



Potential of nanofiltration technology in recirculating aquaculture systems in a context of circular economy

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ABSTRACT

In recirculating aquaculture systems (RAS), high degrees of recirculation are beneficial from an environmental perspective, but they also imply high risks of accumulation of unwanted substances in the water loop. The fundamental features and the recent developments of nanofiltration (NF) potentially make this technology attractive for applications in intensive RAS. Indeed, NF membranes can retain dissolved contaminants of emerging concern, off-flavor molecules, and inorganic species (e.g. nitrate and nitrite), and thus they can in principle be applied in RAS in order to remove such substances. On the other hand, the water productivity and the need for pre-treatments remain causes of concern for the integration of NF in RAS. Moreover, NF membranes partially retain all the dissolved ions and the nontoxic organic matter, thus altering the composition of the water in a way that might not be beneficial for the farmed fishes. For this reason, it is hard to foresee the use of NF as an alternative for the present biological treatments. On the contrary, NF technologies appear highly suitable to treat side-streams of the fish tank effluents after the biological treatments to prevent unwanted substances to accumulate and reaching critical concentrations in the water loop. Furthermore, the ongoing innovations in NF technologies are expected to facilitate their integration in RAS.

1. Introduction

Wastewater effluents generated by fish breeding and farming are potential sources of contamination for surface waters, as they may contain fodder leftovers, metabolic waste products (e.g. ammonia and urea), pharmaceuticals, and other contaminants of emerging concern (CECs) [1, 2, 3]. In reason of that, over the past years, fish farming has been gradually implementing Recirculating Aquaculture Systems (RAS). In such land-based facilities, water consumption and wastewater disposal are minimized by the continuous treatment and recirculation of the water effluents from the fish tanks. As shown in Fig. 1, in a RAS loop the fish tank effluent is treated by a series of technologies with the aim to remove undesirable substances and pathogens and to adjust water composition before its reuse. In short, the water from the fish tank is treated first with mechanical filters (e.g., drum filters) for the removal of most of the suspended solids. Then, there are one or more biological treatments, which reduce the organic carbon content and the biological oxygen demand of the effluent. As even low concentrations of ammonia

are already harmful to most of the fish and shrimps' cultures, the biological treatment has also the function to nitrify the potentially toxic ammonia. Nitrate ions (and nitrite ions to a less extent), which are the end products of the nitrification process, tend to accumulate in RAS. This issue can be addressed by substituting a fraction of the water in the loop with fresh water or by adding a biological denitrification step. After the biological treatments, accumulated CO₂ and N₂ are stripped out of the affluent, while the concentration of the dissolved oxygen is raised to a level optimal for fish growth. Before recirculation in the fish tank, the effluent is treated with UV light or ozone to remove pathogens and other (micro)organisms, which can harm the fish culture. Other possible steps include the adjustment of pH, salinity, and temperature of the effluent. Besides the obvious benefits in reducing water consumption, RAS have several advantages compared to the traditional linear systems. Indeed, RAS allow collecting waste and controlling culture conditions, which makes it possible to move fish farms close to the corresponding markets and reduce their footprint. In addition, the land-based RAS highly reduce the risks of external transmission of diseases and escape of the

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farmed species to natural waters. On the other hand, RAS are typically more expensive than traditional systems, and the well-being of the fishes and the taste of their meat is highly affected by fluctuations in water composition or by the malfunctioning of the purification systems, which might bring to the accumulation of the unwanted compounds in the water loop.

In RAS an important parameter is the degree of recirculation, which is defined according to Eq. (1).

$$\text{Degree of recirculation (\%)} = \frac{\text{Recirculation flow}}{\text{Recirculation flow} + \text{Fresh water flow}} \times 100 \quad (1)$$

Full recirculation of water in RAS remains a virtual target, because part of the water is lost with the solids waste after mechanical filtration, and because in many systems the water in the loop is partially substituted with fresh water in order to control the concentration of unwanted substances, such as off-flavor compounds, contaminants of emerging concern, potentially toxic elements, nitrites, etc. The current transition towards a circular economy, which aims to reduce pressure on natural resources, such as water, to produce no waste, and at the same time to boost sustainable economic growth, is strongly driving towards super-intensive RAS with a degree of water recirculation of 99.6% or higher [4]. However, such high degrees of recirculation imply high risks of accumulation of unwanted substances in the loop and therefore make RAS strongly dependent on the efficiency and reliability of their separation and purification systems. In this context, membrane technology can play a key role in improving the current RAS concepts. Microfiltration (MF) and ultrafiltration (UF) membrane units have recently been proposed to reduce the concentration of dispersed and dissolved organics in wastewater [5, 6]. Nevertheless, the potential of membrane technology in RAS remains largely unexplored. In this mini-review, we wish to investigate the perspectives of nanofiltration (NF) technologies in intensive RAS. NF membranes have pore size allowing for the retention of dissolved small organic molecules, including CECs (e.g. antibiotics [7, 8, 9], and pesticides [10, 11]) and off-flavor molecules (e.g. geosmin and 2-methylisoborneol [12, 13, 14, 15]), which can be accumulated in the closed RAS loop and eventually in the meat of the fish. Moreover, NF membranes can totally or partially retain dissolved inorganic nitrogen and phosphorous species that can be reused as nutrients. Hence, based on their selectivities, NF membranes can be used to treat side-streams of RAS effluents to keep contaminant species in the loop, below levels of concern for human and fish health and well-being. Specifically, by reviewing the recent literature in the field, here we discuss those limitations that still hamper the application of NF in aquaculture, the recent developments in NF materials and technologies, and thus the future perspectives for integrating NF technologies in RAS.

