluxes on performance of both MM and SM modules was observed; the amount of hydraulically irreversible fouling was almost the same for the same membrane despite of changing backwashing fluxes. This may indicate that hydrogel coating could mitigate fouling; however, it was hard to remove adhered oil once the membrane was fouled. Subsequently, shortening filtration cycles might be advantageous for further mitigating irreversible fouling for MM modules.

3.2 Influence of Testing Conditions

The conditions for 28 experiments set to study the influence of testing conditions on fouling propensity (expressed by F_{HI}) of MM vs SM modules are listed in Tab. 1. Since F_{HI} values for center experiments, i.e., 25–28, showed comparatively certain fluctuations that were large for SM, no conclusive statements can be established; however rather general trends can be identified.

For instance, experiments 1–8, performed at constant SDS concentration of 0.24 g L⁻¹, revealed that high CEB frequency was associated with lower membrane fouling. Besides, for certain CEB, high salt concentration accompanied by high oil concentration showed low fouling, while it

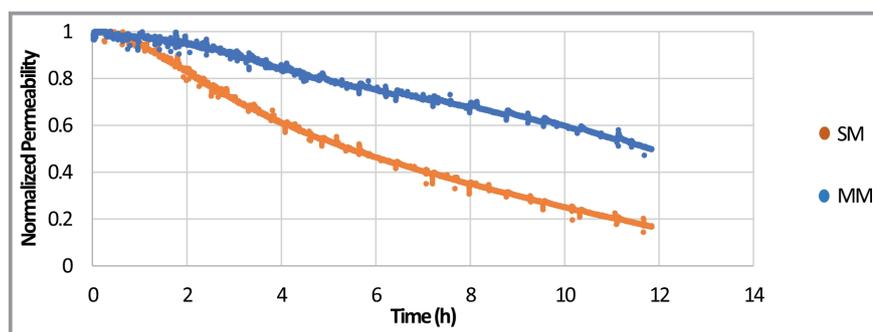


Figure 4. Performance curves for MM vs SM modules during dead-end mini-plant filtration experiments at constant flux of 240 L m⁻²h⁻¹ using oily feed water of 1 mg L⁻¹ TOC and average oil droplet size of $d_{32} = 500$ nm.

resulted in relatively more fouling in case of low oil concentration experiments, considering that fouling by low oil concentration is already low.

Experiments 9–16, performed at high SDS and salt concentrations, showed a generally significant decrease of permeability at the beginning of filtration experiments. Such a decrease could be restored in certain experiments while not in others that led to inconsistent behavior. Additionally, higher CEB frequency resulted in low membrane fouling in case of low oil concentration, while the opposite behavior was noticed at high oil concentration. Severe membrane fouling was clearly seen at high oil, SDS, and salt concentrations. Addition of salt and surfactant was reported to change the oil/water interfacial tension leading to droplet deformation and membrane fouling via pore penetration mechanism [17, 18]. Besides, salts can decrease the surfactant solubility (salting out effect) in water and influence its CMC [18], which may lead to surfactant micellization and blocking of membrane pores.

Overall, in most of the filtration tests at high SDS concentration, no consistent and/or significant difference in fouling propensity was, unexpectedly, observed for SM and MM modules. Besides, increasing both salt and SDS concentrations showed comparable performance of SM and MM modules, either improvement or deterioration depending on the salt and SDS concentrations set.

Furthermore, additional insights were obtained from Minitab® analysis, results are plotted in Fig. 5. Oil concentration and interaction between salt and SDS were the most

influencing parameters. High salt concentrations significantly reduced membrane fouling when SDS concentration was at low to medium level, whereas fouling is drastic if both concentrations were high. The interaction between salt and SDS had more dominant influence than both parameters individually. On the other hand, the results showed no or minimal influence of CEB frequency on SM and MM module performance, which should be related to employed range (being not wide enough), and/or dominant influence of salt and SDS effects being too dominant.

