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Hollow fiber nanofiltration: From lab-scale research to full-scale applications

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ABSTRACT

This review provides a comprehensive overview on the quickly developing field of polymeric hollow fiber (HF) nanofiltration (NF), including membrane (module) and process design, operational parameters, and full-scale applications. Six different methods are currently used to produce HF NF membranes: phase inversion, interfacial polymerization, grafting, coating, polyelectrolyte multilayers (PEM) and chemistry in a spinneret. While all methods have their strengths and weaknesses, several PEM based membranes stand out because of their high chemical stability. This combination of geometry and chemical stability can make HF NF a sustainable alternative to spiral wound NF. This is especially the case for applications with a high fouling load where, in contrast to spiral wound NF, HF NF typically does not require an intensive pre-treatment. In academic settings, experiments are typically done in small modules with single-component feeds. Several studies showed that it is important, but not always straightforward, to correlate these lab scale results to full scale performance. Indeed, process design parameters such as crossflow velocity and staging partly determine energy consumption and retention and need to be taken into account. Partly based on these insights and developments, in the last five years commercial HF NF modules have rapidly become available. At least 59 pilot-scale and 26 full-scale HF NF plants are currently in operation or under construction, mostly focusing on water treatment. A comparison between these plants shows that HF NF can be applied for a broad range of applications with excellent scalability, highlighting the growth potential for HF NF in the coming years.

1. Introduction

Nanofiltration (NF) membranes are widely used in a variety of industries [1]; In drinking water applications, they are often employed for softening and removal of colour or metals. In the food industry they are used for concentration and demineralization. In chemical and petrochemical industries, nanofiltration membranes are often used for recovery of reactants and catalysts. The total NF market alone is expected to rise from \$500–660 M in 2019 to \$1200–1550 M in 2024 [1,2]. Polymeric NF membrane modules can be produced with different membrane geometries; spiral wound (SW), tubular, and hollow fiber (HF) (also referred to as capillary) are possible. Spiral wound modules have been on the market since at least 1984 [3], and are currently still dominant in the market. In 2019, spiral wound membranes had a market share of NF membrane sales of >90%. HF modules still have a much smaller market share, but are expected to have the highest annual growth rate [1]. These data clearly show the potential of the NF market in general, and the HF NF specifically.

NF membranes are commonly characterised as membranes with pore diameters between 1 and 10 nm, and a molecular weight cut-off (MWCO) between 200 and 1000 Da, although there is not a single universally accepted definition [4]. Alternately, a MWCO of 100–2000 Da and pore diameters <2 nm has been used as a definition [5]. Membranes with substantially higher MWCO's are sometimes also classified as NF membranes, but only when their ion retentions (e.g., 10–90% NaCl) are in the NF range [6,7].

Commercial polyamide based HF membranes with a 1.5 mm inner diameter were briefly available on the market around the year 2000 [8]. Though, at that time they were not competitive due to the higher module price [8], environmental concerns and legislation issues [9].

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Subsequently, the production of this type of modules was discontinued. Currently, several commercial polymeric HF NF products are available and applied in a variety of processes; ranging from dense NF membranes from e.g. NX filtration, to more open membranes introduced by Pentair X-Flow. Even though to date the commercial availability of HF modules is still significantly lower than that of SW modules, their availability is rapidly increasing. Still, within the academic community this availability of commercial HF modules remains relatively unknown and it is sometimes even incorrectly claimed that there are no mature HF NF membranes [10]. Despite the commercial success, academic publications on full-scale applications of HF NF are scarce. An overview of possible applications for HF NF was recently published [11], but an overview of current full-scale HF NF plants is due but has not been published yet.

This review aims to fill these gaps in the current scientific understanding by offering a field-broad overview of polymeric HF NF. We will focus on three questions: 1) Which processes are currently being used to produce HF NF membranes? 2) What is the key difference between the SW and HF module configurations? 3) What can we learn from lab-scale and full-scale case studies? By connecting these aspects, we aim to create an improved knowledge base for the upscaling and utilization of polymeric HF NF membranes.

2. Processes & materials for HF NF fabrication

Polymeric NF membranes can be produced in a variety of ways. Five general categories of production methods for HF NF membranes were previously defined by Urper et al. [12]. This includes phase inversion (PI), interfacial polymerization (IP), coating, grafting and polyelectrolyte multilayers (PEMs). Next to this, we propose adding chemistry in a spinneret as a sixth category. In this section, we aim to give an overview of the different fabrication methods which are available for HF NF membranes. It should be noted that many of these methods are also applicable to SW membranes, but the HF geometry comes with an extra set of challenges and tuning parameters. As this section gives an overview of the available production methods, not all recent advances will be included. For more details, the reader is referred to some excellent reviews which are available. For HF NF specifically, a detailed review comparing the IP and PI methods was previously written [12]. Next to that, reviews which focus on NF more generally are available for PI [13,14], IP [15,16] and PEMs [17–19].

2.1. Phase inversion

Phase inversion (phase separation) is one of the more established techniques to produce porous membranes. Besides being able to synthesize fully functioning HF NF membranes, PI membranes typically function as support membranes for thin film composite membranes made via other techniques. PI is a technique in which a membrane is created by precipitation of a polymer solution into two phases: a polymer-rich phase which forms the membrane matrix and a polymer-poor phase which forms the pores. There are four main ways in which this precipitation can take place: via immersion in non-solvent (NIPS or the Loeb-Soerirajan method), solvent evaporation (SIPS), adsorption of vapor from the atmosphere (VIPS) or cooling of a hot casting solution (TIPS) [20]. Combinations of these methods can be used [21–23], but in practice NIPS is the most common method. A more detailed description of PI methods can be found in the textbook by Baker [20].

When fabricating membranes with a HF geometry, a polymer solution (dope) is extruded through a hollow orifice spinneret, into a coagulation bath containing a non-solvent. Another non-solvent (bore solution) is fed through the inside of the fibers and causes coagulation of the inside. The choice for either a double (Fig. 1A) or a triple (Fig. 1B) spinneret allows to make single layer (SL) or dual layer (DL) membranes, respectively [24]. SL membranes consist of one type of polymer, whereas DL membranes consist of two different types of polymers layered on top of each other. The main advantage of DL PI is that less of a, usually more expensive, functional polymer is needed for only the separating layer. However, a disadvantage of this method is the low mechanical stability of the membrane that results from the limited adhesion between the two polymer layers [12,25]. This can be prevented by increasing the polymer concentration of the polymer solution for the selective layer [24].

The process of PI is commonly theoretically understood via the three-component phase diagram [26–28]. This model stresses the importance of the ratio between solvent, polymer, and non-solvent in the initial casting solution for the properties of the final membrane. Other tuning parameters include chemical properties such as the composition of the bore fluid [29,30] and dope solution [26] and physical spinning parameters such as dope flow rate, air gap length, take-up speed [29], temperature of the spinneret [27] and coagulation bath [25]. Traditionally, NIPS is based on (aprotic) organic solvents. More sustainable alternatives for these organic solvents are being developed that open new opportunities for dense hollow fiber development. For example, aqueous phase separation has been performed with tubular NF membranes [31] and HF microfiltration (MF) and ultrafiltration (UF) membranes [32], but these developments are yet to be translated to HF NF.

2.2. Interfacial polymerization

The IP reaction was developed in 1959 by Wittbecker and Morgan [33] and first applied onto reverse osmosis (RO) membranes by Cadotte in 1972 [34]. In this reaction, two polymer precursors, commonly a diamine and a diacid chloride, are dissolved in two immiscible phases (commonly water and an organic solvent, respectively). When these solvents are brought into contact, a polymerization reaction occurs at the interface of these phases (Fig. 1D). The layer can be post-treated further with a heat treatment. The IP reaction is performed on a support membrane, which is typically made via PI. The details of the IP process have been extensively described. It follows that there are two regimes in the IP process. At first the reaction rate is purely kinetically controlled by the reaction rate of the monomers, followed by a regime in which the reaction rate is diffusion controlled by the transport of monomers to the reaction zone [35]. Therefore, the reaction is self-limiting. Membrane properties can be tuned by changing the support membrane [36], heat treatment [36] and, lastly, the type [37], concentration [38], reactivity and number of reactive groups of the monomers [35].

IP shares the advantage of DL PI of being able to individually select a mechanically strong and highly permeable support layer and a selective top layer, albeit with commonly better adhesion between support and top layer [12]. The main gain of IP is that the separating layer can be much thinner than the separating layer in DL PI. Because of this, IP was a major breakthrough compared to PI. Notably, the majority of commercial flat sheet NF membranes are currently made via IP [4,39].

However, it is challenging to apply IP to a HF geometry. In a HF membrane, excess monomer cannot be removed from the surface of the membranes with a roller, as would be done during flat sheet manufacturing. Additionally, the liquid-liquid interface cannot be managed with gravity due to the curvature of the surface. This leads to a high number of defects such as pinholes and delamination [39,40], though the high number of defects could be overcome by the addition of an interlayer [40].