2. State of the art in NF membranes

Nanofiltration (NF) is a pressure-driven process, i.e. water (or another solvent) is forced through a selective membrane by establishing a difference in hydraulic pressure between the feed and the permeate side. NF differs from microfiltration (MF) and ultrafiltration (UF)

because it relies on membranes, which are either dense or have active pores with a size typically smaller than 2 nm, thus allowing the rejection of small organic molecules and multivalent ions. However, contrary to the dense reverse osmosis (RO) membranes, which are used for water desalination, NF membranes show scarce rejection for monovalent ions such as sodium and chloride. In pressure-driven membrane processes, the permeate flux (J_w) is proportional to the applied pressure trans-membrane pressure (ΔP) corrected for the osmotic pressure across the membrane layer (Π):

$$J_w = F(\Delta P - \Pi) \quad (2)$$

The permeability coefficient (F), also called permeance, is a property of the membrane and can be described according to different models, depending on the nature of the membrane, e.g. if dense [16] or microporous [17]. In general, water permeance ($L h^{-1} m^{-2} bar^{-1}$) is inversely proportional to the thickness of the membrane active layer. Therefore, NF exploits asymmetric systems consisting of a filtering layer as thin as a few hundred nanometers, which is supported on a macroporous support that confers mechanical stability to the membrane under the operating pressure.

A range of polymeric (e.g. polyamide, polypiperazineamide, cellulose acetate, and polyethersulfone) NF membranes with diversified module design (e.g. spiral or hollow fiber), costs, permeabilities, and selectivities is already available on the market. Such membranes are often fabricated by the interfacial polymerization method, which consists of the reaction and copolymerization of two reactive monomers at the surface of the porous support to form the active NF layer Fig. 2.a shows a schematic of this process when applied to the synthesis of a polyamide membrane: after soaking in an aqueous diamine solution, polysulfone support is contacted with an organic phase with trimethyl chloride, which is not mixable with water. The monomers diffuse and react at the interphase of the two solutions, thus forming the thin NF layer, whose SEM and EDX pictures are depicted on the right side of Fig. 2a. Recent progress in the field includes the incorporation of nanoparticles in the thin film layer to obtain nanocomposites with enhanced separation performances or anti-fouling activity [18]. Other fabrication methods encompass grafting polymerization methods such as UV/photo-grafting, electron beam irradiation, plasma treatment, and layer-by-layer deposition.

At present, the NF market is dominated by polymeric membranes, which can offer a good compromise among costs, footprint, selectivity, and water production rate. Nevertheless, they present also important drawbacks such as low tolerance for temperature, mechanical stresses, and harsh chemical conditions, making it difficult to clean and sterilize them without affecting their lifespan [19]. For this reason, various types of inorganic materials have been applied for the fabrication of NF membranes. Such membranes typically consist of oxides. The selective top-layer, which can be made of $\gamma\text{-Al}_2\text{O}_3$ [20], TiO_2 [21, 22], ZrO_2 [23, 24], or surfactant-templated amorphous silica [25, 26], can be relatively easily deposited on a porous ceramic support by the sol-gel method as described in Fig. 2b. The porous support is dipped in a sol of oxide nanoparticles. The solvent is drained in the support pores, and the nanoparticles form a film while withdrawing the support from the

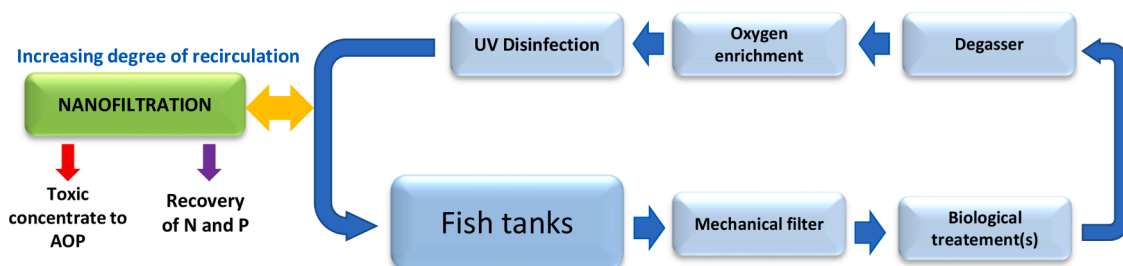


Fig. 1. Scheme of the units in a typical Recirculating Aquaculture System (RAS) and possible integration of Nanofiltration (NF) technology in the loop.

