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Development of a hybrid water treatment process using forward osmosis with thermal regeneration of a surfactant draw solution

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ABSTRACT

A hybrid process of forward osmosis (FO) in combination with thermal regeneration of the draw solution is proposed and investigated experimentally. On the side of the draw solution, a surfactant water emulsion is contacting the FO membrane. The solubility of non-ionic surfactants in water is exceptional in that it decreases at elevated temperatures. Depleted surfactant/water draw solution can thus easily be separated into an aqueous phase (product water) and a surfactant-rich phase (regenerated draw solution) by increasing temperature in order to induce liquid phase separation. The optimal choice of a surfactant as active draw agent will need to account for the surfactants performance in the thermal separation as well as in FO. In this work, 12 different surfactants were evaluated and discussed for their usability as draw solution. The surfactant L31 showed the best performance considering both criteria: high affinity toward water in FO and the lowest temperatures in thermal regeneration at 50°C. At such low temperatures, waste heat and solar heat can be sufficient to cover the energy demand, offering new opportunities in energy efficient and sustainable process design. In some cases, further purification of the product water is necessary. The requirements for this fine cleaning step are determined by the respective application in which the purified water is to be used. Highest requirements need to be met in the production of drinking water. For this, the product water from thermal separation is easily further purified to yield high-quality water which is desalinated (FO) and purified from surfactants (thermal separation and fine cleaning). In our study, three fine cleaning methods (foam fractionation, ultrafiltration, and nanofiltration) were screened and discussed for their product water quality. The most suited fine cleaning method to produce drinking water quality was nanofiltration with surfactant retentions of more than 99%. The proposed process combines the advantages of applicability of energy from sustainable sources, application of standard chemicals, and high product water quality.

Keywords: Forward osmosis; Surfactant; Tenside; Nanofiltration; Water treatment

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1. Introduction

Although the majority of our planet is covered by ocean, only 0.8% of the water on earth is directly accessible as drinking water [1]. This makes water a valuable good that is one of the basic needs of human existence. One of the major challenges in our century is the supply of water in water scarce regions. A total of 884 million people worldwide do not have access to clean water [2], and the numbers are expected to increase in the future. The international energy agency predicts an 85% increase in water consumption by 2035 [3]. Membrane technology, and here foremost reverse osmosis, already plays an important role in combating water scarcity. However, with an energy consumption of 2–4 kWh per m^3 of purified water, reverse osmosis is still a relatively energy intensive process [4]. Forward osmosis (FO) is a very promising membrane technology without the need of high gauge pressures and thus reduced energy consumption compared to reverse osmosis. In FO, a thin membrane is contacted on one side, the feed side, with a water source of low osmotic pressure (relative to the draw solution) that requires further treatment in order to be used as purified water; this can be, e.g. sea water or waste water. On the other side of the membrane, the draw solution side, a solution of high osmotic pressure is creating a large chemical potential gradient that yields a water flux through the membrane. One of the obstacles that need to be overcome before FO can be a competitive technology is the development of a suitable draw solution [5].

This paper explores the use of surfactant mixtures as a novel draw solution and thermal regeneration of such a draw solution. Surfactants are known to induce high osmotic pressure which is the fundamental criterion for a draw solution in FO [6]. The surfactants that are subject of this study are listed in Section 2.2.

The use of surfactants as a draw agent in FO has been described before, as will be shown in Section 1.1. However, no attention was paid to the phenomenon of phase splitting of surfactant/water mixtures which offers a potential approach for the regeneration of depleted surfactant draw solution which can already be induced at moderately high temperatures.

1.1. Literature review

In the field of FO, besides the development of efficient and robust membranes, the determination of suitable draw solutions is one of the most researched topics. Table 1 summarizes well-known examples of draw solutions, as a complete overview is beyond the scope of this article. For a more comprehensive review, refer to the study by Coday and Cath [7].

However, in continuous processes where the diluted draw solution itself is not the final product, a regeneration step is necessary. In the ammonia–carbon dioxide FO process [15], a mixture of ammonium bicarbonate, ammonium carbonate, and ammonium carbamate is used as draw solution. The salt mixture is well rejected by the FO membrane and creates high osmotic pressures to draw water from the feed solution. The diluted draw solution can be regenerated by heating which causes the salts to decompose into ammonia and carbon dioxide.

Surfactants offer the advantages of high osmotic pressure [6], being non-toxic, inexpensive standard chemicals and exhibiting low reverse flux [21]. These beneficial properties for forward osmosis have been shown in the literature as summarized in the following.

In 2014, two studies explored the applicability of surfactant/water emulsions for use as draw solution in FO. Roach et al. [6] used cetylpyridinium chloride, sodium dodecylsulfate, and Triton X100 for FO with flat sheet cellulose acetate membranes from HTI (Hydration Technologies Inc., OR, USA). The concept of forwards osmosis with a surfactant draw solution was shown to be a promising approach especially due to the low values of reverse flux. Elevated surfactant concentrations yielded high fluxes in FO but at the same time, regeneration in ultrafiltration became increasingly ineffective and fluxes through the ultrafiltration membrane decreased considerably. The authors, therefore, recommend application in environmental or pharmaceutical applications where recovery of the surfactant is not necessary.

In the study by Gadelha et al. [22], a similar approach was taken with five different surfactants and two membranes, the HTI cellulose triacetate FO flat sheet membrane and a hollow fiber membrane prepared in-house. Regeneration was accomplished by two different approaches, ultrafiltration and crystallization. Crystallization was achieved for sodium dodecyl sulfate below 18˚C and for meristyltrimethyl ammonium bromide below 10˚C. However, for both regeneration methods, the surfactant concentrations in the product water were relatively high, and the authors concluded that further process steps for a complete regeneration are necessary.

In 2015, a similar study using a mixture of Triton X100 and sodium phosphate also with the FO membrane by HTI was published by Nguyen et al. [21]. The authors focused on reverse salt flux which was extremely low compared to values of other draw

Table 1
Available literature on draw solutions for FO

Year	Draw solution	Regeneration method	Source
1964	Ammonium bicarbonate	Heating to ca. 60°C	[8]
1965	Volatile solutes	Heating or stripping	[9]
1965	Aqueous solution of gases (SO_2) or liquids (aliphatic alcohols)	Distillation	[10]
1970	Organic acid and inorganic salts	Temperature variation or chemical reaction	[11]
1972	Aluminum sulfate	Precipitation with calcium hydroxide	[12]
1989	Fructose	None	[13]
1997	Magnesium chloride	None	[14]
2005	Ammonium bicarbonate	Heating to ca. 60°C	[15]
2007	Magnetic nanoparticles	Solid separation	[16]
2008	Salt, ethanol	Pervaporation	[17]
2011	Fertilizer	None	[18,19]
2012	Sucrose	None	[20]

solutions found in the literature. Regeneration was performed by a two-stage ultrafiltration–nanofiltration system and reached combined surfactant rejections of 98%. To further enhance the product water quality, the authors recommend the use of higher pressure or membrane distillation.