The NF50 M10 module initially developed by Stork B.V. and later introduced by NORIT X-Flow was based on 1.5 mm membranes with a separation layer produced via an IP process [41]. However, these IP HF membranes did not gain the same popularity as their SW counterparts due to their higher costs [8], challenging production process and the issues concerning high chemical use and associated difficulties with environmental legislation [9]. Another drawback of the IP process is the sensitivity to chlorine degradation due to the polyamide backbone, which is commonly present in the selective layer [42,43]. This either

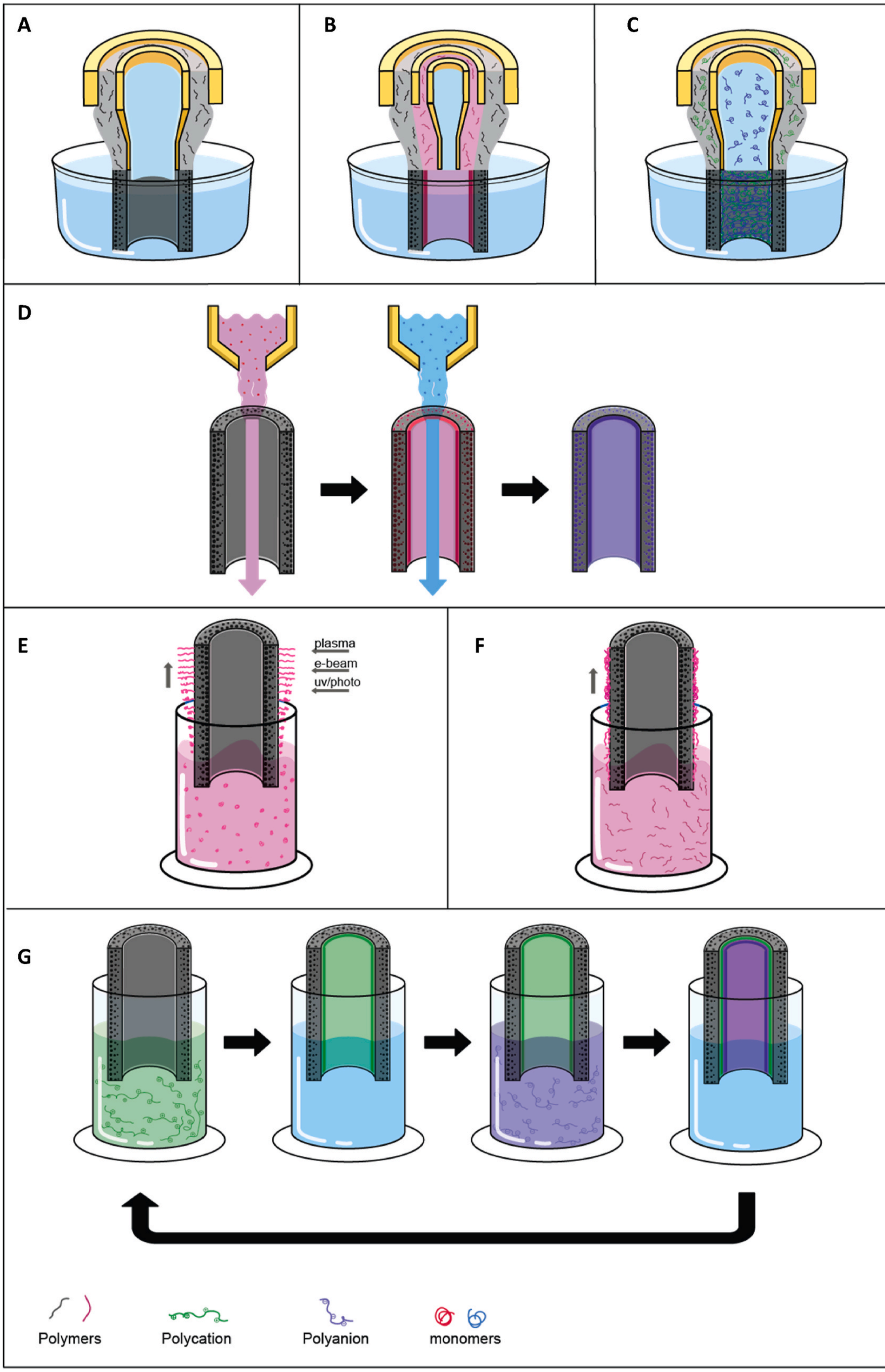

Fig. 1. Methods to fabricate hollow fiber nanofiltration membranes. It should be stressed that most of these methods, save grafting, can be performed on either the inside or the outside of the hollow fiber. For simplicity, only one of these options is displayed per method. A) Single layer phase inversion B) Dual layer phase inversion C) Chemistry in a spinneret D) Interfacial polymerization E) Grafting F) Dip-coating G) Polyelectrolyte multilayers.

limits their application, as chlorine is often used for membrane cleaning, or necessitates a much more extensive pre-treatment, negating one of the advantages of HF NF membranes.

2.3. Grafting

A very limited amount of research has been done on HF NF grafting. Grafting is possible on HF membranes, and the procedure would be easy to implement in a spinning line (Fig. 1E). However, due to the geometry, modifications with UV and plasma are mostly limited to the outside of the membranes as irradiation of the membranes from the inside is not possible. Grafting methods with an e-beam [44], plasma [45], and UV/photoirradiation [46–48] have been performed, and the UV/photoirradiation process has even been modelled [49]. These methods have shown to be able to produce very open NF membranes by tuning parameters such as line rate, irradiation dose and polymer concentration, amongst others. Little is known about the mechanical and chemical stability of these membranes.

2.4. Dip-coating and spray-coating

A variety of coating methods is possible for SW NF membranes. However, coating on the HF NF geometry mostly takes place via dip-coating (Fig. 1F). One instance of spray-coating on the outside of hollow fibers was reported [50]. Other coating methods, such as spin-coating, are not suited for the HF geometry. One of the main advantages of coating is that it allows for a large variety of surface modifications. In the early 2010's, homopolymers were coated on HF supports [51,52]. More recently, the dip-coating method was combined with PI to coat alternating copolymers [53] and block copolymers [23,54] on the outside of hollow fibers. Coating and subsequently sintering of colloids has also been performed on inorganic supports [7,55]. Because of the large variety of surface modifications, chemical stability is highly dependent on applied coating.

2.5. Polyelectrolyte multilayers

During the fabrication of PEM membranes, a coating approach is used as well. However, the Layer-by-Layer (LbL) approach relies specifically on the self-assembly of charged polyelectrolytes and yields membranes which are more complex and contain much more tuning parameters than other coating methods. It is therefore discussed as a distinct category here.

The method was developed by the group of Decher in the early 90's [56] and was quickly adapted onto membranes later in that decade [57,58]. However, the application onto HF NF membranes only took off in the 2010's [59]. PEM membranes are created by alternately coating layers of positively and negatively charged polyelectrolytes onto a charged support membrane (Fig. 1G). Coating of hollow fibers can be done statically (also referred to as dip-coating, see paragraph 2.4) or dynamically (both in dead-end and crossflow mode) [60,61]. The driving forces of this reaction are electrostatic interactions between polyelectrolytes, an increase in entropy due to the release of counterions and hydrophobic interactions [17].

The main advantage of the LbL method is that layer properties are highly tuneable. Common tuning parameters during coating include salt concentration [62], pH [63], choice of polyelectrolytes [64,65], number of layers [62,66], degree of crosslinking [64,67], and choice of support membrane [68]. Additionally, with the LbL method, membranes with a high chlorine stability can be produced [68]. Besides that, this method is relatively sustainable due to the mild conditions and aqueous solvents which are used. However, a disadvantage is that this technique consists of many coating steps and can therefore be relatively time-consuming, though the coating time could be substantially shortened by applying dynamic coating at a high flux [61].

Recently, a surge in research around more advanced membranes which incorporate functional compounds into the membranes to improve functionality has been seen. Examples include the inclusion proteins such as aquaporins to improve flux [69] or laccase to improve organic micropollutant (OMP) degradation [70]. Another way to incorporate the use of these LbL polyelectrolytes is by using the PEM layer as sacrificial layer against fouling [60]. A recent advance is asymmetric LbL coating, where the pores of the support membranes are first closed off with a very open PE pair, and a couple layers of a very dense PE are applied on top. This yields membranes with both a high flux, high OMP retention and low salt retention [71].

2.6. Chemistry in a spinneret

To simplify the multistep process required for IP, the group of Wessling developed the chemistry in a spinneret process, where formation of a support via PI and crosslinking are combined in a single-step process [72–77]. At first they focused on covalent crosslinking [72], later on ionic bonds in polyelectrolyte complexes [75]. More recently they combined these two methods [76] (Fig. 1C) and also explored further coating of the extruded membrane with a polyelectrolyte [77]. They proved to be able to make both dense and open NF membranes with this method. However, a downside of this approach is that the PI and crosslinking processes affect each other when they are executed at the same time [72]. This leads in practice to very complicated reaction mechanics which are poorly understood [73]. The chemical stability of these membranes is highly dependent on the used materials [77].

2.7. Potential for commercialization

The advantages and disadvantages of all production methods for HF NF membranes are summarized in Table 1. PI plays a very important role

Table 1
Advantages and disadvantages of HF NF production methods.

Method	Advantages	Disadvantages
Single layer Phase inversion	- Single-step fabrication process	- High occurrence of defects - Selecting a material with high permeability, mechanical strength and good separation properties is challenging
Dual layer phase inversion	- Single-step fabrication process - Compared with SL PI less of the more expensive polymers which are used for the separation layer is needed.	- High occurrence of defects - Often poor attachment between support and separating layers - Relatively thick separating layer
Interfacial polymerization	- Good attachment between support and separating layer - Thin separating layer	- Multi-step fabrication process - Poor reproducibility - Generally poor chlorine resistance
Grafting	- Modifications can be done in spinning line	- Modifications only possible on outside membrane - Only very open NF membranes
Coating	- High flexibility in coating compounds	- Multi-step fabrication process - Thick separation layers
Polyelectrolyte multilayers	- Membrane properties are highly tuneable - Thin separating layer - Aqueous solvent - Good chlorine resistance	- Multi-step fabrication process
Chemistry in a spinneret	- Single-step fabrication process	- Poorly understood reaction mechanics - Kinetics for phase separation and complexation need to be optimized

in developing support membranes which can further be modified with other techniques. For stand-alone membranes, DL PI is often preferred over SL PI because of its higher tunability. However, DL PI still often suffers from thick separating layers. Much thinner separating layers can be made with IP, and a big fraction of the lab-scale research focusses on this technique. A major drawback for their commercialization is their poor chlorine resistance, but this could be overcome in the coming years when research focusses more on less sensitive building blocks. Research on grafting is limited and has thus far not been successful to produce denser NF membranes. Coating allows for the largest variety of compounds to be applied to the membrane, which makes the technique very versatile. However, the thick separation layers limit the flux of these membranes in practice. PEM membranes show great potential for scale-up, as reflected by their commercial presence [78]. Even though this multi-step fabrication process can be time-consuming, thin separating layers are produced, membrane properties are highly tuneable, and membranes show a good chlorine resistance, which is relevant for industrial cleaning methods. Research on chemistry in a spinneret is still very limited, but future commercialization might be possible when the technique has matured, and its mechanics are fully understood.