Subsequently, the mathematical models correlating the main influencing parameters with relative total hydraulic irreversible fouling for both SM and MM modules are shown in Tab. 2. The results of model fitting for the MM module were less significant since the p -value was < 0.05 .

Furthermore, the influence of oil (B), salt (C), and SDS concentrations (D) on F_{HI} (Y) was studied using 3D response plots (see Fig. 6). The oil concentration was emphasized to have major influence with more severe fouling at increasing oil concentration. Fouling is particularly strong at medium salt and SDS concentrations, while the influence decreases at low and high salt and SDS concentrations. Also, as aforementioned, salt and SDS concentrations had a major combined influence, and they interacted with each other. Therefore, it was complicated to make conclusive statements based on the employed small set of experiments; only rather general trends were identified. For instance, it is well-known that the higher the salt concentrations, the more destabilized the oil emulsion and the larger

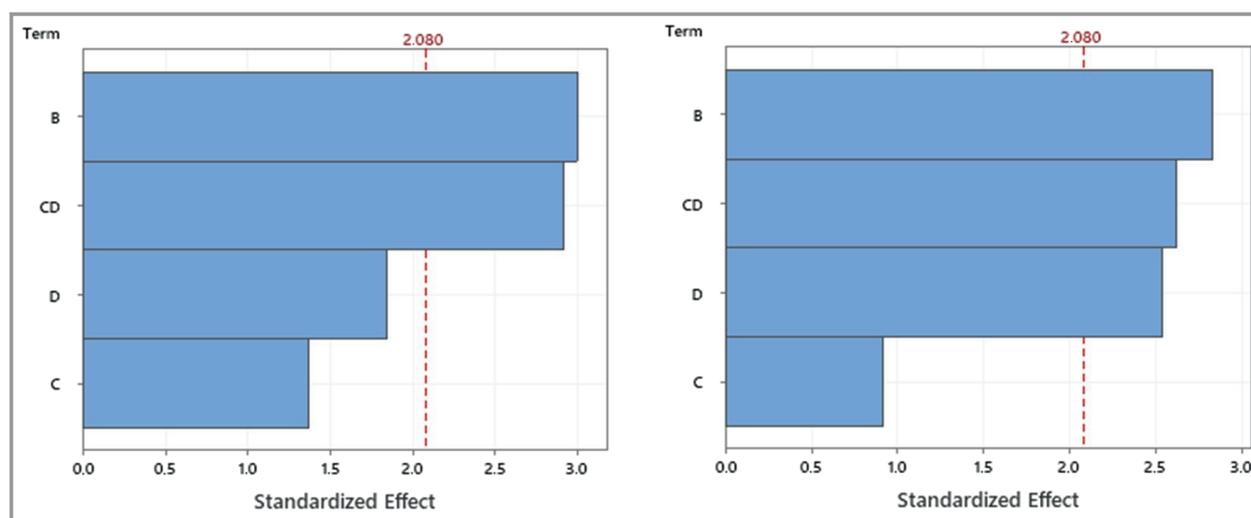


Figure 5. Standardized influences of oil concentration (B , mg L^{-1}), salinity (C , $-\log(\text{ionic strength})$), and SDS concentration (D , g L^{-1}) on fouling behavior of SM (left) and MM (right) modules.

Table 2. Mathematical models for SM and MM modules.

Membrane	Mathematical models	p -value [-]	R^2 [-]
SM	$F_{HI}^{0.5} = -2.35 + 0.492B + 1.364C + 14.97D - 7.22CD$	0.093	0.52
MM	$F_{HI}^{0.5} = -2.52 + 0.459B + 1.306C + 15.04D - 6.4CD$	0.003	0.51

