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Removal of a cyanotoxins mixture by loose nanofiltration membranes applied in drinking water production

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ABSTRACT

Cyanobacterial toxins may threaten human health if their levels in drinking water exceed certain thresholds. Therefore, it is important for water works that use raw water sources prone to cyanobacterial blooms to have efficient barriers against such toxins. Nanofiltration (NF) is one potential barrier. The efficacy and mechanism of removing four cyanotoxins, namely microcystins (MCs), cylindrospermopsin (CYN), saxitoxins (STXs), and anatoxin (ATX), were studied at bench-scale using NF membranes commonly applied in Norwegian drinking water facilities. The average removal of the different cyanotoxins under the tested operating conditions ranged from 15 % to 96 %. The membrane with the lowest molecular weight cut-off (MWCO) of 0.3 kDa made of polyamide (PA) was deemed the most suitable for the removal of all studied cyanotoxins. A gradual improvement of rejection observed with the 2 kDa cellulose acetate (CA) membrane was linked to the formation of fouling on the membrane surface. Sulfonated polyethersulfone (SPES) membranes with MWCO of 1 and 3 kDa could not efficiently and consistently remove cyanotoxins, except for MCs. The rejection of MCs over time was over 80 % by the SPES membranes during two days of filtration. The influence of pressure and pH as relevant operating parameters was evaluated. However, the analysis of the cyanotoxin concentrations in the permeate indicated that the investigated NF membranes alone would generally not be able to meet the WHO guidelines for drinking water during a severe cyanobacterial bloom. Thus, incorporating other water treatment technologies should be considered to effectively remove cyanotoxins.

1. Introduction

One of the consequences of global warming and the degradation of aquatic environments by the growing urbanization, sewage discharges and the excessive use of fertilizers in agriculture, is the proliferation and dominance of harmful cyanobacteria [1]. Surplus of nutrients combined with factors such as increasing temperatures, reduced water volumes and more stagnant waters create conditions that favor the growth of cyanobacteria. During harmful algal blooms (HABs), the cyanobacterial masses deplete the oxygen and worsen light conditions in the water, produce taste and odor compounds, creating aesthetic problems and impairing consumptive and recreational use of water resources. Furthermore, at least 19 of the >50 known cyanobacteria genera are capable of producing lethal toxins known as cyanotoxins [2]. It has been estimated that between 25 and 75 % of cyanobacterial blooms are associated with toxin-producing events [3]. The ingestion of cyanotoxins is associated with symptoms such as skin irritation, vomiting, diarrhea, gastroenteritis and pneumonia [4,5]. In more severe cases, they may be fatal for both animals and humans, due to respiratory arrest and liver failure [5–7]. If present in drinking water, they will pose a potential risk to public health. For example, in Lake Taihu in China a bloom of cyanobacteria hampered the water supply for two million people for over one week [8].

If cyanobacteria and their associated cyanotoxins reach the intake of a water work, measures to reduce their presence prior to sending the water into the distribution mains may become necessary. The World Health Organisation (WHO) has provided guidance to alert levels for the presence of microcystins (MCs), cylindrospermopsin (CYN), saxitoxins (STXs), and anatoxin (ATX) in the raw water source [5]. Alert Level 1 that induce the need for measures requires 1 μg/L for MCs, 0.7 μg/L for

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CYNs, 0.3 μg/L for STXs and 3 μg/L for ATX. Alert Level 2 (12 μg MCs/L, 3 μg CYNs/L, 3 μg STXs/L and 30 μg ATX/L) indicates elevated risk to human health.

Cyanobacterial toxins can enter waterworks as intracellular (inside the cell) or extracellular (outside the cell) toxins. The latter is often the case for CYN; >50 % of CYN has been found as extracellular toxins in water [9]. Chemical precipitation combined with rapid media filtration, which is applied at many waterworks to remove natural organic matter, has been shown to be very effective in removing cell-bound cyanotoxins, but much less effective for the removal of extracellular cyanotoxins [10–12]. Extracellular toxins are in general more challenging to remove and require either physical removal by adsorption (using an adsorbent) or size exclusion (using e.g., membrane) or chemical transformation by oxidation (using e.g., ozonation or chlorination). Satisfactory results were obtained for dissolved cyanotoxins removal from water sources when using adsorption with PAC or GAC, and complete removal was achieved under optimal conditions [13–16]. However, the presence of competing organic matter in water, energy consumption during regeneration of exhausted adsorbents and high operational costs discourages its implementation as a pre-treatment at large scale.