3. Process conditions

Next to the materials of the membrane, there are many more factors which influence the performance of the membranes in practise, though this gets less attention from the scientific community. Section 3.1 focusses on the design of HF NF modules and highlights the differences with regards to SW NF modules. Optimizing plant design and operational parameters is crucial for amongst others controlling concentration polarization and specific energy consumption (SEC). This is discussed in section 3.2. Plants need to be designed with the feed stream in mind, as the feed characteristics can influence membrane performance in a variety of ways, as discussed in section 3.3. Lastly, fouling remains a crucial factor in membrane longevity and performance, thus section 3.4 is dedicated to fouling and cleaning of the membranes.

3.1. Module configuration

When comparing the SW and HF configurations, it becomes clear that each configuration has distinct characteristics (Table 2). For SW modules, a large selection of module types is available (>65 commercial full-scale module types, see Supporting Information). On top of that, these modules are often available with a range of different spacer sizes, which can be chosen for the application. SW membranes are typically placed in RO-type pressure vessels. This leads to a standardised size of SW modules at 1016 × 200 mm [79–84] and their ability to be operated at high pressures, with the maximum operating pressure form modules ranging between 28 and 55 bar [79–83], but specific energy consumption will be high when these modules are operated at high pressures. The SW configuration is prone to fouling due to the presence of a feed spacer [85]. Additionally, the direct (0.1–100 ppm) and cumulative (up to 500 ppm h) chlorine resistance of SW membranes are limited [79–84], because the separating layer of most SW NF membranes is based on polyamides. Necessary pre-treatment often starts with a safety screen. However, due to the higher fouling rate and poor cleaning potential of SW membranes, further pre-treatment of the feed stream is essential. This is often done via a variety of process steps, such as combinations of coagulation/flocculation, sedimentation, rapid sand filtration, and UF [8], which gives rise to a higher energy demand and need for extra chemicals for the pre-treatment, and consequently more brine disposal issues due to the added chemicals.

HF configurations, on the other hand, have a much lower availability (14 commercial full-scale modules [86–98]), and the dimensions of the modules differ per supplier [86–88]. Their maximum operating pressure is much lower, ranging between 4 and 8 bar [88–90]. The SEC of the operation will be reduced when the modules are operated at a low pressure, but more membrane surface area will be required. HF NF modules are void of the spacer, because of this, concentration polarization factors are typically higher in HF NF than for SW NF [99–101]. However, the absence of a spacer also leaves HF NF modules less prone to spacer-related fouling and clogging problems. It is important to mention that hollow fibers can become blocked due to fouling by larger particles, but this can easily be circumvented by applying a large enough inner diameter and a simple strainer. In addition to that, the configuration offers much more possibilities for hydraulic and chemical cleaning. First of all, backwashing is possible in this geometry. Secondly, due to the use of more stable polymers in the separating layer, their direct (0.1–500 ppm) and cumulative (up to 250,000 ppm h) chlorine resistance can be much higher than SW membranes [86–94]. Potentially, SW type membranes could be prepared with the same highly stable materials, yet in practice this has not been done. As a result of the high chemical stability of HF NF membranes, limited pre-treatment of the feed stream is sufficient for this geometry. HF NF modules only require a 0.1–0.3 mm micron safety screen [102,103] to prevent fiber clogging as a pre-treatment. After that, the process can be continued with direct filtration of the feed [41]. Thus, saving energy and chemicals by omitting the intensive pre-treatment that is required for SW NF.

Due to their lower proneness for spacer-related fouling, increased possibilities for chemical and mechanical cleaning, and lower chemical and energetical demand of the pre-treatment, the HF configuration has potential to be a more sustainable treatment method than the SW configuration, especially for applications with a higher (bio)fouling potential. HF NF has shown to be competitive for drinking water production compared with SW membranes [41,104] and non-membrane based drinking water production techniques [104]. Whether HF NF or SW NF is more favourable should be determined on a case-by-case basis.

Module design is a vital aspect in membrane operations. There are many parameters which can be tuned during module design. A HF module generally consists of four parts; the membranes itself, membrane housing, potting and end caps (Fig. 2A) [105]. Some reviews have been written about HF modules in the past few years [105,106], However, published scientific research on module optimization for HF NF is scarce and usually targeting at lab-scale research. Commercial modules are commonly around 1.5 m length whereas in academia typically modules of 10–30 cm length are used [107]. Effects such as flux decline [108] and increased concentration polarization due to lower crossflow velocities [107] along the fiber length need to be properly accounted for when assessing full-scale installations. Thus, it is important to realise that research on small, lab-scale hollow fibers cannot be simply translated into performance of full-scale membrane modules due to membrane length being an important factor in recovery and retention [107,109].

Within this review, the distinction between HF membranes and tubular membranes is based on inner diameter; with HF membranes having an inner diameter <1 mm and tubular membranes having an inner diameter ≥ 1 mm. However, it should be noted that this distinction is also incidentally based on production method, where HF membranes are produced in a single extrusion step in a spinneret and tubular membranes are cast on a helically wound backing material. The typical commercial HF NF membrane has a single bore with an inner diameter of 0.7–0.8 mm. However, in academia, variations of this membrane geometry can be found. Some multichannel membranes with 3 and 7

Table 2
Comparison between commercial full-scale spiral wound and hollow fiber nanofiltration modules.

Configuration	Spiral wound	Hollow Fiber
Module size	Standardised	Varied
Commercial availability full-scale module types	>65	14
Max. operating pressure	High	Low
Chlorine tolerance	Low	Low - High
Pre-treatment	Extensive	Limited
Cleaning methods	Limited	Extensive

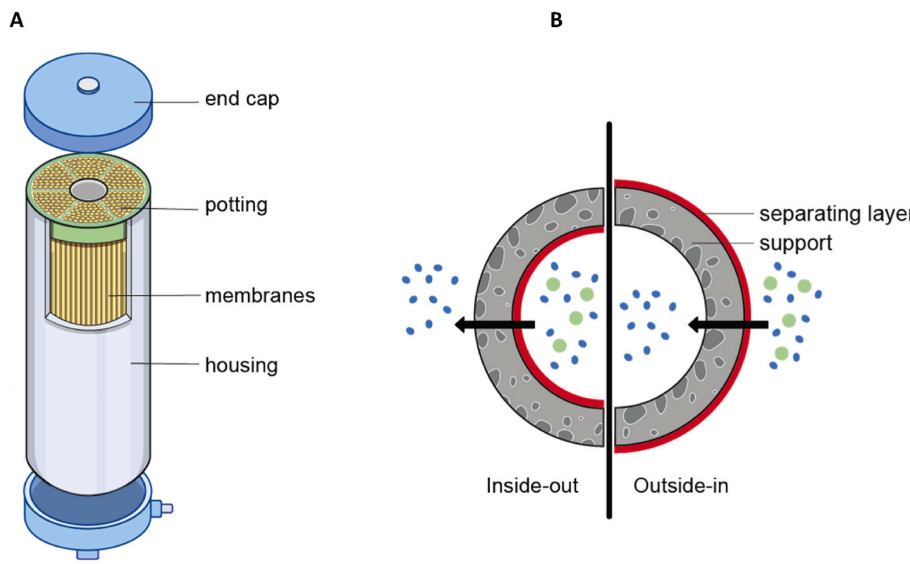

Fig. 2. A) Schematic representation of a hollow fiber module B) Inside-out vs outside-in filtration.

bores were previously produced [110–113], albeit with rather large bore sizes (>0.9 mm). These multichannel membranes are claimed to have increased packing density [111]. In addition to that, single-bore sinusoidal-shaped fibers were developed [74]. The aim was to mitigate concentration polarization effects, but the modification showed little effect in aqueous separations in practice. Besides that, variations in bore diameter occur. The fiber diameter, in combination with the crossflow velocity, determines the Reynolds number [109], and thus the mass transfer near the membrane surface.

Another important factor in module design is the operation mode. HF modules can be operated in inside-out (bore-side feed) or outside-in (shell-side feed) mode (Fig. 2B). Fibers with respectively selective layers on the inside or the outside are used for these modes. The choice between inside-out and outside-in depends on the application. Both modes have their specific advantages. On the one hand, inside-out membranes are less prone to abrasive wear [114] due to reduced fiber movement, and concentration polarization is better controlled in this mode [114,115], while the outside-in configuration yields a higher specific surface area (Supporting Information).

All in all, module design impacts the efficiency of a plant using HF NF. The operation mode and fiber length impact the magnitude of concentration polarization, and thereby the solute rejection and flux of the membranes. However, knowledge on optimization of module design for HF NF is still scarce and mainly present with manufacturers. Academic literature mostly focuses on membrane development. Other important aspects, such as design of the potting, end caps and housing lack nearly entirely in academic literature. Therefore, more research on module optimization is called for.

3.2. Operational design and parameters

During the design of full-scale plants, operational design aspects such as number of modules, operation mode and staging allow for more optimization tools for the specific application. Within this paper, full-scale plants are defined as plants with a production or demonstration focus, whereas pilot-scale plants are defined as plants with a research focus. The size of full-scale plants can vary wildly, from as little as 3 modules in Strathgordon and Windigo Island [9], up to 140 in Benkalis [116]. A plant with a capacity of 7200 modules has been modelled but has not been build [108], showing the large degree of scalability for this technique.

Membrane modules can be operated in dead-end or crossflow mode. In dead-end mode, all the feed is passed through the membrane. In contrast, in crossflow mode, a part of the feed flows tangentially across the membrane surface. Dead-end filtration is commonly performed in batch mode whereas crossflow filtration is commonly performed continuously. Dead-end operation has lower fluxes and retentions [8] due to increased concentration polarization and fouling. Therefore, crossflow operation is favoured in practice.