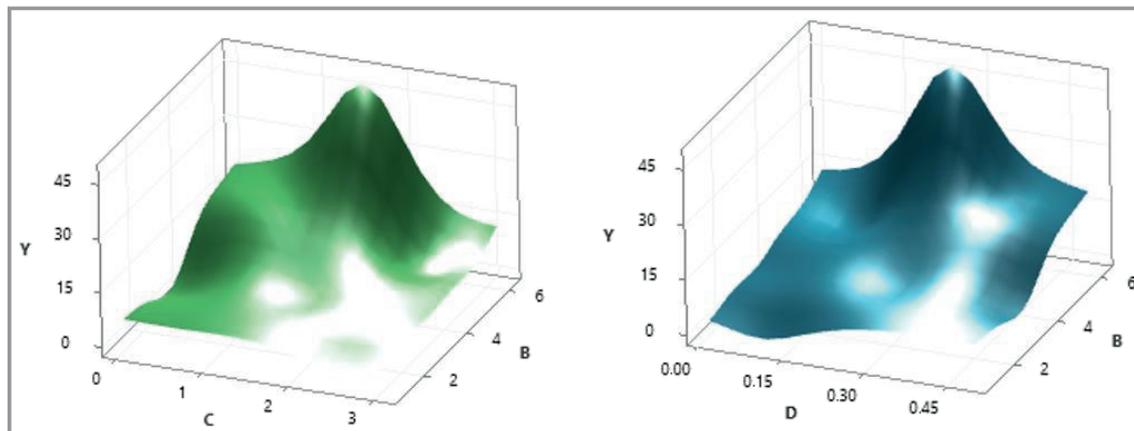


Figure 6. 3D plots of the influences of oil concentration (B , mg L^{-1}), salt concentration (C , $-\log(\text{ionic strength})$), and SDS concentration (D , g L^{-1}) on hydraulic irreversible fouling per cycle (Y , $\%/ \text{cycle}$) for SM.

the oil droplets due to agglomeration. This may have positive influence on mitigating fouling. Increasing SDS concentration may stabilize oil emulsion, and thus, reduce the impact of salt addition.

4 Conclusions

Surface modification of ready-to-use hollow fiber UF membranes by in-situ polyzwitterionic hydrogel coating was emphasized to promote antifouling propensity during multiple-cycles challenging oil/water separation tests. Nevertheless, the systematic study of the impact of testing conditions via DOE showed no significant effect for surface modification compared to standard membranes. Instead, oil concentration and combined salt-SDS concentrations were identified as the main influencing parameters. Further experiments are planned to understand possible interrelationships between different testing parameters employing reliable ranges.

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Symbols used

A_m	$[\text{m}^2]$	membrane active surface area
F_{HI}	$[\%/ \text{cycle}]$	hydraulic irreversible fouling
N_Z	$[-]$	number of performed filtration cycles
P_{feed}	$[\text{bar}]$	pressure at feed side

P_{perm}	$[\text{bar}]$	pressure at permeate side
$Perm$	$[\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}]$	membrane permeability
PWP_0	$[\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}]$	initial pure water permeability
PWP_f	$[\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}]$	pure water permeability at the end of filtration test
TMP	$[\text{bar}]$	transmembrane pressure
TOC	$[\text{mg L}^{-1}]$	total organic carbon

Abbreviations

APS	ammonium persulfate
CEB	chemical enhanced backwash
CMC	critical micelle concentration
DOE	design of experiment
MBAA	N,N' -methylene-bis-acrylamide
MM	modified module
MWCO	molecular weight cut-off
OM	open membranes
PBD	poly(2-dimethylamino)-ethyl methacrylate-co-butyl methacrylate
PW	produced water
PWP	pure water permeability
SDS	sodium dodecyl sulfate
SM	standard membranes
SPP	N -(3-methacryloylimino)propyl- N,N -dimethylammoniumpropanesulfonate
UF	ultrafiltration

References

- [1] Y. Liang, Y. Ning, L. Liao, B. Yuan, in *Formation Damage during Improved Oil Recovery* (Eds: B. Yuan, D. A. Wood), Gulf Professional Publishing, Kidlington **2018**, 515–586.
- [2] *Produced Water: Technological/Environmental Issues and Solutions* (Eds: J. P. Ray, F. R. Engelhardt), Environmental Science Research, Vol. 46, Plenum Press, New York **1992**.