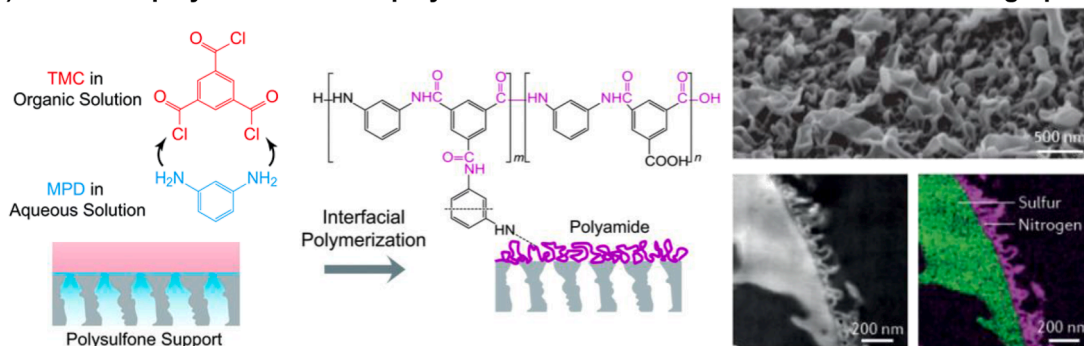
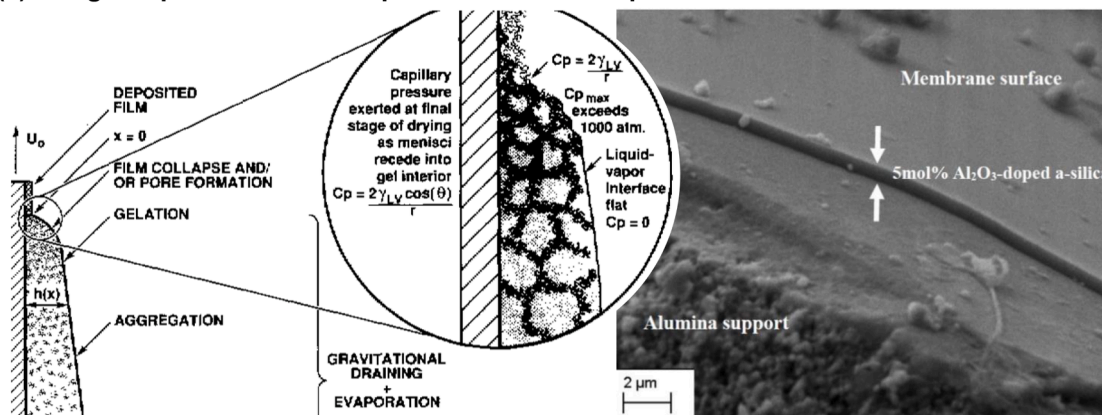
(b) Interfacial polymerization of a polyamide NF membrane with SEM and EDX micrographs**(a) Sol-gel deposition and SEM picture of a Al_2O_3 -doped silica NF membrane**

Fig. 2. Membrane fabrication. (a) Interfacial polymerization is commonly used for the synthesis of polymeric NF membranes on an industrial scale: scheme of the interfacial polymerization of a polyamide NF membrane with corresponding the SEM and EDX micrographs; (b) ceramic NF membranes are typically prepared by dip-coating via the sol-gel method: scheme of the membrane formation during sol-gel coating and SEM micrograph of a Al_2O_3 -doped silica NF membrane. The left section of part a is reproduced from Ref [27] with permission from the Royal Society of Chemistry. The right-up section of part a is adapted with permission from Ref [28], American Chemical Society. The right-down section of part a is adapted with permission from Ref [29], American Chemical Society. The left section of part b is reprinted from Ref [30] with permission from Elsevier. The right section of part b is reprinted from Ref. [31].

coating sol. The thickness of the film will depend on sol concentration and viscosity, support porosity, and withdrawing rate. The film is then dried and calcined to yield the final consolidated filtration layers. An Al_2O_3 -doped silica NF membrane is depicted on the right side of Fig. 2b. Inorganic membranes are easier to be cleaned and present a longer usage time than their polymeric counterpart. Nevertheless, they are typically more expensive to produce and present lower filtering area density when compared to polymer membranes.