Crossflow operation can be performed in single-pass mode (Fig. 3A) or in feed-and-bleed mode (Fig. 3B). Introducing a recirculation pump and recirculation loop to the plant allows for operation in feed-and-bleed mode. Here, a large part of the feed is recycled through the system. An advantage of feed-and-bleed is that a high crossflow velocity can be maintained over the length of the module, thus minimizing fouling [117]. Besides that, higher recoveries can be obtained in this mode. However, the solute retention is lower due to the increased concentrate concentration which is caused by the feed recirculation. In addition to that, the circulation pump poses extra energy demand [118] and extra purchase cost.

Besides that, modules can be operated in a single-stage design or in a multi-stage design. The aim of staging is to reduce the average feed concentration in the first stages. It can be an effective tool to increase recovery or purity, or reduce the SEC. Typically, flow mixing takes place in the connection between the two stages [108]. Because of this, the concentration polarization profile that builds up along the length of the fiber is disrupted. Consequently, adding another module is not equivalent to installing a module that's twice as long. For NF, staging in the form of a tapered cascade, also called Christmas-tree configuration, is common (Fig. 3C) [119]. Due to the tapered design, repressurizing between stages is usually not necessary. Keucken et al. modelled a three-stage and a four-stage HF NF Christmas-tree array and they found that, at equal module amount, the four-stage array had a higher natural organic matter (NOM) removal and a lower energy consumption than the three-stage array [108]. Considerations for staging of NF modules have been elaborated upon elsewhere [119].

In addition to the range of choices that can be made during the design of full-scale plants, use of different process conditions gives additional operational freedom. Process conditions influence membrane performance in a variety of ways. An increase in operating pressure leads to an increased flux and is associated with increased dye and salt rejection [37]. However, increasing the flux also leads to an increase in concentration polarization [119]. Therefore, especially at low crossflow velocities, and high module lengths, the retention tends to decrease at high fluxes [107,120]. This increase of concentration polarization is also likely to be the cause of increased fouling at higher fluxes [119,121,

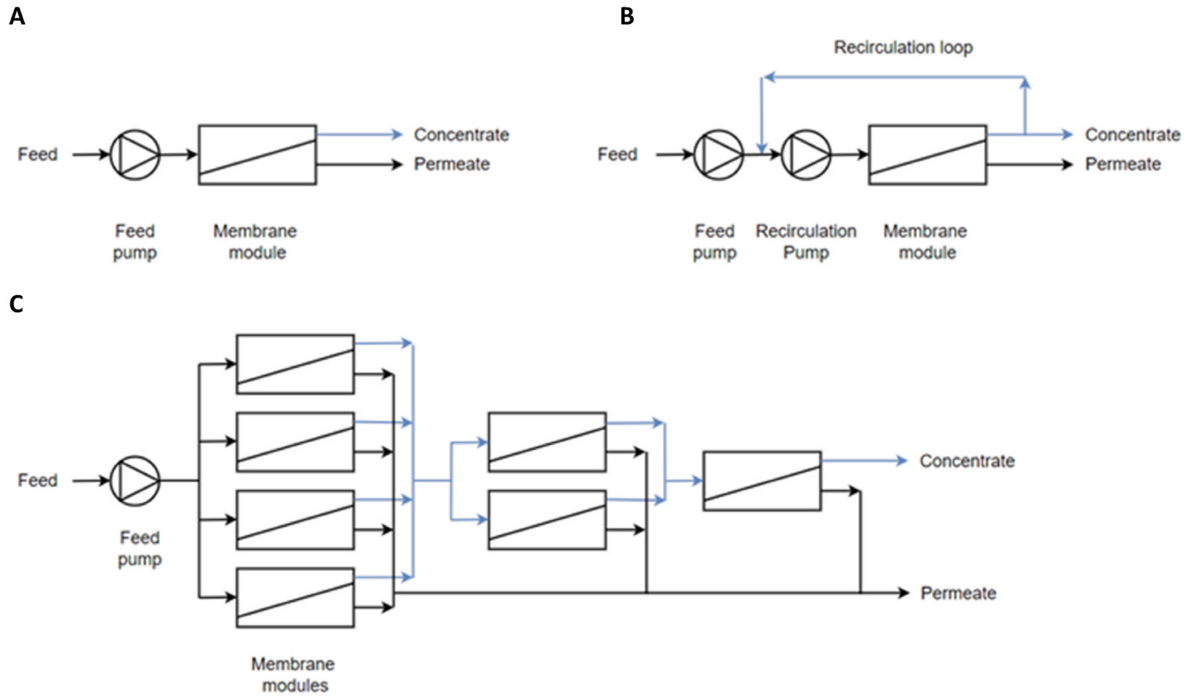

Fig. 3. Several process designs for a plant with hollow fiber nanofiltration modules A) Single-stage, single-pass design B) Single stage feed-and-bleed design C) Christmas-tree staging with seven modules, single-pass design.

122]. Next to that, an increase in recovery can reduce retention due to increased concentration polarization [108,114]. Another important process condition is crossflow velocity. An increase of the crossflow velocity has been associated with an increased retention of solutes [8, 108,120], likely due to decreased concentration polarization, and an increased pressure drop alongst the membrane [108]. In contrast, the effect of temperature on retention is often limited [51].

However, altering operational conditions can have a substantial effect on SEC. The effect of operational parameters on SEC has been investigated by Jährig et al., and is displayed in Fig. 4 [114]. It can be seen here that increasing the flux can substantially increase the energy demand of the process, because more concentration polarization and fouling takes place. In contrast, increasing the recovery slightly reduces the SEC of a process (Fig. 4). This is because at high recoveries, you need to pressurize less feed per m^3 of permeate. In this figure, it can also be seen that crossflow velocity has a major impact on SEC, as an increase in crossflow velocity from 0.5 to 1.0 m/s leads to a 3-fold increase in SEC [114]. It should be noted here that the crossflow velocity is not plotted in an ascending manner. The increase in SEC can be explained by a higher pressure drop at high crossflow velocities, and a lower single pass

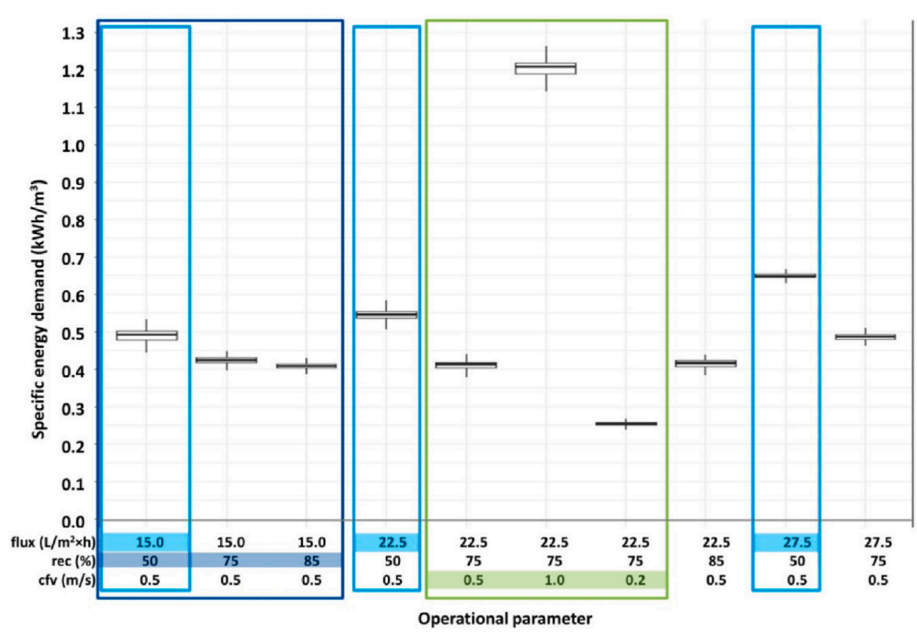

Fig. 4. Impact of operating conditions on the specific energy demand of drinking water filtration. Light blue: increase of flux, dark blue: increase of recovery and green: increase of crossflow velocity. Reprinted with permission from [114]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

recovery (at equal flux). In addition to the parameters shown in Fig. 4, the effect of temperature on SEC is relevant to mention. An increase in temperature reduces the water viscosity [51,123–125]. This allows modules to be operated at a lower pressure while maintaining similar fluxes, and thus a reduction in energy consumption can be seen at higher temperatures [120].

All things considered, there are many parameters which play a role during plant design and operation. This allows for a high degree of optimization for the specific application, but also introduces complexity when designing these plants. Unfortunately, the amount of academic research on HF NF plant design is relatively scarce, and knowledge on these topics, especially filtration mode and staging remains mostly at manufacturers.

3.3. Parameters of the feed

To an extent, the chosen operational parameters discussed in the previous chapter are dependent on the properties of the feed, as membrane performance depends strongly on the type and concentration of the solutes [38,123,124,126]. We discuss the influence of feed parameters on HF NF here, but it should be noted that most of these parameters are also relevant for SW NF. For charged solutes, an increase in concentration can lead to a decrease in rejection [38,126] due to the suppression of the electric double layer of the charged membrane and/or solute, thereby mitigating the effect of charge repulsion. An increase in molecular weight, size (Stokes radius), and a decrease in diffusivity of the solute generally leads to an increase in rejection [124,127]. On the other hand, an increase in solute valency can lead to both an increase or a decrease in rejection, depending on the dominant separation mechanism and membrane charge [123]. The effect of pH on membrane performance in HF NF is twofold: Firstly, pH influences the charge of the solutes, resulting in either a higher or a lower retention or fouling rate for these solutes [37,123], depending on membrane charge. Secondly, the membrane structure can change both reversibly and irreversibly at extreme pH values. The effects range from swelling [128] and hysteresis [23] to complete delamination [4] and decomposition [129]. However, with proper choice of the chemistry of the separation layers, this can be avoided [129].

The effect of feed parameters becomes more complicated when rejection of solutes is not determined in single-component solutions, but in mixtures. This is especially important for NF membranes, where, also depending in the specific chemistry of the separation layers, different separation mechanism play an important role. In multicomponent solutions, mixture effects such as negative retentions [127] and reduced dye retention at increased ionic pressure [130] might occur. Despite these interactions being very relevant for separation efficiency, it is still very common in academia to measure rejections in single-salt solutions or in simple synthetic waste waters. Therefore, these results often do not give an accurate impression of performance with real waste waters and more studies exploring mechanisms in multicomponent mixtures are paramount for the future developments of NF membranes.