The here presented research goes one step further in order to make alternative energy sources accessible. As will be described in the next section, the approach taken here is to induce thermal phase separation of the draw solution. The above-mentioned complications of ultrafiltration can be overcome, while at the same time using energy from low temperature sources such as waste heat and solar heat is possible.

1.2. Description of the proposed hybrid process concept

Instead of ultrafiltration, the phenomenon of phase separation can be utilized to regenerate the draw solution. The extraction of a solvent from a given feed stream is achieved by a two-stage process comprised of FO together with thermally induced phase separation. Hence, the extracted solvent, in our case water, is demineralized by FO and purified from the osmotic agent of the draw solution by thermal separation. A brief schematic of the process is shown in Fig. 1.

A more detailed description of the proposed hybrid process can be found in Fig. 2. An aqueous feed stream enters the process and is concentrated in the FO stage resulting in a concentrate stream and a diluted draw solution stream. The dilution of the draw solution will decrease the driving force of the extraction, i.e. the osmotic pressure difference, and the draw solution will require regeneration. In light of the global energy crisis, low-temperature energy sources such as waste or solar heat increasingly attract attention. Thermal regeneration will then separate the depleted draw solution into a regenerated draw solution (which can be replenished by a make-up stream) and product water. Eventually, this product water can be used in applications where demineralized water is required. In case of the production of drinking water also, the concentration of the surfactant in the product water needs to fulfill regulatory limits. In such a case, fine cleaning might be necessary.

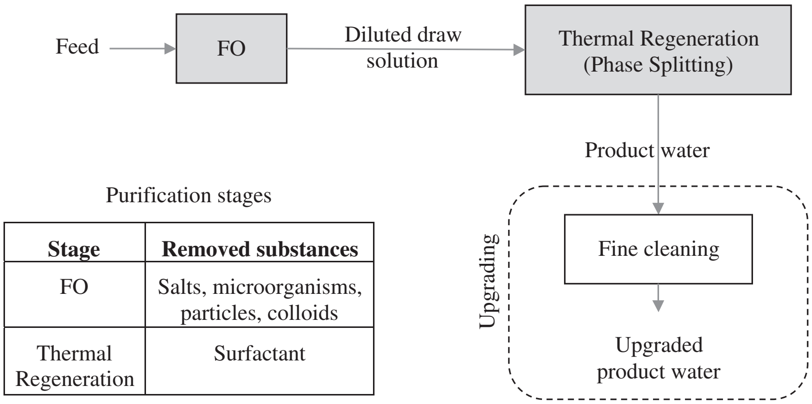
Separate laboratory experiments on the individual process stages, FO and thermal regeneration and also for 3 different fine cleaning methods, were performed and will be presented and discussed in later sections.

1.3. Objectives

As presented in Section 1.1, surfactants make excellent draw agents based on the following criteria:

1. High osmotic pressure in order to induce strong water flux through the membrane.
2. Inexpensive, non-toxic, non-hazardous (depending on the choice of the surfactant).
3. Small reverse flux in order to avoid surfactant loss.

The criterion of economic regeneration of the depleted surfactant draw solution is still of important interest and crucial for industrial applications. The objective of this study was to evaluate and discuss suitable surfactants for their use in FO and thermal regeneration in order to use low-temperature sources such as waste or solar heat. As presented in Section 2.2, a choice of 12 surfactants was preselected by a literature survey and further refined by the following criteria:



Purification stages

Stage	Removed substances
FO	Salts, microorganisms, particles, colloids
Thermal Regeneration	Surfactant

Fig. 1. Simplified schematic of the proposed process. The fine cleaning step is an upgrade when high product water qualities are required.

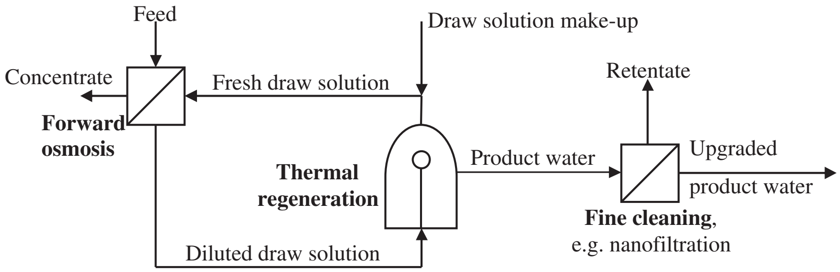


Fig. 2. Flow sheet of the novel FO process [23].

(1) Water flux through the FO membrane as a measure for process efficiency.
(2) Reverse flux of the surfactant into the feed solution which would result in increased costs due to loss of surfactant and pollution of the feed water source.
(3) Further criteria specific to each surfactant, as described in Table 2.

These screening experiments will then be followed by experiments which aim at the evaluation of the process stability. In batch tests, the dependency of water flux on time and feed/draw concentration is determined as well as the time dependency of surfactant reverse flux and the NaCl flux from the feed into the draw solution.

In the next step, the study aims at water quality at the drinking water level. Consequently, fine cleaning will be necessary in order to ensure high water quality. The options which will be considered for the fine cleaning step are NF, UF, and foam fractionation. The formation of micelles could enhance fine cleaning by UF, and for this the critical micelle concentration (CMC) will be investigated for the surfactant which is chosen in the experiments on FO and thermal regeneration.

2. Experimental

2.1. Laboratory facilities

The FO cell for all experiments is sketched in Fig. 3. The cell has 5 cm^2 of open membrane area and a maximum draw volume of 70 ml with an initial feed volume of 460 ml. Homogeneous distribution of the feed and draw solution is ensured with a magnetic stirrer for the feed side, and motor stirrer on the draw side, respectively.