Transport and therefore the rejection of solutes in NF membranes occur according to different mechanisms, which depend on size effects and electrical (Donnan) contributions [32, 33], i.e. on the porosity and the surface charge of the membrane material. NF membranes are typically operated at pressures ranging from 2 to 20 bar and a pre-treatment such as UF is needed to avoid suspended solids to clog membrane modules. Water permeabilities for NF membranes typically range between 1 and 10 L (h m² bar)⁻¹ [26] and specific energy consumption for NF is typically > 0.2 kWh per cubic meter of permeate [34]. Membrane permeance decreases during filtration, due to the accumulation of rejected organics (fouling) and precipitated salts (scaling) on the membrane surface and pore-clogging. Thus, NF membranes are subject to frequent washing cycles, which might have a negative impact on their service time [35]. Membrane selectivity depends on the type of membrane and the feed solution. NF membranes often show high rejection towards organic matter and multivalent ions (e.g. SO_4^{2-} , Mg^{2+} , and Ca^{2+}), and a moderate rejection (< 20%) towards monovalent ions [35]. Thus, NF membranes are in principle suitable to remove unwanted substances from RAS, but they can also have a strong impact on the salinity and the concentration of nontoxic organic matter in the water

loop.

3. Abatement of undesired compounds in RAS by NF

NF membranes have been showing high efficiency in the rejection of organic compounds dissolved in water. Therefore, they can be applied in RAS for the removal of the substances that can spoil the taste of the fish meat, and of those compounds that can be potentially harmful to fishes or humans.

3.1. Off-flavor compounds

The accumulation of off-flavor compounds, as geosmin and 2-methylisoborneol (2-MIB), is a problem often encountered in RAS [36], since they are produced as secondary metabolites by various microorganisms that are often present in aquaculture ecosystems [37]. The accumulation of geosmin and 2-MIB is a financial threat for RAS because their adsorption in the lipid-rich tissues of fishes makes their meat unmarketable due to the unpleasant muddy taste and odor [38]. A simple approach to address this problem is to place fish into tanks with water of high purity and rich in oxygen, to release off-flavor compounds. However, this method is relatively costly, has a large footprint, and proper removal requires large quantities of pure water. On the contrary, the best strategy appears to minimize the concentration of these compounds in the water loop, thus preventing their absorption in the fish meat. This approach involves proper control of the microbiological characteristics of the water in the loop and the abatement of off-flavor compounds, which can be achieved by advanced oxidation systems (AOPs), such as

ozonation [39] or UV treatment [40]. While the implementation of these AOPs is under development, the control of the concentrations of geosmin and 2-MIB in RAS is usually achieved by replacing part of the water in the loop with fresh water. However, this operation has an obvious negative effect on the degree of water recirculation (Eq. (1)). In this context, an NF membrane can be used to treat a stream from the fish tank effluent and reuse the permeate in the loop once purified from geosmin and 2-MIB, thus achieving intensive degrees of recirculation and avoiding the accumulation of these substances at the same time Table 1. shows that most of the commercial polymeric membranes and a lab-made alumina-zirconia (as an example of ceramic NF membrane) have high rejection for both 2-MIB and geosmin. Thus, these membranes (except NTR7450) can be potentially used for this application.

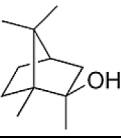
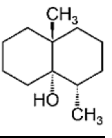
3.2. Contaminants of emerging concern

In RAS systems, drugs and chemical products are applied to promote aquatic growth and to control diseases. Thus, an increasing number of contaminants of emerging concern (CECs) have been found in the water loop or in the fish meat from RAS [41]. Moreover, other contaminants can be introduced with the inlet water or can be formed during the production cycle. Potential CECs in aquaculture systems are antibiotics [42, 43, 44], disinfectants, pesticides [44, 45], and polycyclic aromatic hydrocarbons (PAHs) [46]. Although the concentrations at which these CECs are present in the water loop are often too low (ng L^{-1}) to make fish meat unsafe for human consumption, they need to be monitored and new abatement strategies to prevent their accumulation in RAS are desired. In this context, NF membranes can play an important role, as they can typically retain most of these CECs Table 2. reports the rejections of NF membranes for different CECs, whose presence has been reported in aquaculture facilities, as obtained from the recent literature. All the NF membranes taken into consideration by this study show rejections values not smaller than 82% for RAS relevant CECs. Although the filtered water matrix influences both membrane selectivity and permeance [14], NF membranes can potentially be applied to treat a side stream in the RAS loop and therefore to keep CECs concentrations under control with negligible impact on the degree of water recirculation. Moreover, it will be more convenient to apply advanced oxidation processes (AOPs) to the mineralization of CECs in the NF concentrate than in the RAS loop, because it will require treating a smaller volume of water. Integration of NF and AOPs in RAS is becoming progressively attractive since an increasing number of integrated systems are reported and validated [47, 48].