- [3] A. Fakhru'l-Razi, A. Pendashteh, L. C. Abdullah, D. R. A. Biak, S. S. Madaeni, Z. Z. Abidin, *J. Hazard. Mater.* **2009**, *170* (2), 530–551. DOI: <https://doi.org/10.1016/j.jhazmat.2009.05.044>
- [4] S. Jiménez, M. M. Micó, M. Arnaldos, F. Medina, S. Contreras, *Chemosphere* **2018**, *192*, 186–208. DOI: <https://doi.org/10.1016/j.chemosphere.2017.10.139>
- [5] T. I. Røe Utvik, *Chemosphere* **1999**, *39* (15), 2593–2606. DOI: [https://doi.org/10.1016/S0045-6535\(99\)00171-X](https://doi.org/10.1016/S0045-6535(99)00171-X)
- [6] J. M. Neff, K. Lee, E. Deblois, in *Produced Water: Environmental Risks and Advances in Mitigation Technologies* (Eds: K. Lee, J. Neff), Springer, New York **2011**, 3–54.
- [7] E. T. Igunnu, G. Z. Chen, *Int. J. Low-Carbon Technol.* **2014**, *9* (3), 157–177. DOI: <https://doi.org/10.1093/ijlct/cts049>
- [8] R. T. Duraisamy, A. H. Beni, A. Henni, in *Water Treatment* (Eds: W. Elshorbagy, R. K. Chowdhury), InTech, Rijeka **2013**, Ch. 9.
- [9] T. Bilstad, E. Espedal, *Water Sci. Technol.* **1996**, *34* (9), 239–246. DOI: [https://doi.org/10.1016/S0273-1223\(96\)00810-4](https://doi.org/10.1016/S0273-1223(96)00810-4)
- [10] L. Yu, M. Han, F. He, *Arabian J. Chem.* **2017**, *10*, S1913–S1922. DOI: <https://doi.org/10.1016/j.arabjc.2013.07.020>
- [11] Y. Ji, in *Advances in Membrane Technologies in Water Treatment* (Eds: A. Basile, A. Cassano, N. Rastogi), Woodhead Publishing, Amsterdam **2015**.
- [12] M. Quilitzsch, R. Osmond, M. Krug, M. Heijnen, M. Ulbricht, *J. Membr. Sci.* **2016**, *518*, 328–337. DOI: <https://doi.org/10.1016/j.memsci.2016.07.007>
- [13] N. L. Le, M. Ulbricht, S. P. Nunes, *Ind. Eng. Chem. Res.* **2017**, *56* (23), 6785–6795. DOI: <https://doi.org/10.1021/acs.iecr.7b01241>
- [14] A. Kouchaki Shalmani, I. M. A. ElSherbiny, S. Panglisch, *Sep. Purif. Technol.* **2020**, *251*, 117345. DOI: <https://doi.org/10.1016/j.seppur.2020.117345>
- [15] W. Kleppmann, *Versuchsplanung: Produkte und Prozesse optimieren* (Ed: K. Matyas), Hanser, München **2016**, 209–233.
- [16] R. S. Nickerson, *Psychol. Methods* **2000**, *5* (2), 241–301. DOI: <https://doi.org/10.1037/1082-989X.5.2.241>
- [17] E. Dutkiewicz, A. Jakubowska, *Colloid Polym. Sci.* **2002**, *280* (11), 1009–1014. DOI: <https://doi.org/10.1007/s00396-002-0723-y>
- [18] E. N. Tummmons, J. W. Chew, A. G. Fane, V. V. Tarabara, *J. Membr. Sci.* **2017**, *537*, 384–395. DOI: <https://doi.org/10.1016/j.memsci.2017.05.012>

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