The application of oxidants, such as chlorine or ozone demonstrated the potential for high degradation of dissolved cyanotoxins, particularly MCs [10,11,17]. At incorrect conditions, oxidation can, however, cause cell rupture and the consequent release of intracellular compounds [18,19]. Moreover, the use of high chlorine doses for the oxidation of extracellular and other natural organic materials will increase the risk of formation of carcinogenic trihalomethanes (THMs) to elevated levels [20], and should therefore be used with care.

In recent years, the application of membrane technologies has increased in the drinking water treatment sector due to their abilities to remove various pollutants as well as pathogenic microorganisms. Removal of algal cells and various cyanotoxins via membrane technologies has been increasingly studied at laboratory and pilot scale. While microfiltration and ultrafiltration can completely remove cyanobacteria cells, they are not a reliable barrier for dissolved cyanotoxins as they have a pore range larger than the size of cyanotoxin molecules in solution. Accordingly, very poor rejection rates have been observed when filtering different surface water sources [21–23]. Conversely, the pore sizes of nanofiltration (NF) and reverse osmosis (RO) membranes span the size of the cyanotoxin molecules and can therefore be expected to at least partially retain these compounds. The NF membrane has been proven to be effective in removing cyanotoxins with rejection as high as 99 % in some cases [21,24–26].

Despite the interest, little attention has been devoted to the effectiveness of NF membranes in removing cyanotoxins other than MCs. Therefore, this study aimed particularly to investigate for the first time the removal of a mixture of four cyanotoxins with different properties (MCs, CYN, ATX and STXs). All the cyanotoxins were spiked to the same test waters in order to mimic a naturally occurring harmful algal bloom, under controlled conditions using a bench-scale membrane system to study their rejection by selected NF membranes. Furthermore, publications on the impact of physico-chemical properties variation of the feed water on the interactions that occur between algal metabolites and NF membranes are rare. Ribau Teixeira and Rosa [52] demonstrated that calcium hardness and pH showed no influence on MCs and ATX removal. Nevertheless, the authors used a single and a tight NF membrane of 150 Da and the filtration experiments were carried out for a short time (app. 130 min) where the removal mechanism is rather governed by adsorption. To our knowledge, this is the first study which tried to assess the effect of operational conditions such as initial pressure and pH on the rejection of cyanotoxins and the fouling propensity of particularly loose NF membranes with relatively large molecular weight cut-off (MWCO) (usually >200–500 Da) by algal metabolites.

This is particularly relevant owing that loose nanofiltration is a promising technology for advanced treatment of drinking water, primarily due to the potentially high rejection of natural organic matter (NOM), high passage of mineral salts (particularly multivalent cations) and lower energy consumption compared to RO and tight NF membranes. On the other hand, most of the membrane-based waterworks in Norway were reported to use loose nanofiltration in a spiral-wound configuration as treatment process according to a recent survey done by Sivertsen et al. [34].

For this purpose, four loose NF membranes having different porosities, surface charges, and hydrophilicities and commonly used in Norwegian drinking water facilities were applied in this study using a crossflow filtration system.

2. Material and methods

2.1. Cultivation of cyanobacteria

Four cyanobacterial strains producing MCs, ATX, STXs or CYN were obtained from the Norwegian Culture Collection of Algae (NORCCA) as described in Table 1. The cultures were maintained in Z8 medium at room temperature of 23–24 °C under continuous light [27]. A description of the morphology of the cyanobacterial strains used in this study can be found elsewhere [28–32]. The growth of the NIVA-CYA 98 strain was noticeably very slow (see Fig. S1) and fewer MCs were produced, thus a long-term preserved freeze-dried (Leybold Heraeus Lyovac GT 2 freeze dryer, Labexchange, Germany) toxin sample from the same strain was used.