3.3. Inorganic nitrogen and phosphorous

Fish tank effluents contain a large amount of nitrogen, arising from

Table 1
Rejection of the off-flavor compounds 2-methylisoborneol (2-MIB) and geosmin for commercial and lab-made nanofiltration membranes.

Membrane			Ref.
	2-MIB	Geosmin	
Polymeric			
NF 90 (DOW Filmtec)	75.7%	58.2%	[12]
DK4040F (GE Osmonics)	97%	96%	[13]
NF90 (DOW Filmtec)	92–99.9%	75–92%	[14]
NF270 (DOW Filmtec)	72–90%	65–85%	[14]
NTR7450 (DOW Filmtec)	0–30%	5–50%	[14]
Desal 5-DK (GE Osmonics)	95–99%	80–90%	[14]
Ceramic			
Alumina-Zirconia (lab-made)	–	65%	[15]

the catabolic processes of fishes [49]. RAS requires quick abatement of ammonia, because of the high toxicity on fish. For instance, ammonia concentrations as low as $30 \mu\text{g L}^{-1}$ are sufficient to induce mortality in salmonids [50]. NF technology has been recently proposed to remove ammonia directly from RAS, either as an alternative or as a backup to the present biological nitrification processes [51], the effectiveness of which is heavily dependent on microorganisms and water composition. Several types of commercial polyamide NF membranes were evaluated for ammonium removal in model RAS solutions [51], some of which presented the good ability for ammonia abatement. However, in this case, membrane selectivity is strongly dependent on the pH [52], since, as previously discussed, mechanisms of rejections are different for the neutral ammonia molecules and the ammonium ions [53]. Moreover, as mentioned above, NF membranes are likely to change salinity, the concentration of nontoxic organic matter, and the microbiological characteristics of the water, which might be not beneficial for the fish culture. On the other hand, NF technology can be applied to treat a side effluent downstream of the nitrification step, thus controlling the concentration of nitrite and nitrate ions in substitution to the biological denitrification process for intensive RAS. With this aim, model RAS effluents were tested over a NF 270 membrane (FilmTec, DuPont), which showed rejection of between 45 and 55% for both nitrite and nitrate ions [54]; although, membrane rejection for these species was dependent on water hardness and N concentration. This study suggested that the permeate of the membrane system can be returned to the fish tank, hence increasing the degree of recirculation.

NF technology has also been applied in combination with coagulation pre-treatment for the treatment of effluents from RAS culture of African catfish in absence of biological filters [55]. In this study, coagulation with either iron or aluminum was used to mitigate fouling of a lanthanum-modified bentonite ceramic NF membrane, thus increasing filtration efficiency. This integrated system allowed to achieve about 100% of removal of the total suspended solids and turbidity, and the abatement of above 96% for nitrites, while the reduction of the total nitrogen and total phosphorous were in the ranges 26.6%–41.3% and 34.7%–47.4%, respectively. These performances can be theoretically improved by selecting a different NF membrane. For instance, a 90% removal of polyphosphate from the concentrated feed was achieved by Leo et al [56]. with a commercial NF polyamide membrane, although separation performances were reported to be strongly dependent on the pH and ammonium concentration. Two problems for the implementation of this approach are the use of coagulant and the disposal of the coagulation sludge and NF concentrates. Indeed, coagulation with Al or Fe is often unwanted in aquaculture, as these elements may cause problems with fish gills [57]. However, it should be mentioned here that the NF membrane was highly effective in removing these elements from the solution [55] before recirculation of the water in the fish tank. In this integrated process, the inactivation and disposal of the sludges arising from the coagulant use should be considered, although the side-streams with a high concentration of ammonium and phosphorous could be used to produce fertilizers with economic and environmental benefits [58, 99–101].

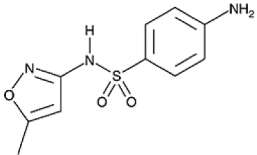
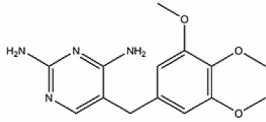
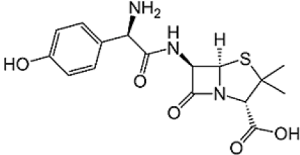
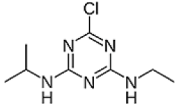
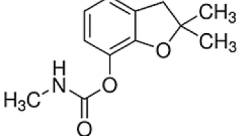
4. Upcoming NF membranes

Despite the last developments in NF materials and modules, various authors [17, 59, 60, 61] have identified three major challenges, which still curb the full-scale application of NF membranes in water filtration and therefore also in RAS. These challenges are: (i) permeability-selectivity trade-off, (ii) improving chemical and mechanical resistance, and (iii) the need for new functionalities such as anti-fouling, anti-microbial, and depolluting properties.