Each FO experiment followed the same routine: the same amount of substance for each surfactant, i.e. 9.1 mmol, was filled inside the batch cell while outside, into the glass beaker, 460 ml of the feed solution (deionized water or NaCl solution) was filled. The amount of draw solution was determined by a series of tests and is a compromise between experimental accuracy and the limited equipment size. The progress was monitored by sampling from the diluted draw

Table 2
Performance of the draw solutions considered in this study

	Water flux	Thermal separation	Decision
Pluronic® L31	Medium	Good	Chosen, TC in aqueous phase 4.1 g/l @ 80°C
Brij30®	Low	Good	Not chosen, TC in aqueous phase 4.3 g/l @ 80°C
Pluronic® L35	High	Poor	Not chosen, separation not possible below 80°C, TC in aqueous phase 4.0 g/l @ 97°C
Butoxyethanol (BE)	High	/rb	Not chosen, leaks through the FO membrane into the feed, is toxic
PNIPAM—poly(N) isopropylacrylamide	/rb	Not possible	Not chosen, hydrogel formed, water could not be separated from draw solution
PAM—poly(acrylamide)	/rb	Not possible	Not chosen, hydrogel formed, water could not be separated from draw solution
PSA—poly(sodium acrylate)	/rb	Not possible	Not chosen, hydrogel formed, water could not be separated from draw solution
Brij10®	/rb	/rb	Not chosen, draw solution unstable, gel layer on membrane formed
Brij 23®	/rb	/rb	Not chosen, draw solution unstable, gel layer on membrane formed
Brij52®	/rb	/rb	Not chosen, draw solution unstable, gel layer on membrane formed
Pluronic® F127 (powder)	/rb	/rb	Not chosen, because the powder did not disperse and a draw solution could not be generated
Pluronic® F68 (powder)	/rb	/rb	Not chosen, because the powder did not disperse and a draw solution could not be generated

Notes: TC = total carbon content/rb stands for “rejected before criterion was evaluated.”

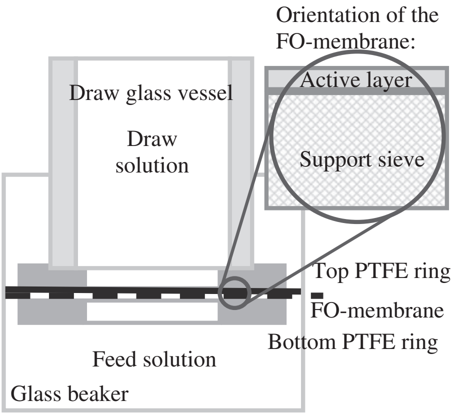


Fig. 3. Schematic representation of the FO test rack (stirrers not shown). The membrane orientation shown here was used in all experiments unless explicitly mentioned.

solution (water flux, NaCl flux) and from the feed solution (reverse flux).

Thermal phase separation was performed with 18 ml samples of each surfactant/water mixture in test tubes which were heated in a laboratory heating oven. Temperature was varied between 50 and 98°C (±1°C) in order to avoid to reach the boiling condition of the solution.

After the thermal phase separation, samples were taken of the aqueous and the organic phase and the quality of the separation was assessed. To upgrade the water purity in order to reach drinking water quality, three different fine cleaning methods were used: nanofiltration (NF), ultrafiltration (UF), and foam fractionation.

The cross-flow filtration unit that was used for UF and NF experiments is described in the study by Hoyer et al. [24]. A piping and instrumentation diagram of the test unit is shown in Fig. 4. Since the filtration temperature influences the feed viscosity and consequently the permeate flux the temperature was adjusted with a thermostat that connects to a heating jacket around the feed tank. The experiments were conducted in recirculation mode in which the permeate is returned to the feed tank and the concentration of surfactant is kept at a stable level before probing.

The third alternative for fine cleaning, foam fractionation, was performed inside a glass funnel (6.6 cm in diameter and 7 cm height) with an integrated ceramic frit (0.5 cm high with a pore size of 0.6 mm). Air at a pressure below 1 bar is introduced at the lower

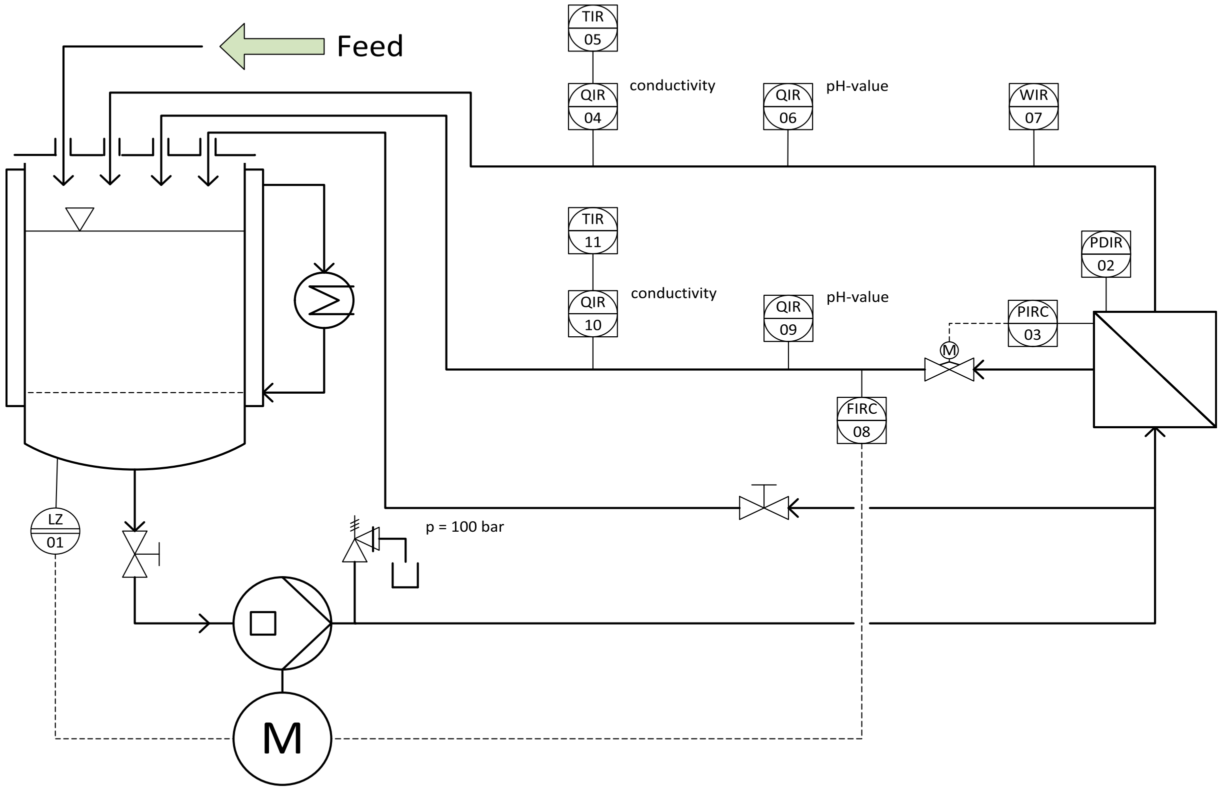


Fig. 4. Piping and instrumentation diagram of the cross-flow membrane laboratory test unit.

end of the funnel through the frit and that way dispersed creating bubbles. Foam forms at the upper end of the glass funnel and can be separated mechanically. The total carbon (TC) content of the solution before and after foam fractionation is measured with a TC analyzer in order to evaluate the separation performance.