3.4. Fouling and cleaning

Membrane fouling is undesirable as it can cause reversible and irreversible flux decline [41,131] and contributes to operating costs. A study by Jafari et al. showed that, in SW NF systems, early membrane replacement is the biggest contributor (~52%) to the cost of fouling, followed by increased energy use due to a pressure drop (~29%) and decreased water permeability (~15%) and cost of chemical cleaning, including chemical costs and downtime (~4%) [132]. They concluded that, for SW NF, costs of fouling range from 11% of operational costs for water with a low fouling potential to potentially much higher percentages for water with a high fouling potential.

HF membranes are much less prone to fouling than SW membranes [99,133] due to the lack of a spacer. In addition to that, SW NF membranes commonly use HF UF membranes as a pre-treatment to minimize fouling. Even though these UF membranes also have a HF geometry, they are still more prone to fouling than HF NF membranes: the open pores of the UF membrane allow foulants to penetrate inside the pores, which leads to irreversible fouling [10]. Therefore, filtration aids are often added to the UF feed, causing additional concentrate disposal challenges. HF NF membranes, on the other hand, have a denser and smooth surface layer and subsequently fouling is much less severe.

Nevertheless, even though direct HF NF is much less prone to fouling than UF + SW-NF, fouling still occurs. Both reversible and irreversible adsorption and cake layer formation can be the cause of fouling in HF NF membranes [131]. The range of possible foulants is huge and includes, but is not limited to ions (scaling) [134], heavy metal hydroxides [123], surfactants [135], proteins [136], pharmaceuticals [137], dyes [130] and natural organic matter (NOM) [131].

Fouling can be countered by using several hydraulic or chemical cleaning methods (Table 3). To the best of our knowledge, mechanical cleaning has not been explored for HF NF membranes. Hydraulic cleanings are often scheduled with regular intervals while chemical cleanings are performed when a flux decline above a threshold value is measured. The required cleaning frequency is highly dependent on the fouling potential of the feed. For drinking water applications, the required cleaning strategy can be predicted quite accurately [116]. However, for waste water applications, the cleaning strategy often needs to be optimized on a case-by-case basis, often based on pilot data [116]. This is because wastewater applications have much more variety in the feed streams. Thus, the values in Table 3 represent a rough estimate rather than exact values.

Hydraulic cleanings include flow reversal, draining, forward flushes, backward flushes, and air sparging. Flow reversal can be performed during operation and helps to reduce pore blocking at the feed side of the module and it has shown to reduce concentration polarization in UF [138]. However, to be effective, flow reversal should occur with short intervals, which is unpractical for full scale systems. Draining is done to remove accumulated particles at the feed side and can be performed under gravity or with air pressure [117]. Forward and backward flushes are the most common hydraulic cleaning methods. They can be performed with feed and permeate water, respectively. Forward and backward flushing can also be performed simultaneously [114]. Air sparging (also called air flush or air scouring) can even be performed continuously, to reduce concentration polarization [139], but it is more common to perform it as a separate cleaning action [8,41,134], to improve physical cleaning efficacy [140].

Chemical cleaning often consists of an acid cleaning to act on organic bounds and a caustic cleaning to dissolve precipitates and remove them [103]. For the acid cleaning step, chemicals like hydrochloric, oxalic, citric, and ascorbic acid can be used [103,114]. The base cleaning step is often executed with sodium hydroxide [114] and combined with hypochlorite or hydrogen peroxide, which perform an oxidating function [117]. The latter chemicals require a degree of membrane stability. Two

Table 3
Cleaning methods for hollow fiber nanofiltration membranes.

Method	Category	Frequency	Downtime
Reverse flow direction	Operation	Every 1–4 h [117]	n.a.
Drain	Hydraulic	1 per hour – 1 per day [117]	30–200 s [117]
Forward flush	Hydraulic	1 per hour [102,141]	30–60 s [142]
Backflush	Hydraulic	1 per hour [41,114]	60–120 s [103,142,143]
Forward flush with air sparging	Hydraulic	2 per hour – 1 per day [8,41,117,134]	5–120 s [8,41,117,134]
Chemically enhanced flush (CEF)	Chemical	2 per week – 2 per month [114,125]	20–60 min [103,120,125]
Cleaning-in-place (CIP)	Chemical	2 per week – 4 per year [103,141,144]	Several hours – 1 day [103]

types of chemical cleaning are distinguished: the chemically enhanced flush (CEF) and cleaning-in-place (CIP). The main difference between the two is the duration. Whereas CEF only takes 20–60 min, during CIP contact time between the chemicals and foulants are increased by increasing soaking time and recirculating the chemicals [117].

Energy consumption of hydraulic cleaning and chemical costs are only a small percentage of total operating costs. Energy consumption of hydraulic HF NF membrane cleaning is only around 0.5% of total energy consumption [114] and chemical use contributes about 2% of operational expenses [103]. However, cleaning also leads to a membrane downtime of up to 8% [103], which indicates a substantial contributor to costs. Besides that, for high fouling applications the use of chemical can amount to 12% of the CO_2 footprint of the NF process [103]. Additionally, membrane integrity may suffer from chemical exposure

Table 4
Overview of properties of full-scale hollow fiber nanofiltration modules.

Company	Pentair X-Flow	NX Filtration	Ochemate	3E Memtech	De.mem	Century Water
Module	HFW-1000 [9,88,144]	WMC200 dNF 40 [86] WMC200 dNF 80 [87] WRC200 dNF40 [96] WRC200 dNF80 [97] [78]	NÜF N80-6040 [89] NÜF N80-6060 [153] [11]	3E – NF20 [90] 3E – NF40 [91] 3E – NF60 [92] 3E – NF80 [93] 3E – NF90 [94]	[95,154]	NanoPure LPNFP8060 [98,152,155]
Indicated uses	Treatment of surface water, potable water and WWTP effluent for colour removal (typically humic or fulvic acids) and minimal salt retention.	Treatment of ground and surface water, reuse of industrial and municipal wastewater effluent, micropollutant removal	Hardness removal, partial desalination	Bacteria and virus removal, heavy metal reduction, heavy metal removal, organic pollution etc.	Dye concentration, dye effluent recovery, wastewater treatment in dye plants	Treatment of ground and surface water, colour removal, organics removal, water reclamation, SW RO pre-treatment
Operation mode	inside-out	inside-out	outside-in	Inside-out	Inside-out	–
Module dimensions	200 × 1537.5 mm	200 × 1537 mm	160 × 1150 mm	25-254 × 200-2000 mm	–	225 × 1600 mm
Membrane surface area	40 m^2	43 m^2 (WMC200) 50 m^2 (WRC200)	40 m^2 (N80-6040) 55 m^2 (N80-6060)	47 m^2 100 m^2	–	–
Membrane inner diameter	0.8 mm	0.7 mm	–	customised	0.8 mm	0.7 mm
Packing density	828 m^2/m^3	891 m^2/m^3 (WMC200) 1036 m^2/m^3 (WRC200)	1730 m^2/m^3 (N80-6040) 1824 m^2/m^3 (N80-6060)	–	–	–
Membrane material:	PES/PES modified with PEM layers	PES/PES modified with PEM layers	modified polyamide/TPFP integrated film forming technology	PES/PVDF + NF coating	PEI	PES-based
Membrane charge at pH 7:	negative	negative	–	–	positive	positive
MWCO	1000 Da	400 Da (dNF40) 800 Da (dNF80)	200–500 Da	–	500 Da	–
Salt retention	<20% Ca_2^+, Mg_2^+ ~0% Na^+, K^+	>91% $MgSO_4$ (dNF40) >76% $MgSO_4$ (dNF80)	≥90% $MgSO_4$ ≥60% $CaCl_2$ ≤25% NaCl	75% NaCl, 24% $MgSO_4$ (NF20) 28% NaCl, 42% $MgSO_4$ (NF40) 51% NaCl, 64% $MgSO_4$ (NF60) 75% NaCl, 85% $MgSO_4$ (NF80) 87% NaCl, 91% $MgSO_4$ (NF90)	–	80–90% Ca^{2+} and Mg^{2+}
pH range						
Filtration	3 < pH < 10	2 < pH < 12	4 <pH < 10	1 < pH < 10	–	–
Cleaning	2 < pH < 11	1 < pH < 13			–	–
Chlorine resistance						
Cumulative	100,000 ppm h	250,000 ppm h	–	1000 ppm	–	400,000 ppm h
Cleaning	Typically 200 ppm	500 ppm	<0.1 ppm	–	–	–
Max. operating pressure	7 bar	6 bar	4 bar	8 bar	–	5 bar
Crossflow velocity range:	Typically 0.3 m/s	0.1–2.0 m/s	–	–	–	–
Recovery	–	–	–	≤60% (NF20A), ≤43% (NF40), ≤38.4% (NF60), ≤30% (NF80), ≤20% (NF90)	–	≤66%
Flux	15–25 L m^{-2} h^{-1}	20–40 L m^{-2} h^{-1} (dNF 40) 20–50 L m^{-2} h^{-1} (dNF 80)	30 L m^{-2} h^{-1}	–	5–15 l L m^{-2} h^{-1}	–
Housing	PVC	PVC-U	–	–	–	ABS, 304 SS

and extreme pH, leading to membrane stiffening [141] and performance loss [68]. This leads to a need for early replacement.

As the downtime, increased CO_2 footprint and reduced membrane lifetime resulting from cleaning are undesirable, prevention of fouling could be seen as favourable to extensive cleaning. Several process design parameters are possible for reduction of fouling, including increasing crossflow velocity [131], pre-treatment [114] or modifying the pH [131]. Academia has also focused on the development of membranes with anti-fouling properties [136,145]. However, because real feed streams are complex and often contain multiple foulants, creating anti-fouling coatings is challenging in practise. Therefore, the industry is still very much reliant on cleaning.