Various approaches have been proposed to overcome the permeability-selectivity boundaries of the current NF membranes, i.e. to increase their water permeability without compromising their selectivity. Most of the strategies are based on the alignment of sub-

Table 2

Rejection of the contaminants of emerging concerns, whose presence has been reported in RAS, by selected polymeric and ceramic NF membranes.

CECs	Membrane	Rejection	Ref.
Antibiotics Sulphamethoxazole	NF90 (Dow FilmTec)	>90%	[7]
			
Trimethoprim	NF90 (Dow FilmTec)	>95%	[8]
			
Amoxicillin	polyelectrolyte (lab-made) NF270 (Dow FilmTec)	>85% >86%	[9] [9]
			
Pesticides Atrazine	Desal 5-DK (GE Osmonics)	96%	[10]
			
Carbofuran	Ceramic (8YSZ) (lab-made)	82–89%	[11]
			

nanoporous channels orthogonally to the membrane surface. One example is the aquaporin-based artificial membranes [62, 63, 64, 65]. Aquaporins are membrane proteins, which can be found in the cells of bacteria, archaea, plants, and animals, where they are responsible for water transport. Their water channel has hourglass shape with a wide hydrophilic entrance and a narrow hydrophobic center which allow for single-file transport of water molecules. Synthetic water nanochannels [66] can also be prepared by self-assembling organic molecules to achieve enhanced permeability and processability compared to biological aquaporins. Among these structures are those obtained from the so-called imidazole-quartets, which can form chiral self-assembled with water channels <0.3 nm [67, 68]. These membranes present high salt rejection and permeabilities 75% higher than the commercial desalination membranes [69]. Synthetic water nanochannels with enhanced permeabilities compared to aquaporins were also obtained from self-assembly of m-oligophenylethynyl macrocycles [70] and pillararene derivatives [71, 72] [73]. Single-wall carbon nanotubes offer also nanochannels for fast water transport and therefore have been considered for water purification membranes [74]. Although many proof-of-concept studies have been showing that these approaches have the potential to overcome the selectivity-permeability trade-off of the current systems, nanochannel surface density, and alignment remain unsolved challenges for the real-scale production of this new generation of membranes. On the contrary, graphene oxide materials can be easily applied for coating large areas of membranes. Graphene oxide is a 2D material, which combines pristine graphene domains and oxidized regions containing a significant amount of epoxy, hydroxyl, and carboxylic groups, which make it processable from water solutions. In a consolidated membrane, graphene oxide (GO) sheets pile over the support surface, forming 3–5 Å water nanochannels between the pristine graphene domains, in which frictionless water transport can occur [75] [76]. Graphene oxide sheets staking are subject to degradation under real crossflow filtration conditions, but they can be stabilized by chemical cross-linking. Cross-linked graphene oxide membranes have

been reported to have good NF performances in terms of selectivity and water productivity [77, 78, 79]. Moreover, cross-linkers length and connectivity allow controlling the thickness of the interlayer space between the GO sheets, thus tailoring membrane selectivity, which is a paramount goal concerning the application in RAS. Indeed, in such systems, the membrane should retain unwanted compounds, while allowing part of the salts and nontoxic organic matter to permeate and thus to be recycled in the loop.

RAS deals with water streams containing a high concentration of dissolved organic matter and of dispersed microorganisms, which can eventually clog membrane pores and deposit on the membrane surface. An important feature for NF membranes in RAS, and food-related application in general, is indeed their ability to withstand frequent sterilization or cleaning cycles. In this context, the fabrication of NF membranes consisting of materials with outstanding mechanical and chemical stability, such as zirconium dioxide (ZrO₂) and silicon carbide (SiC), has also been attempted. Both materials are currently used to fabricate commercial MF membranes, which find application for instance in microbiological reactors [61]. However, these membranes are fabricated from pre-formed particles with procedures involving sintering at temperatures higher than 1200 °C. It is not possible to obtain NF membranes under these conditions, due to grain growth and pore expansion during densification [61]. Therefore, fabrication of ZrO₂ and SiC NF layers typically occurs via sol-gel deposition and from polymer precursors, respectively. In principle, both methods allow obtaining continuous NF layers with good adhesion to the support, and with no need for high-temperature sintering. ZrO₂ and TiO₂-ZrO₂ membranes with molecular weight cut-off (MWCO) lower than 300 [80] and 900 Da, respectively, were prepared by the sol-gel method [81]. SiC membranes NF membranes can be potentially fabricated by polymer precursors, such as allylhydrido polycarbosilane, which is converted to porous SiC by pyrolysis at about 750 °C [82]. The two major challenges in this procedure are to avoid penetration of the precursor in the pores of the membrane support and to avoid crack-formation in the active layer film

during pyrolysis. Both problems are eased by adding dense SiC particles to the coating solution, but membranes fabricated with this approach are characterized by low water permeability [82].