2.2. Selection of suitable draw solutions

A plethora of surfactants for various applications exist. In this study, 12 surfactants were selected and investigated more closely which were chosen based on their HLB (hydrophilic–lipophilic balance) value and their molecular weight. The HLB value developed by Griffin [25] can be used to give an estimate of the osmotic pressure that a surfactant develops in solution. This value can be calculated for a specific surfactant of molar mass M_{total}, a molar mass of hydrophilic groups M_{h}, and a molar mass of its lipophilic groups M_{l} as follows:

$$M_{\text{total}} = M_{\text{h}} + M_{\text{l}} \quad (1)$$

$$\text{HLB} = 20\left(1 - \frac{M_{\text{l}}}{M_{\text{total}}}\right) \quad (2)$$

Literature data on the ratio of hydrophilic groups will be used here as criteria for the draw solution selection. At HLB values 0–9, the surfactant is soluble in oil, and at a HLB value of 10, it is soluble in water and oil, and for HLB between 11 and 20, the surfactant dissolves in water. This means at high HLB values, the surfactant shows higher affinity toward water, i.e. it develops a higher osmotic pressure and is potentially a draw solution with a higher driving force.

Furthermore, the HLB value and the molecular weight also influence the tendency for concentration polarization. Concentration polarization is an effect in which a component accumulates at the membrane surface thereby reducing the mass transfer driving force, i.e. the osmotic pressure difference. Draw solutes with a low molecular weight and low viscosity offer the advantage of reducing concentration polarization as their diffusion coefficient in water is high.

However, the HLB value also indicates the phase separation temperature, where surfactants with a higher HLB value also have a higher phase inversion temperature [26].

Consequently, the choice of surfactants that will initially be included in this study is a compromise between high osmotic pressure and low phase separation temperature. The investigated draw solutions are listed in Table 2. All draw solutions were employed at an initial amount of substances of 9.1 mmol.

The surfactant that performed best in FO and thermal separation is Pluronic® L31. Phase separation for L31 could already be achieved at a temperature as low as 50˚C.

2.3. Analytical methods

Appropriate methods for the determination of NaCl and TOC concentrations were employed to evaluate the efficacy of the performed experiments. During the experiments, the draw solution concentration was determined using a refractometer. Additionally, at the end of each experiment, the draw solution concentration was determined using Karl Fischer titration with hydranal (Toledo volumetric KF titrator by METTLER, accuracy 0.1%) as well as by TC analysis (multi N/C® 2100S TOC analyzer, Analytik Jena Analytical Instrumentation).

The thermal separation was performed in glass tubes that were heated in a laboratory heating oven (ULM 500 by Memmert). Samples from the aqueous and tensidic phases were taken with a thin cannula. Salt concentrations in the feed solution were measured using a conductivity meter with a precision of ±0.5% of the measured conductivity (TetraCON 315 by WTW).

2.4. Membranes

The FO membrane employed in the experiments is the 081118-ES-2 supplied by Hydration Technologies, Albany OR. This cellulose triacetate membrane with a PE support sieve will reach a volumetric flux of 13–17 $l/m^2/h$ (@ 45-% glucose, 20˚C) and has 93–95% rejection of NaCl [27]. This commercial membrane offers the advantage of high flux and has thus been used in numerous studies on FO.

For the fine cleaning of the produced water, three different membranes were tested: one hydrophilic NF membrane (DK by GE osmonics; MWCO 150–300 Da; Flux 72 $l/m^2/h$ @ 5 bar), a hydrophilic UF membrane (ETNA01PP by Alfa Laval; MWCO 1,000 Da; Flux 59 $l/m^2/h$ @ 2 bar), and one hydrophobic UF membrane (P005F by Microdyn Nadir; MWCO 1,850 Da; Flux 53 $l/m^2/h$ @ 7 bar). Employing membranes of different hydrophobicities was done with the intention to operate fine cleaning in different modes: the hydrophilic membrane will produce aqueous permeate while the hydrophobic membrane was tested to produce a surfactant-rich permeate. The membranes were specifically chosen to exhibit different MWCO and to be typical commercial membranes for drinking water applications.

The orientation toward the feed side for two membranes is different. The FO membrane contacts the feed solution with the support sieve (rough side) while the NF contacts the feed with its active separation layer (smooth side). Microscopic images showing the differences in the morphology of the support layer for NF and FO are shown in Fig. 5. The effect of the FO membrane's orientation will be described in Section 3.1.

2.5. Experimental procedure

An overview of all experiments is given in Table 3. Feed solutions in the FO experiments were deionized water which is used as a baseline value, and NaCl solutions at two concentrations resembling brackish water (1-wt.% NaCl), and saline water (2.5-wt.% NaCl). In light of global water scarcity especially those regions with access to sea water offer potential applications for the here described water purification process. The experiments were thus designed to suit the conditions in such an application.

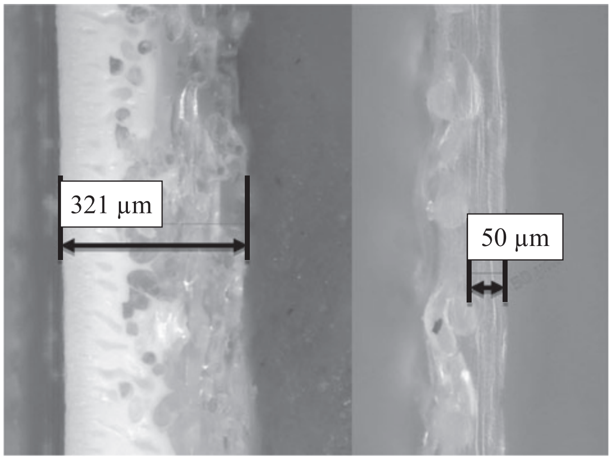


Fig. 5. Microscopy of the NF membrane (left) and the FO membrane (right). Feed side of the membranes is on the left side. The length scales give an idea of the difference in thickness which allows much higher diffusive fluxes through the FO membrane and the mechanical stability of the NF membrane. The two membranes are oriented with their rough side toward each other.

Table 3
Experimental protocol

	FO experiments	Thermal separation	Fine cleaning
Applied surfactant	L31, L35, Brij30	12 surfactants (from Table 1)	L31
Temperature	20˚C	50–100˚C	20–60˚C
Experiments	(1) draw concentration (2) reverse flux (3) salt flux (4) membrane orientation (5) long termed experiment	(1) Pure surfactant (2) Surfactant and oil mixture	(1) Ultrafiltration (2) Nanofiltration (3) Foam fractionation

An overview of the experiments is shown in Table 3 and in the following. All 12 surfactants were first screened for their use in thermal separation, and the 3 that performed best in the thermal separation were used in FO where L31 showed the best performance and was, therefore, also tested in 3 separate fine cleaning experiments.