Overall, fouling is undesirable as it causes flux decline. HF NF membranes observe a lower fouling rate and have more possibilities for cleaning than the UF + SW-NF alternative, which could result in more stable and sustainable processes. Even though fouling is much less, fouling control is still required for efficient operation. Unfortunately, little knowledge on optimization of cleaning strategies is available in academic literature. More knowledge on this aspect is necessary to guarantee successful market introduction of this technique.

4. Applications

In recent years, several commercial HF NF modules have been introduced to the market. In section 4.1 an overview of these commercially available HF NF modules is offered. Furthermore, an inventory is made on the applications of HF NF membranes in sections 4.2-4.4. Here, the distinction is made between applications that are being researched on lab-scale, pilot-scale and full-scale in order to show the differences and similarities and highlight applications worthy of further exploration. It should be noted that scientific literature on these commercial modules and their use in pilot-scale and full-scale plants is still relatively scare. Therefore, all identified commercial suppliers were contacted by us with a request for more information on their modules and their applications, to which some replied. These communications are reported here as an addition to the information that is publicly available.

4.1. Commercial suppliers

Data from a variety of HF NF modules is available at the websites of membrane suppliers, with a range in maturity of the commercial products. Pentair X-Flow, NX Filtration, Ochemate, 3E Memtech, De.mem, and Century water all offer commercial full-scale (>40 m^2 membrane area) HF NF modules (Table 4), although the commercial availability of all these modules is unknown to us. With these modules, a range from dense (200 Da) to open (1000 Da) NF membranes is available. This is also reflected in a range of the $MgSO_4$ retention of these HF NF modules, between 20 and 91%. However, it should be noted that testing conditions are not standardised for NF membranes, this complicates the comparison of modules produced by different suppliers.

The exact membrane composition and used production methods are often trade secrets. NX Filtration mentions the use of the PEM membranes [78], but does not disclose exactly which polyelectrolytes are used. Pentair X-Flow probably utilizes PEM membranes as well [11]. None of the other companies disclose any information on their production process, though the low chlorine resistance of the Ochemate modules (<0.1 ppm), in combination with their use of polyamide can be indicative of an IP approach. De.mem currently uses polyethyleneimine (PEI), but is developing membranes infused with graphene oxide nanoparticles for increased water flux and rejection [95].

The high packing density of HF membranes compared with SW membranes is frequently mentioned in literature as one of the main advantages of HF membranes [51,123,125,146,147]. Theoretically, hollow fibers can have a packing density between 1000 and 2000 m^2/m^3 and SW modules between 600 and 1300 m^2/m^3 [115]. However, in practice the expectation of a higher packing density is mainly correct for outside-in modules, or for small inner diameters. For example, Ochemate modules (1730–1824 m^2/m^3) have higher packing densities than SW modules (931–1281 m^2/m^3). On the other hand, inside-out modules such as the modules from Pentair X-Flow (828 m^2/m^3) and NX Filtration (891 m^2/m^3, 1036 m^2/m^3) have packing densities comparable to SW modules (Supporting Information).

A clear distinguishment of the HF NF modules is their lower pressure tolerance (max. 8 bar), compared to SW NF. This is partly a consequence of the mechanical stability of the housing materials used in the modules, as the membrane fibers themselves can withstand up to 18 bar collapse pressure and 20 bar burst pressure [120]. As a result, HF NF membranes are typically operated at lower transmembrane pressures, which does reduce the SEC of the membrane filtration.

NX Filtration [148,149], Ochemate [150], 3E Memtech [90–94] and De.mem [138,139] also offer smaller, pilot-scale (9.8–14.5 m^2 membrane area) versions of their full-scale modules. Besides that, Ochemate also offers residential-scale modules [151], of which the membrane area is not disclosed and Century Water offers several different module sizes with a non-disclosed membrane area [152]. Upscaling from pilot-scale to full-scale modules happens in different ways. NX Filtration increases the surface area of the modules by increasing the diameter of the modules, keeping the module length unaltered, and thereby increasing the number of fibers in a module. Ochemate, however, varies either the length of the modules or both the length and the diameter of the modules. As the length of the fibers may influence performance [107,108], this may cause considerable performance differences in full scale installations.

4.2. Lab-scale studies

In academia, a wide variety of applications is being examined for HF NF (Fig. 5A). Academic research tends to focus more on fundamental aspects of membrane performance and the application is more implicit. Nevertheless, most papers appear to focus on topics related to drinking water production or treatment of municipal wastewater. Research in these areas tends to focus on removal of small solutes, such as heavy metals [156], per-and polyfluoroalkyl substances (PFAS) [157], pesticides [158] and other OMPs [159]. Sometimes water softening is also mentioned as a goal [160].

Another major application of HF NF membranes in academia is in the textile industry [48,125,126,161]. Wastewater from this industry commonly contains a mixture of dye molecules, a high salt concentration, and a variety of other compounds. HF NF membranes are typically used to separate the dye from the salts, so that the salt might be reused in the dying process [126]. An additional advantage is the removal of colour in the wastewater. Lab-scale research focusses on pure water permeability, salt and dye retention and fouling/long term flux.

In addition, HF NF membranes are also frequently used for organic solvent nanofiltration (OSN) [26,30,36,147,162,163] in academia. This often involves separation of dye and solvents. The use of solvents poses a challenge for the operation as they can induce either membrane swelling or shrinkage [147,162]. Besides that, the choice of solvent impacts permeability [26,147]. Therefore, very stable membranes are required for OSN. Although OSN membrane development gets quite some attention in academic context, larger scale pilot studies are currently few and far between.

Furthermore, the use of HF NF-type membranes in forward and pressure retarded osmosis has been frequently mentioned [164–166] in academia. However, the forward osmosis process shows fundamental differences from the NF process. An elaborate examination of these mechanisms is beyond the scope of this paper.

There are also several more niche applications for HF NF. Most of these applications involve the treatment of industrial waste streams or targeting specific solutes. For example, these membranes can be used for heavy metal removal from waste streams from the electroplating industry [123,167] and they have been used for removal of oil, surfactants

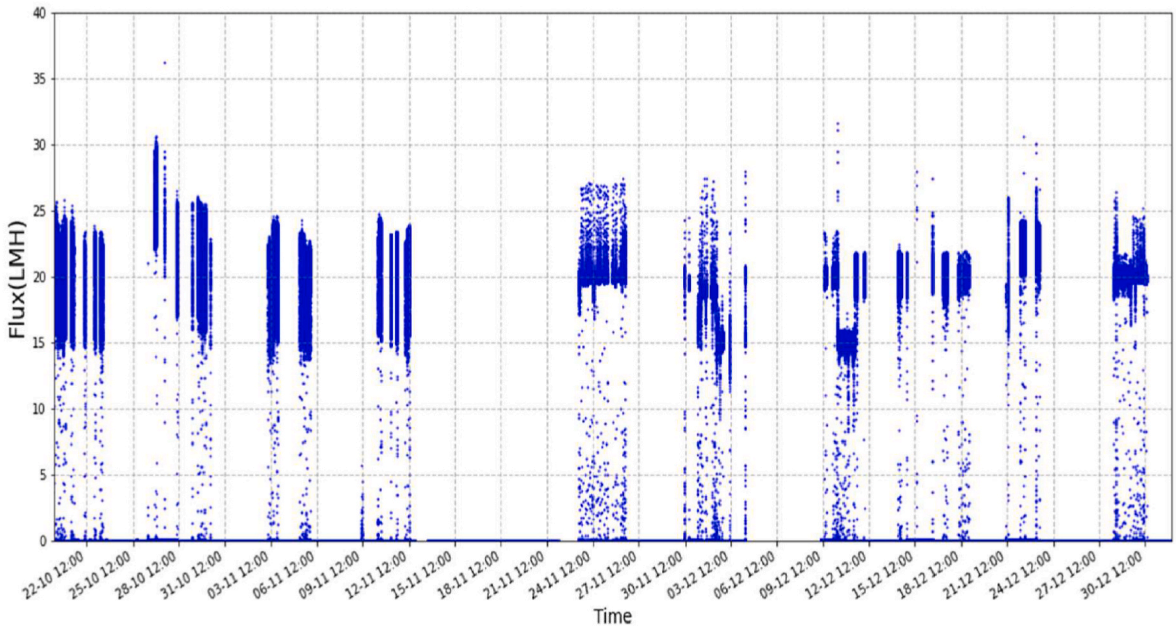

Fig. 5. Flux of dNF40 membranes (in L m^{-2} h^{-1}) at a pilot at La Zaragozana beer brewery in Spain over a 2-month period. Production stops during the COVID-19 pandemic are the cause of the discontinuous data. Reproduced from [184].

and ions from produced water [135,168]. Waste waters from a petrochemical plant [169], landfill leachate [170], domestic waste [142], and an RO plant [22] have been treated with HF NF. Besides, potential applications in the food [10,171], chemical [172,173] and pharmaceutical [173] industries have been reported. These are just a few examples showing the multidisciplinary character of these membranes. It is expected that the range of possible uses will expand in the coming years.

4.3. Pilot studies

A range of larger pilot studies is being conducted world-wide (Fig. 6A, Supporting Information). These pilot study often serve as a first step towards full scale implementation of the HF NF membranes in water treatment processes. Drinking water production was the first application to be studied on a pilot scale. In the 2000's, several studies were performed with the NF50 M10 modules [8,134,142,174–176]. Later, also the HFW-1000 [102,120,141,177,178], NX Filtration modules [179,180] and De.mem modules [181] were used in pilot-scale studies for drinking water. These pilot-scale studies highlight some aspects which are often overlooked during lab-scale research. First of all, whereas lab-scale studies frequently use synthetic feeds, in pilot-studies often more realistic and more complex feed streams are used. Production of drinking water from lake water [102,177], groundwater [182] and river water [41] was studied. Pilot studies also target other compounds in drinking water. Whereas lab-scale research is focussed mostly on removal of small compounds, pilot scale research tends to focus more on topics like removal of NOM [102,177,182], water softening [134] or disinfection [177]. One study focused on anoxic operation of HF NF modules to prevent iron and manganese precipitation and showed that HFW-1000 modules could be operated under anoxic conditions with a flux up to 22.5 L m^{-2} h^{-1} [114].