Among the major drawbacks of the membrane processes are fouling that reduces water productivity and membrane service time, and the creation of a potentially unsafe concentrate, which needs to be treated and disposed of. Both problems can be faced by integrating membrane technologies with advanced oxidation processes (AOPs), such as (photo) Fenton [83, 84], photocatalysis [85, 86], thermocatalysis [87], UV/H₂O₂ [88] etc. or advanced reduction processes (ARPs) e.g. UV/SO₃ [89]. The advanced oxidation/reduction can be performed as a separate step, or the membrane can be directly modified to perform advanced oxidation/reduction [90, 91]. For instance, a PVDF (polyvinylidene fluoride) NF membrane coated with TiO₂ nanoparticles and with a lacase enzyme was shown to be able to retain and degrade bisphenol A, as a model pollutant [92]. The promising performances of GO membranes in terms of water permeability and CECs rejection, coupled with the synergistic interaction of GO with photocatalytic materials, such as TiO₂, have led to develop various photocatalytic GO membrane concepts, which are able simultaneously to retain organics, to degrade CECs, and to mitigate fouling [93, 94, 95, 96, 97, 98]. These features are particularly interesting for potential RAS application, where NF membranes should simultaneously retain and degrade CECs and off-taste compounds. For example, Fig. 3a and 3b show the functioning and the structure, respectively, of a nanocomposite photocatalytic NF membrane consisting of graphitic carbon nitride (g-C₃N₄), TiO₂ nanoparticles carbon nanotubes (CNTs), and GO, which was used to treat a real aquaculture effluent. CNTs are used to facilitate water transport across

the membrane and to confer mechanical strength to the GO structure. At the same time, the photocatalytic g-C₃N₄/TiO₂ nanoparticles enhance membrane hydrophilicity and degrade retained organic species. Moreover, the fouled membrane can be regenerated and the permeate flow restored by exposure to UV light, as shown in Fig. 3c. When used to filter aquaculture wastewater, the functional membrane showed high retention for dispersed solids and organic molecules in the dark. Moreover, when the photocatalytic nanoparticles are activated by light exposure, the membrane performed better in terms of water productivity and the abatement of organic molecules and dissolved nitrogen species (e.g. ammonia), as shown in Fig. 3d.

5. Conclusions

Nowadays, nanofiltration is an established filtration technique and a wide range of polymeric NF membranes is available on the market. Moreover, new materials including polymers, ceramics, and hybrids are developed to push the permeability-selectivity trade-off of NF membranes beyond the present limits and to integrate new functionalities in the NF systems. The current literature has demonstrated that commercial membranes can already retain off-flavor compounds and the contaminants of emerging concern (CECs), which are relevant for RAS. Furthermore, NF membranes can partially reject ammonia, nitrite, and nitrate ions, and therefore it is possible to foresee their application in the control of inorganic nitrogen species in the RAS loop. Despite these features, NF technologies seldom have been proposed for integration in RAS. Few studies suggest NF either as a replacement or as a backup of the current biological processes in RAS [55, 57]. However, based on