The experiments were performed in the following order:

Six of the 12 surfactants listed in Table 2 were considered in the thermal separation experiments. For each of those 6 surfactants, 18 ml of a 1:1 mixture with water was kept for 2 h at a certain temperature. When phase separation was achieved, samples of the upper (aqueous) and lower (surfactant-rich) phase were taken and analyzed by TC analysis and Karl Fischer titration, respectively. Three of the 6 surfactants were then tested in FO experiments in batch mode. About 9.1 mmol of the undiluted surfactant was added inside the FO batch cell and the water flux was monitored over time. One of the 3 surfactants, namely L31, was considered for the 3 separate fine cleaning tests.

3. Results and discussion

The experimental results are presented and discussed in the order of the three process steps: FO, thermal separation, and fine cleaning. The surfactant screening started at the thermal separation which means that surfactants were first investigated for their thermal regeneration properties, and only the three best performing surfactants were investigated in FO.

3.1. FO experiments

As shown in Table 2, most of the 12 draw solutions from preliminary experiments could be excluded regarding their water flux in FO. Three solvents were tested in separate FO experiments following the procedure described in Section 2.1. Each surfactant draw solution was tested with the three different feed solutions resembling pure water (0% NaCl), brackish water (1%), and saline water (2.5%). The three surfactants shown in Fig. 6 proved to be suitable draw solutions and are compared by their performance in FO. The highest water flux was achieved with L35. The influence of different feed concentrations as shown in Fig. 6 is stronger for the surfactants that induce higher flux. Remarkably, the flux induced by Brij30 was relatively stable for different concentrations. This could be attributed to kinetic effects or

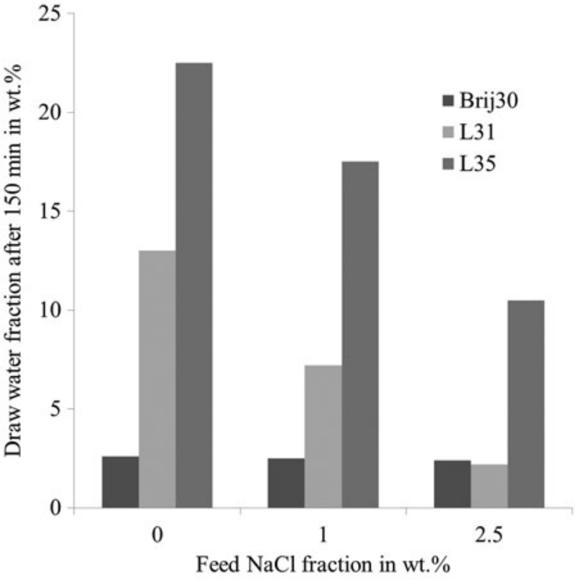


Fig. 6. Water content of the three draw solutions for three different feed concentrations. After 150 min, at 20˚C.

differences in the mechanisms in which the water is absorbed by the different draw solutions.

For the two surfactants with the highest fluxes, the influence of membrane orientation was determined. The FO membrane performs better with the rough side (Ref. to Fig. 5) toward the feed solution which means that concentration polarization effects are stronger for the surfactant than for the feed salt solution which agrees with the expectations considering the increased viscosity. Roach et al. [6] performed a similar experiment and also found that diffusion of surfactant through the membrane support layer leads to a lower osmotic pressure difference across the membrane. This can also be observed in Fig. 7 for two different draw solutions.

Increasing the draw solution concentration increases the osmotic pressure difference and that way also the flux rate. This behavior is shown in Fig. 8 for different surfactant concentrations at different feed concentrations. The dependence on concentration is also important since the regeneration of the draw solution will not be complete and a small fraction of water will remain in the draw in practical applications. As data in Fig. 8 suggest higher surfactant concentrations will improve water flux and the influence has significant effects at high concentrations. The feed solution osmotic pressure, in the experiments adjusted using NaCl solution, is a parameter that reduces water flux which can be overcome at high draw solution purities. Consequently, highest draw solution purities after the regeneration step are desirable.

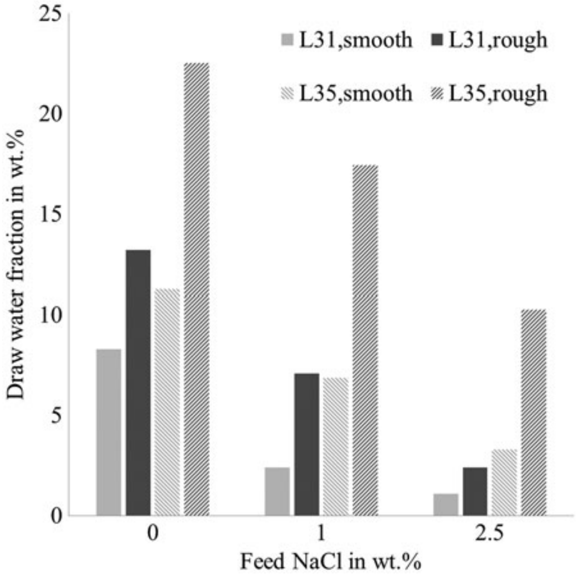


Fig. 7. Influence of the FO membrane orientation (which side, smooth side or rough side, contacts the feed solution). After 150 min, at 20˚C.

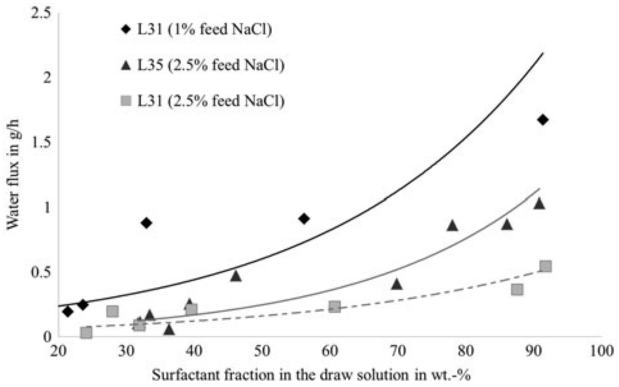


Fig. 8. Water flux as a function of feed NaCl concentration and draw surfactant concentration. After 150 min, at 20˚C.

The dilution of the draw solution is an important consideration for module design and operation of FO applications. To determine the rate of flux decline, a long-term experiment was performed, as shown in Fig. 9. Here, the flux was monitored over the period of two weeks. In particular, at low feed concentrations, a nearly linear behavior is observed during the first day which corresponds to constant water flux. If the flux is constant despite progressing dilution, regeneration is not necessary yet. This means that the investigated draw solutions can be used for more than 24 h before they need to be regenerated.