A few pilot-scale studies were performed on textile wastewater, but information on this application is relatively scarce. De.mem membranes have shown to be able to remove visual traces of dyes from waste water [154]. Some studies with in-house produced pilot modules were performed as well [125,183]. In one of those studies, the HF NF concentrate was further treated with coagulation-flocculation [183], coagulation-flocculation could remove up to 91% of colour from the concentrate.

HF NF membranes can also be used for other sources of wastewater. In La Zaragozana beer brewery, dNF40 membranes were used for treatment of RO concentrate in order to reduce the water foot print of the brewery [184]. The permeate of the NF membranes was re-used in the brewery, which resulted in an 80–85% reduction of the RO concentrate waste stream. During a 2-month operation, membrane flux was shown to be stable (Fig. 5), and no fouling was observed on the membrane. Additionally, treatment of municipal wastewater has been studied [142], and both Pentair X-Flow and NX Filtration mention use of pilots for grey water re-use, process water production, treatment of MBR effluent and leachate (Supporting information).

Another matter that is highlighted during pilot-scale studies is the importance of monitoring fiber integrity during drinking water production [177]. HF NF membranes can be used as a microbial barrier. However, incidental breaking of a fiber in a module can take place. Lidén et al. show that when a fiber in an HFW-1000 module breaks, a doubling of total organic carbon (TOC) and 2% increase of permeate flow can occur. Besides that, the removal of virus-like particles goes down from 5 to 6 log to $<$2 log [177]. Modules with broken fibers can be repaired by closing the broken fibers with a pin [117].

Generally, these pilot studies show that HF NF membranes are capable of stable removal of organic compounds [125,141]. In one case it was noticed that ion retention decreased over time [182]. This was attributed to the adsorption of ions to charged groups on the membrane, thereby reducing rejection by charge exclusion. Although flux decline takes place during long-term pilot studies, usually chemical cleaning can restore the flux without affecting performance [114,125].

The pilot studies highlight several environmental aspects which should be taken into consideration when using NF. Generally, energy use of water treatment plants with HF NF treatment is high compared with other, non-membrane-based techniques for water treatment [114,178]. This is especially the case during winter, where the energy demand can increase with as much as 50% compared to the average HF NF energy use [178]. Due to the low temperature during this period, the viscosity of the water goes up, thus leading to a larger energy demand for pumping. Despite the high operational energy demand of HF NF, one study in Sweden concluded that the greenhouse gas emissions of HF NF are lower than a traditional water treatment consisting of coagulation-flocculation combined with sand filtration, if energy use for production of chemicals is factored in [178]. This can be attributed to the fact that HF NF membranes in general require few chemicals, as opposed to the traditional water treatment, which requires coagulants. It should be mentioned here though that a large part of energy in Sweden is green energy. Therefore, considering the higher operational energy use of HF NF membranes, using green energy sources is important for its future as a sustainable technique.

Another factor that could influence the environment is that membrane treatment always leaves a waste stream in the form of water from the concentrate stream and water used for cleaning the membranes, which contains cleaning chemicals. The volume and concentration of this stream is dependent on the process recovery. Disposal in surrounding waters could impact the local ecosystem. Thus, appropriate treatment or disposal of the concentrate and cleaning water is paramount, but unfortunately HF NF concentrate treatment gets little attention in the scientific literature.

In conclusion, larger pilot-scale research allows studying the performance of membranes with real feed waters, over a longer period. Besides that, it shows that these membranes are able to deliver a stable performance. This pilot-scale research is performed world-wide (Fig. 6B, Supporting information), in a range of applications (Fig. 6A). In academic literature, drinking water production is the most prevalent application on a pilot scale, with textile water treatment coming in second. However, data from manufactures shows that these membranes are already applied in a much broader range.

4.4. Full-scale applications

Pilot-scale studies are frequently used in combination with modelling to provide further information on the scale-up of drinking water production [108,120]. During the design of full-scale plants, knowledge from pilot-plants is often used as input for a model to determine the optimal plant design and operation. Such models require variables such as quality, flow and temperature of the feed and can give an indication of the required number of membrane modules, as well as giving an indication of flux, recovery, energy demand and membrane rejection [185]. Table 5 gives a non-exhaustive overview of the different full-scale applications. We used (open) literature and direct communication with the membrane suppliers as sources. It must be noted that little to no information from Ochemate, 3E Memtech, De.mem, and Century water was found, also after reaching out to the companies for specific information.

The first full-scale HF NF setups were built in two locations in western Europe and Asia for the treatment of landfill leachate [9]. For this, NF50 M10 modules were used. Our analysis shows that especially in 2021 the amount of full-scale HF NF based has increased substantially. Nowadays, full-scale systems are being constructed world-wide (Fig. 6B, supporting information), and a variety of applications can be distinguished. Drinking water production appears to be the most prevalent application for these membranes (Table 5). For this application, HF NF can be coupled with chlorination to kill microbes, and sometimes more extensive post-treatments steps are used. Typical crossflow velocities for this application are 0.3–0.5 m/s. The capacity of HF NF drinking water treatment plants ranges from 60 to 6000 m^3/day, illustrating the scalability of HF NF.

An example of a full-scale drinking water production plant with HF NF treatment, is Ringarooma Valley, which is one of the oldest production plants. Its start-up was in 2017 and it is still in operation at the moment of writing. It is not known if any membrane replacement has taken place in the meantime. Feed water is obtained from Ringarooma river and pre-treated with strainers, followed by two units of four skids with 30 HF NF modules, each treating 1500 m^3/day (Fig. 7A). Post-treatment consists of granular activated carbon (GAC) filters to remove small organic compounds that pass the membrane, CO_2 dosing and calcite contractors for mineralization and regulation of corrosivity, UV treatment as microbiological barrier, and lastly chlorination and fluoride dosing for safety and dental protection (Fig. 7B) [144,186]. Discharge water from hydraulic cleaning is used as irrigation water for agricultural purposes in the surrounding area, thus reducing wastewater.

Textile water treatment is also making the transition to full-scale installations. Two full-scale treatment plants for textile wastewater are under construction in India at the time of writing, each with a different purpose. The first treatment plant will focus mainly on full colour removal and partial chemical oxygen demand (COD) and total dissolved solids (TDS) removal from wastewater of a denim jeans company [187]. The second HF NF treatment plant is the common effluent treatment plant in Jetpur [188]. The feed water contains 2–4% sodium hydroxide from the textile industry [116], showing that these membrane can be used even under alkaline conditions. Both systems are designed to run at high recovery rates (90–95%).

Several other applications can be identified. One system for treatment of RO concentrate is operational. This system is run at a low recovery rate of 50%. Besides that, systems for re-use of grey water, process water production and treatment of a variety of waste streams are constructed. Looking at an overview of full-scale systems (Table 5), it is clear that the introduction of full-scale HF NF plants is fairly recent, but the full-scale applications cover a big range both in capacity and type of application. Though it must be stressed that Table 5 is non-exhaustive, it is remarkable that the PEM-type modules, such as the HFW-1000, dNF40 and dNF80 are highly represented in full-scale production locations.

In addition to the applications mentioned in Table 5, based on the applications of SW NF and academic literature, Sewerin et al. also see potential for the application of HF NF in the oil and gas industry, the food and beverage industry and biorefinery [11]. This shows the potential for a much higher number of treatment plants utilizing HF NF modules in the future in a broad range of applications.

5. Conclusions and outlook

In the past 5 years, HF NF membranes have made a significant step in their maturity and should now be considered reliable alternatives for their SW counterparts. Their lower sensitivity to fouling, coupled with a wide range of cleaning possibilities, facilitates their use without intensive pre-treatment steps. Because of the reduced energy and chemical use in the pre-treatment step, HF NF has potential to be a sustainable alternative to SW NF, especially in high-fouling applications. The choice should be made on a case-by-case basis.

But there are certainly also still opportunities for improvement. Unfortunately, still little is known about long-term (i.e. several years) operation of HF NF modules. Besides, HF NF modules are typically operated at lower pressures and have a lower pressure tolerance than SW NF modules. Increasing the pressure tolerance of HF NF modules would benefit the applicability of the technique, especially for feed streams with a high osmotic pressure. Furthermore, HF NF membrane modules currently have a lower commercial availability compared with SW modules. Nevertheless, it can be expected that more commercial modules with a wider range of properties (MWCO, charge, salt retention) will enter the market the coming years.

Six different groups of methods have been developed for production of HF NF membranes. The ability to create defect-free separation layers with high fluxes is key for commercialization of membranes. Besides that, a high chemical stability is paramount as this allows operation of HF NF membranes without extensive pre-treatment, and this gives the HF configuration a competitive edge compared to the SW configuration. Especially PEM membranes have shown to be able to meet these demands, as reflected by their market introduction by Pentair X-Flow and NX Filtration.