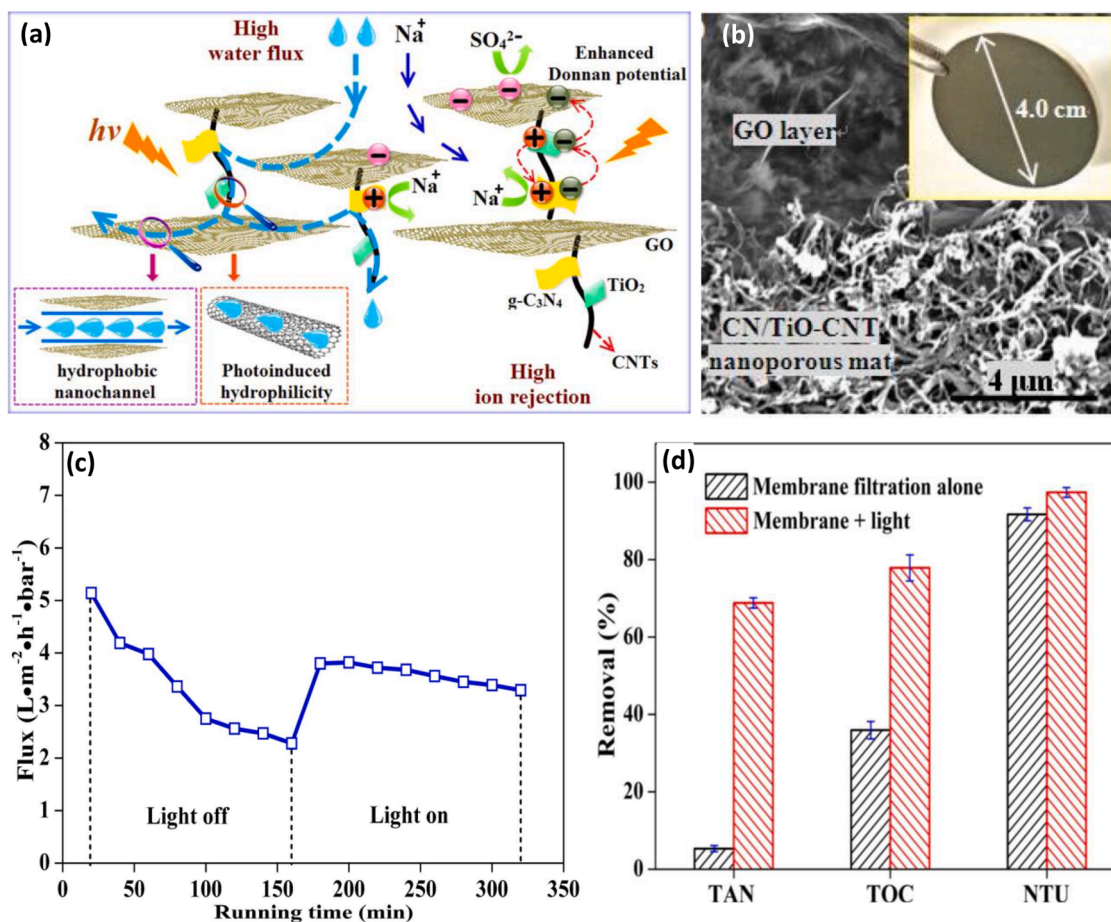


Fig. 3. Nanocomposite (g-C₃N₄/TiO₂/CNTs/GO) photocatalytic membrane used for filtering aquaculture wastewater: (a) scheme of the functioning; (b) membrane structure; (c) anti-fouling properties; (d) total ammonia nitrogen (TAN), total organic carbon (TOC), and turbidity (NTU) abatement from real aquaculture wastewater for the membrane in the dark (alone) or under light irradiation. Reprinted from Ref [95] with permission from Elsevier.

what we discussed in this review, this approach has various drawbacks. NF membranes typically work at trans-membrane pressures of 2–20 bar with permeate production rate from 1 to 10 L (m² L h)⁻¹ with specific energy consumptions > 0.2 kWh m⁻³. This creates concern about investments, footprint (large membrane area), and running costs of NF units in this context. Moreover, NF modules are sensitive to clogging, thus requiring pre-treatments such as microfiltration, ultrafiltration, or coagulation, which increase process complexity and costs. Last but not least, NF membranes partially retain salts and nontoxic organic matter and alter the microbiological compositions of the water in the loop, making this approach realistic only for a limited number of cases, for example, fishes growing in low salinity water.

On the other hand, a common procedure to avoid the accumulation of the unwanted compound in RAS is nowadays the substitution of part of the water in the loop with fresh water. Therefore, in a circular economy context, NF can be potentially used to filter a side stream of the fish tank effluent after biological processes for the abatement of CECs, off-flavor compounds, and unwanted inorganic species. The fraction of the water effluent treated by NF should be optimized, in such a way that the concentrations of these chemical species will remain below their critical limits when steady state is reached, and water pollutants are removed by NF at the same rate at which are formed in the loop. Moreover, to a certain extent, these hypothetical NF-integrated RAS systems will be able to deal with fluctuations of the composition of the water loop, as the NF unit productivity can be readily increased by changing the trans-membrane pressure. The permeate can be recirculated into the loop, thus increasing the overall degree of recirculation. The membrane retentate can be treated by AOPs to mineralize the unwanted organics and then recirculated in the system or used for other processes in the RAS facilities. This study shows that the current development in NF technology can potentially boost the integration of NF in RAS. Indeed, the upcoming NF units will present high water permeability thus allowing for a reduction of installation and running costs. Furthermore, the implementation of robust ceramic NF membranes will reduce the need for pre-treatments and facilitate membrane cleaning and sterilization, which is also an important aspect in RAS, where the microbiological characteristics of the water are important for fish well-being and taste. Last but not least, integration of NF with AOPs, as in photocatalytic membranes, will mitigate the problems related to the fouling in NF units and in principle will create permeate and retentate streams ready to be reused in the RAS loop.

In summary, the literature treated in this mini-review suggests that nanofiltration technologies are already at a maturity stage that allows their implementation in RAS for reaching a higher degree of recirculation, which is desirable based on the global water shortage and within the current transition towards truly circular and sustainable production systems. Moreover, NF integration in RAS is expected to be facilitated by the large number of innovations, which have been proposed for NF technologies in recent years.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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