Another criterion for the draw solution selection is the reverse flux of surfactant through the membrane. High values for the reverse flux are undesirable as the loss of surfactant increases operation costs of the process and will also result in pollution of the feed water source. The loss of draw solution to the feed due to reverse flux was in the range of 1–5 mg/h after 150 min, as shown in Fig. 10. Here, the surfactant

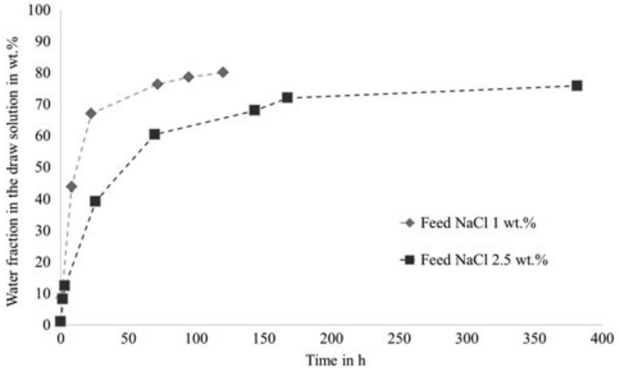


Fig. 9. Water content of the draw solution during a long-term experiment for L31, at 20˚C. The experiments started with a draw solution consisting pure surfactant.

Brij30 performed best which could be due to structural reasons. Surfactants with larger molecules will be better retained by the membrane and reverse flux will thus be lower. On the other hand, as described in Section 2.2, surfactants of small molecular weight will exhibit lower concentration polarization and have higher fluxes. Brij30 exhibited lower dependence on feed concentration and could thus be kinetically inhibited.

Fig. 11 shows the development of water flux and surfactant reverse flux over time for the surfactant L35. Highest surfactant concentrations in the draw solutions are at time 0 while further on the draw solution becomes increasingly diluted. As has been shown above, operating at high draw solution concentrations will yield higher water fluxes through the membrane, as can also be seen in Fig. 11. Although Fig. 11 shows that this high flux also translates to higher loss of draw solution agent via reverse flux (reverse flux decreased to one-third of its initial value after 200 h), it is important to consider that the water flux after 200 h is close to zero. In other words, regeneration of the draw solution after a long time will result in higher surfactant loss per amount of product water; here, a trade-off needs to be identified in case of industrial application. Accordingly, operation of the FO process step should be performed at high draw solution concentrations, i.e. timely draw solution regeneration, considering that reverse flux is not decreasing by orders of magnitude for low draw solution concentrations.

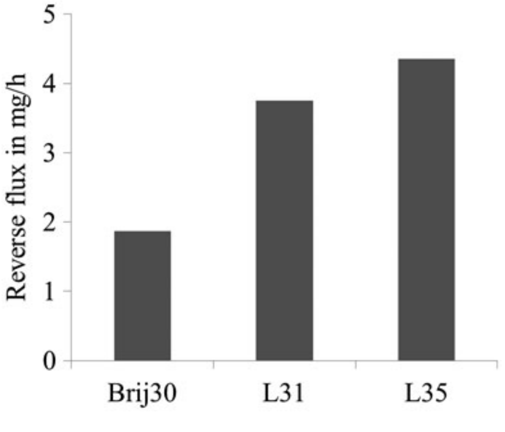


Fig. 10. Reverse flux through the FO membrane of different draw solutions. After 150 min, at 20˚C.

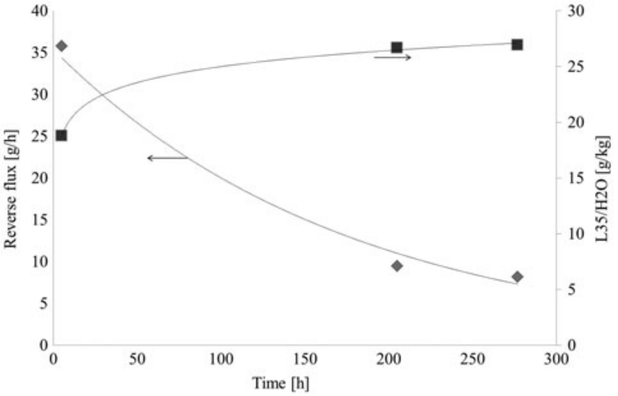


Fig. 11. Reverse flux and accumulative loss of surfactant to feed solution over time. At 20˚C, 2.5 wt.% of L35, and 2.5 wt.% of NaCl.

Besides draw solution reverse flux, salt flux is an undesirable transport process through the membrane. Salt concentration of the feed and draw solution was determined using a conductivity probe and a calibration of conductivity to NaCl concentration prior to the experiment. During these experiments, the NaCl concentration of the feed and the draw solution were measured with a conductivity probe. A change in conductivity was only observed for the draw solution and has been used to calculate the NaCl flux. The development of the accumulated salt flux (determined from the increasing conductivity) is shown in Fig. 12. Salt retention R, calculated according to Eq. (3) from the NaCl concentration in the feed c_{feed} and draw solution c_{draw}, was at 97.5% and thus higher than in the literature [27]:

$$R = 1 - c_{\text{draw}}/c_{\text{feed}} \tag{3}$$

The cumulative flux of NaCl is highest during the first day of operation: half of the NaCl that passed the membrane after 100 h has already passed during the

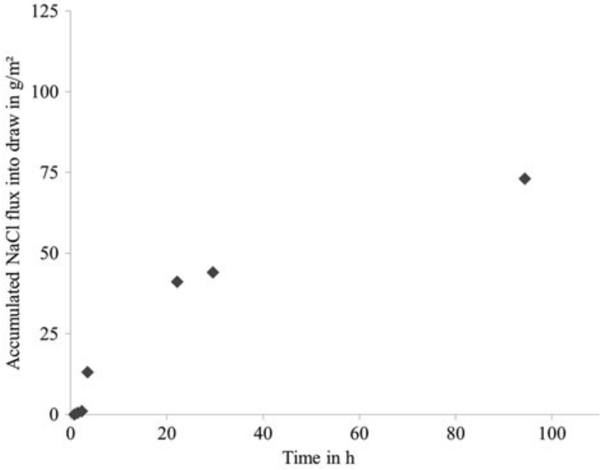


Fig. 12. Accumulated salt flux through the membrane over time. At 20˚C and 2.5 wt.% of NaCl.

first 24 h. In conclusion, the NaCl flux showed that the membrane has a relatively high retention for pollutants and that most of the salt transport happens within the first few hours of operation.

Due to the batch operation of the membrane experiments, the fluxes of water, surfactant, and salt which were reached could also be influenced by changes in the membrane properties, such as fouling, and ongoing swelling that did not reach saturation. Experiments with improved module design in steady-state cross-flow mode could be used to study the influence of membrane activation such as swelling.