It should be noted that, just as for other membrane types, the influence of process design on HF NF performance and energy consumption can be substantial. Lab-scale research often uses different membrane lengths and operational settings than full-scale plants. Therefore, it is not always straightforward to translate lab scale results to full scale

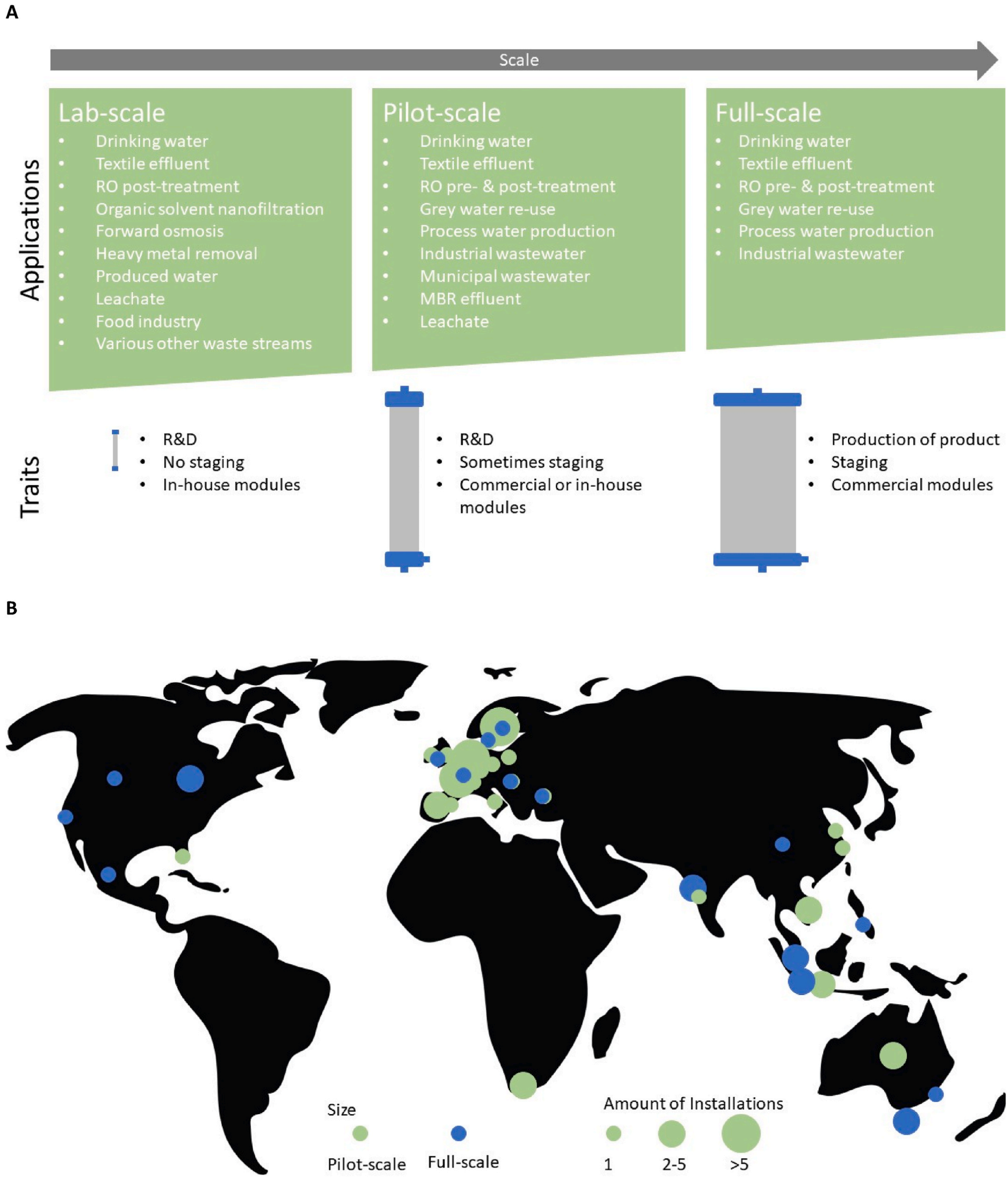

Fig. 6. Non-exhaustive overview of pilot-scale and full-scale HF NF installations. Data and references supporting the information in this figure can be found in the supporting information. A) Properties of hollow fiber nanofiltration modules and their applications on different scales B) World map showing past, current, and prospective pilot-scale and full-scale hollow fiber nanofiltration installations. In case the exact location is unknown, the circle is placed in the middle of the country.

Table 5
Non-exhaustive overview of full-scale production locations with hollow fiber nanofiltration membranes. Limited information from Ochemate, 3E Memtech, De.mem, and Century water was found, also after reaching out to the companies for specific information.

Country	Location	Application	Start-up year	Module type	Capacity [m^3/day]	Number of modules	Crossflow velocity [m/s]	Recovery [%]	Combined techniques	Ref
Australia	Ringarooma Valley	Drinking water production	2017	HFW-1000	1500	120	0.3	–	Strainer, GAC, CO_2, calcite, UV, chlorination, fluoride	[9, 144]
Australia	Strathgordon	Drinking water production	2017	HFW-1000	60	3	0.5	–	strainer, chlorination	[9]
Australia	Rosebery	Drinking water production	2018	HFW-1000	1300	100	0.3	–	Strainer, GAC, CO_2, calcite, UV, chlorination, fluoride	[9, 189]
Canada	Windigo Island hunting camp	Drinking water production	2018	HFW-1000	60	3	0.5	–	strainer, chlorination	[190]
Hungary	Nagykanizsa	Industrial wastewater	2018	dNF40	240	10	–	90	RO, Vapor Compression	[116, 191]
Australia	King Island	Drinking water production	2019	HFW-1000	1000	72	0.3	–	DAF, GAC, CO_2, calcite, UV, chlorination, fluoride	[9, 189]
USA	California	Treatment RO concentrate	2019	dNF40	120	10	–	50	–	[116]
Canada	Calgary	Industrial wastewater	2020	dNF80	360	15	–	75	strainer	[116]
Philippines	Mindenao	Drinking water production	2020	dNF80	450	31	–	85	strainer	[116]
Sweden	Forsmark	Process water production	2020	dNF40	900	74	–	75	strainer	[116]
Canada	Angle Inlet	Drinking water production	2021	HFW-1000	350	36	0.3	–	strainer, chlorination	[9]
Canada	Animakee	Drinking water production	2021	HFW-1000	400	40	0.3	–	strainer, chlorination	[9]
Canada	Washagamis	Drinking water production	2021	HFW-1000	350	36	0.3	–	strainer, chlorination	[9]
Canada	Windigo Island community	Drinking water production	2021	HFW-1000	300	28	0.3	–	strainer, chlorination	[9]
China	–	Industrial wastewater	2021	dNF80	–	20	–	–	–	[116]
India	Gujarat	Textile water treatment	2021	dNF40	–	102	–	95	–	[116]
India	Gujarat	Textile water treatment	2021	dNF40	700	32	–	90	–	[116]
Indonesia	Dumai	Drinking water production	2021	dNF80	4320	120	–	77	strainer	[116]
Indonesia	Jakarta	Drinking water production	2021	dNF80	94	3	–	80	strainer	[116]
Indonesia	Lampung	Drinking water production	2021	–	300	–	–	–	–	[116]
Indonesia	Sumatra	Drinking water production	2021	–	4000	–	–	–	–	[116]
Sweden	Helsingborg	Grey water re-use	2021	dNF40	240	12	–	80	biology	[116]
France	Montataire	Wastewater treatment	2022	dNF80	144	12	–	75	strainer	[116]
Mexico	Leon	Wastewater recovery	2022	dNF40	432	14	0.3	80	strainer	[116, 192]
Turkey	Çorlu	Textile water treatment	2022	dNF40	1200	48	–	77	strainer, RO	[116, 193]
United Kingdom	Rockwool	Wastewater recovery	2022	dNF80	1080	30	0.3	>75	strainer	[116, 194]

performance. Appropriate process parameters and mass transport correlations need to be accounted for. Unfortunately, especially studies concerning staging and using feed-and-bleed versus single-pass mode in HF NF modules are currently scarce in academic literature.

In 2022, at least 59 pilot-scale and 26 full scale HF NF plants are in operation or under construction. This clearly shows that HF NF has grown into a mature technique by now. Full-scale HF NF installations show a broad range in applications and a capacity ranging from 60 to 6000 m^3/day. This shows the substantial growth potential for this technique. When comparing full-scale and pilot-scale research to academic research, the importance of using realistic feed streams becomes clear.

Overall, it can certainly be concluded that HF NF is a quickly growing field. Both academia and industry will benefit when more data from pilot-scale and full-scale HF NF plants becomes available, as it will allow academia to focus on the relevant issues and allow industry to benefit more from academic research. We expect that especially research that focuses on the competitive edge of HF NF due it its enhanced stability and different geometry, could translate to a meaningful contribution in practical applications. The expectation is that in the coming years, substantially more HF NF water treatment plants will become operational, while the membranes and processes will see a continued development in academia.

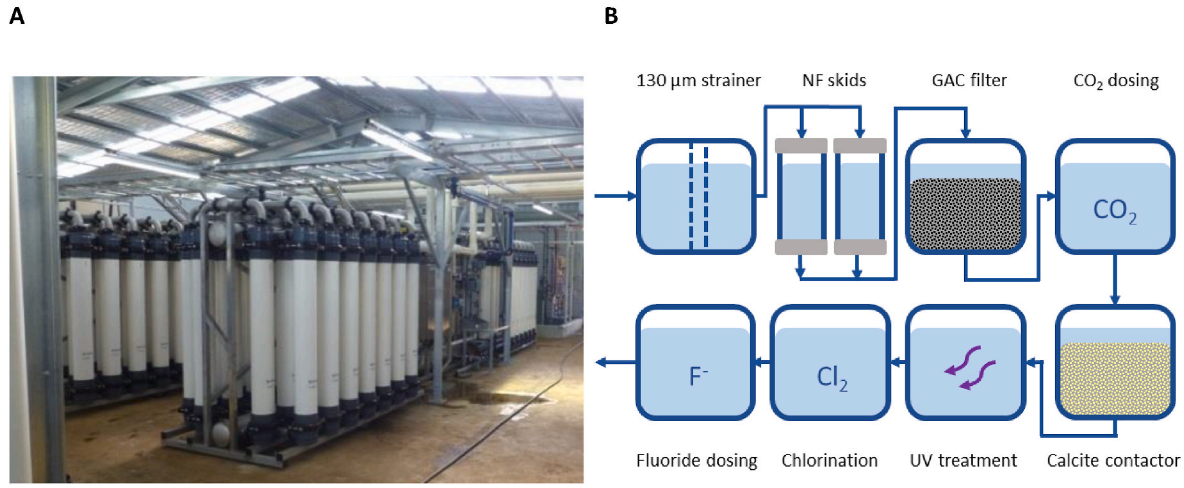

Fig. 7. Full-scale hollow fiber nanofiltration at Ringarooma Valley, Australia. A) Picture of the hollow fiber nanofiltration skids, reproduced from [144] B) Schematic overview of the treatment scheme, image based on information in [144].

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Declaration of competing interest

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Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2022.121234.

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