According to the presented results, surfactant mixtures are an advantageous draw solution. They exhibit a low sensitivity toward feed salt concentrations, and water fluxes are relatively stable over time. For further consideration in the subsequent step, it is important to note the influence of surfactant concentration on water flux: at higher surfactant concentrations, the influence of the surfactant concentration becomes more pronounced, i.e. at high draw solution surfactant concentrations even small increases of surfactant concentration will yield a strong increase in water flux.

Also the influence of membrane side orientation, which will be important for module design, could be established: effects of concentration polarization can be reduced by letting the smooth side of the membrane face the draw solution.

3.2. Thermal regeneration

Thermal regeneration offers a stable and fast regeneration method with a potential for waste heat usage. The thermal regeneration of the selected surfactant, L31, requires temperatures above 50˚C. At these temperatures, L31 decomposes into two phases, a water-rich and a surfactant-rich phase. The composition of the aqueous upper phase is shown in Fig. 13, and the composition of the tensidic bottom phase is shown in Fig. 14.

As can be seen in the diagrams, the separation first improves at higher temperatures. Further temperature increase results in a decreasing quality of water purification and draw solution regeneration. This means that the temperature of the thermal regeneration should be chosen in the temperature range between 50 and 80˚C. A final decision about the optimal separation temperature needs to be based on the required product water quality, available energy sources, and the draw solution purity required by the FO stage. It needs to be highlighted that separation was already achieved at 50˚C which is well within the temperature range at which waste and solar heat is available in many applications.

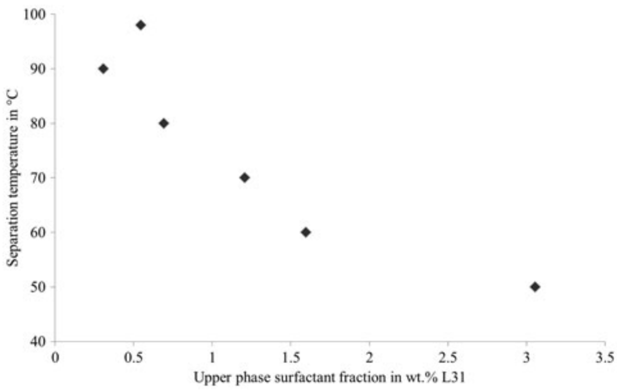


Fig. 13. Composition of the upper phase (extracted aqueous phase). Binary system L31-water.

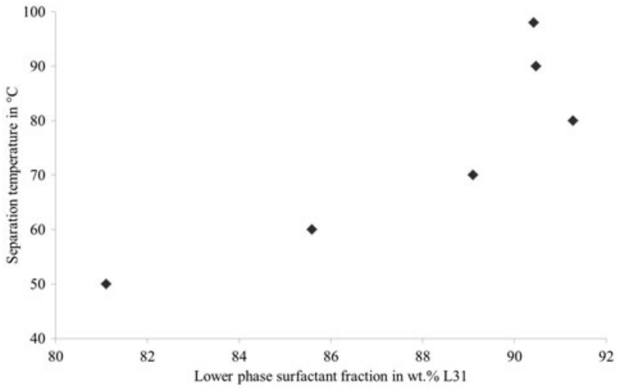


Fig. 14. Composition of the lower phase (regenerated draw solution). Binary system L31-water.

Fig. 13 shows that the product water quality is strongly influenced by the separation temperature. The product water quality can thus be adjusted in the range between 0.31 (90˚C) and 3.05 (50˚C) wt.%, which corresponds to a TC content of 1.64 and 16.1 g/l. According to the German drinking water regulation, this value exceeds the maximum allowable concentration of 1.5 mg/l [28] by orders of magnitude. Even the maximum concentration for seepage water (0.2 g/l according to §7a Wasserhaushaltsgesetz) is exceeded. Consequently, in case, drinking water standards shall be met additional purification steps will be necessary. Upgrading of the product water by means of three different methods will be described in Section 3.3.

Fig. 14 shows the purity of the regenerated draw solution which is in the range between 81 and 92 wt.% of surfactant per draw solution. Comparison with the flux, as presented in Fig. 9, shows that the regenerated draw solution will induce high values of flux, as those within the first few hours of operation of the FO experiments. This means that thermal regeneration is effective and can be used in a hybrid process with FO. It should be mentioned that, as indicated in Fig. 2, a make-up stream for the draw solution is necessary to ensure draw solution quality but also to compensate for the surfactant loss due to reverse flux.

According to research by Katzer [29], oil as an additive will result in improved thermal separation and higher product water quality. The expectation according to this literature source is that addition of oil as an additive will decrease the TC concentration in the aqueous phase, i.e. will improve the water quality. This hypothesis was explored by the following experimentation.

Thermal separation according to the procedure described in Section 2 was performed for the system L31-water and two additives: soy oil and methyl ester of rapeseed. Fig. 15 shows the product water quality as a function of oil addition in wt.%. A trend that was in agreement with the findings described by Katzer [29] was observed. The addition of oil improved the product water quality already at very low weight fractions.

Due to the increased demand for thermal energy (to heat the added oil) and an efficacy of the oil additive which is below the requirements for drinking water, this approach cannot be used as a stand-alone fine cleaning step, but is suitable for process water production. For drinking water, further fine cleaning methods will be presented in the following section.

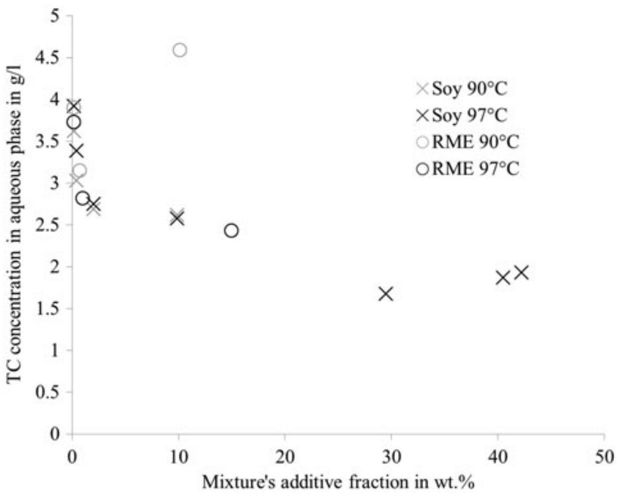


Fig. 15. Effect of soy oil and methyl ester of rapeseed as additives to improve thermal separation. TOC content of the aqueous phase for two different temperatures. Ratio of water to L31 = 1.5.

3.3. Fine cleaning of the aqueous phase

Three alternative approaches for the fine cleaning of the aqueous phase from the thermal regeneration were briefly investigated: NF, UF, and foam fractionation.

Ultrafiltration is performed below the expectations that are based on the membrane's MWCO. In UF, the MWCO is the molecular weight of a theoretical substance that is retained by 90%. This means for the selected surfactant L31 with a molecular weight of 1,100 g/mol, relatively high retentions should be reached by the two UF membranes with MWCO of 1,000 Da (ETNA01PP) and 1,850 Da (P005). The retentions that were actually reached were much lower, 25 and 29% were reached for the UF membranes P005 and ETNA, respectively (at 20°C and 2 bar). These retentions are too low to reach the product water quality that is required for drinking water.

To improve UF of the surfactant, another approach was then pursued. Above a certain concentration of surfactant, micelles form which is expected to strongly improve retention of the UF step. This concentration is called the CMC which can be determined using the du Nouy ring detachment method [30, p. 52]. In this method, the surface tension of the water surfactant solution is determined using a ring which is pulled out of the solution at different concentrations. The CMC is reached when further increases in concentration do not yield a further decrease in the surface tension. However, even at high surfactant concentrations, micelles did not form. Consequently, UF could not be further improved and was discarded as a fine cleaning method.

As an additional method, foam fractionation was analyzed with foam created by bubbling air through a glass frit as described in Section 2.1. Because the hydrophobic tails of the surfactant will adsorb at the interface between air bubbles and solution surfactant will accumulate in the foam and will thus be extracted from the feed solution. The separation was evaluated by enrichment β, which is the ratio of surfactant concentration in the foam to the concentration in the feed, and by the stripping α which is defined by the product water surfactant concentration c_{prod} and the feed surfactant concentration c_{feed} as:

$$\alpha = 1 - c_{\text{prod}}/c_{\text{feed}} \tag{4}$$

The experiments met the expectations in that foam fractionation is ineffective at high surfactant loads. High values for enrichment, $\beta > 10$, were only possible at low surfactant concentrations (<300 mg/l). Stripping remained at high values ($\alpha > 0.7$) over a wide

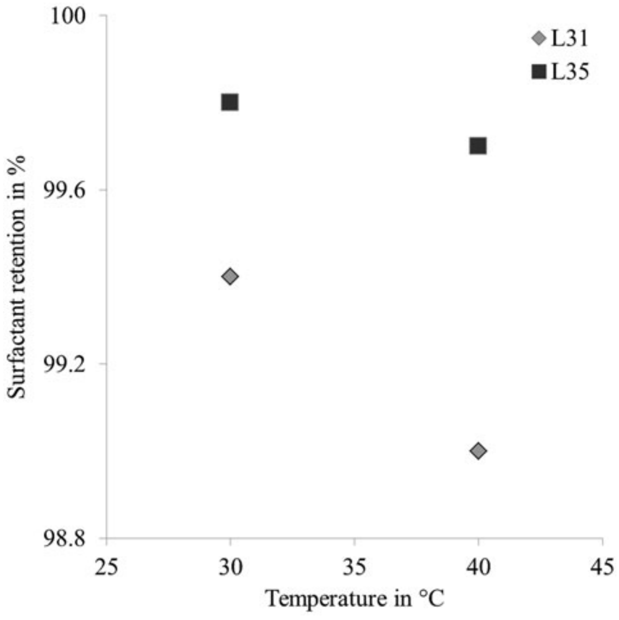


Fig. 16. Surfactant retention in nanofiltration fine cleaning. At a cross-flow velocity of 1 m/s and a pressure of 10 bar.

range of feed concentration (up to 1.2 g/l). In conclusion, fine cleaning using foam fractionation was not effective enough to meet the required product water quality of less than 200 mg/l, but can be used in an additional pretreatment stage.

The third analyzed method and also the purification technique with the highest product water purity was NF. About 10 l of the surfactant solution was generated based on the chemical analysis of the product water from the thermal regeneration. Temperatures and process conditions were adjusted using process control in order to keep all experimental parameters stable. Nanofiltration membranes have pores of about 1 nm in diameter and consequently a low MWCO of a few hundred Da. Hence, the high retentions of the large surfactant molecules were in agreement with the expectations. Retentions of the surfactant of more than 99% were reached, i.e. a product water quality of below 20 mg/l. Thus, the maximum allowable concentration of 1.5 mg/l, according to the German drinking water regulation [28], can be met. Higher temperatures, which could be supplied by the thermal regeneration step, increased flux further and thus have the potential to reduce water purification cost. In the scope of process design, a transfer of the here developed sustainable and effective basic process configuration into an economically feasible and viable industrial process will require optimization in light of a specific application in the water treatment sector (Fig. 16).

4. Conclusions

A novel hybrid FO process using surfactants as draw solution was proposed, and a basic and systematic analysis of performance considerations has been carried out. Among the 12 tested surfactants, L31 is the surfactant that performed best based on the criteria of having high permeate flux in FO and having a low regeneration temperature in the subsequent regeneration.

Water flux for the selected surfactant was monitored over two weeks and for different feed concentrations to analyze water flux over time. Although values of flux decreased considerably over this long period, the flux decline within the first 24 h was low. Consequently, it could be demonstrated that the surfactant-based draw solution can be used for a sufficiently long time before regeneration is necessary.

The water flux through the FO membrane remained stable over more than 24 h which indicates for a future application that the draw solution can remain in the FO module for a relatively long time before it needs to be recirculated to the thermal regeneration stage for regeneration. This is especially important since the two stages will be operated at two different temperatures which makes quick exchange of the draw solution difficult.

The retention of the commercially available and commonly used FO membrane (supplied by HTI technologies) for NaCl was at a high value of 97.5% and the reverse flux was relatively low with 20 g of surfactant per 1 kg of purified water. The experiments were performed with different feed solutions: pure water and NaCl solutions with concentrations between 1 and 2.5 wt.% to reflect the range from brackish water to saline water. Scale-up experiments with real feed solutions will be necessary to determine the degree to which salts build up in the system. The fine cleaning as described in Section 3.3 will be required to remove potentially harmful substances to ensure drinking water quality. Improved module design in steady-state cross-flow mode could be used to test whether FO membrane properties change over the course of the experiments.

The draw solution regeneration using thermally induced phase separation for the selected surfactant L31 was induced already at a temperature as low as 50˚C. This has the potential to offer huge energy savings in those cases in which waste heat or solar heat is available. Hence, ultrafiltration which is the only regeneration method for surfactant draw solutions investigated in the literature can be substituted by this sustainable regeneration approach, and the advantages of using surfactants as draw solution, namely high osmotic pressure und low reverse flux, can fully be used.

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Abbreviations

FO	—	forward osmosis
MWCO	—	molecular weight cut-off
TC	—	total carbon content
NF	—	nanofiltration
UF	—	ultrafiltration
CMC	—	critical micelle concentration

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