2.2. Extraction of cyanotoxins

The toxins (Table 2) were extracted when the cultures were still in their exponential growth phase (see Fig. S1). The extraction process included 4 cycles of freeze-thawing, subsequent ultrasonication to improve the recovery rate of cyanotoxins without impacting the integrity of toxins, and filtration (GF/F Whatman® glass fibre filters with nominal pore size of 0.7 μm) to isolate the toxins from the algal debris. The cell lysis method was optimized for cyanotoxins recovery (Table S1). Each freeze-thaw cycle consisted of freezing 1 L samples in polyethylene terephthalate (PET) bottles at −20 °C until cultures were frozen solid, followed by stepwise thawing in water baths, first at 23–25 °C for 2–3 h and then at 37 °C until no visible ice crystals remained in the samples. The ultrasonication was performed in amber glass bottles using a Branson 5510 ultrasonicator (Branson Ultrasonics Corp., Danbury, CT, USA) at 40 Hz and 185 W for variable times (120–1200 s) depending on the volume of the bottle and the type of algal strain that was sonicated: The applied sonication power ranged from 0.13 to 0.26 W/mL for STXs production and from 0.022 to 0.044 W/mL for CYN and ATX. The bottles were kept on ice during sonication to prevent overheating. The solutions were GF/F-filtered and transferred to PET bottles and frozen until use. Thawed samples were used as relatively dilute stock solutions when preparing the feed water. The freeze-dried MCs sample had a dry weight of 3.56 g and a MCs concentration of

Table 1
Overview of the strains used in this study and their corresponding produced toxins. Dominant toxins produced by each strain shown in bold.

Strain Nr.	Species	Cyanotoxin produced	Reference
NIVA-CYA 626	*Aphanizomenon gracile*	**CYN**	[29]
NIVA-CYA 851	*Aphanizomenon gracile*	**neoSTX** **STX** GTX5	[30]
NIVA-CYA 711	*Cuspidothrix issatschenkoi*	**ATX**	[31]
NIVA-CYA 98	*Planktothrix prolifica*	**[D-Asp3, Dhb7] MC-RR** Oxygenated [D-Asp3, Dhb7] MC-RR [D-Asp3, Dhb7]MC-HtyR [D-Asp3, Dhb7]MC-LR	[33]

Table 2
Dominants/main cyanotoxins included in this study.

Cyanotoxin	Abbr.	CAS No.	Chemical formula	Mw (g/mol)
[D-Asp3]-Microcystin-RR (Desmethyl-Asp3-MC-RR)	D-MC-RR	118389-26-7	$C_{48}H_{73}N_{13}O_{12}$	1024.19
Anatoxin-a	ATX	64285-06-9	$C_{10}H_{15}NO$	165.24
Cylindrospermopsin	CYN	143545-90-8	$C_{15}H_{21}N_5O_7S$	415.42
Saxitoxin	STX	35523-89-8	$C_{10}H_{17}N_7O_4$	299.29
Neosaxitoxin	neoSTX	64296-20-4	$C_{10}H_{17}N_7O_5$	315.13

5884 μg/g dry weight. The material was diluted with milli-Q water and GF/F-filtered before being transferred to PET bottles to constitute stock solution with no further extraction processing applied.

2.3. Preparation of feed water for the NF tests

10 L feed water was prepared by mixing the volumes shown in Table 3 of each toxin stock solution and filling up with 7.5 L tap water. Feed solutions were homogenized by a magnetic stirrer for 10 min before each test. The concentration ranges in the final feed are shown in Table 3.

2.4. Nanofiltration membranes

Four NF membranes with MWCOs from 0.3 kDa to 3 kDa were used in the NF tests; two hydrophobic (HYDRACoRe-10 and HYDRACoRe-50 from Hydranautics/Nitto) and two hydrophilic (TRISEP from Microdyn-Nadir and NF-270 from DuPont) membranes (Table 4). The HYDRACoRe and TRISEP membranes are common in Norwegian waterworks for production of drinking water [34], while the NF-270 membrane has previously been assessed for the rejection of cyanotoxins [24–26].

The clean water permeability (CWP) of the flat sheet membrane coupons prior to the tests followed the order of: HYDRACoRe-10 > NF-270 > TRISEP > HYDRACoRe-50 (Table 4). The trend agrees with the findings of Nair [35] who compared the CWP of eight NF membranes including, HYDRACoRe-10, HYDRACoRe-50, and NF-270. The authors observed highest permeability for HYDRACoRe-10 and suggested it was due to higher MWCO compared to the other tested membranes. Moreover, as shown in Table 4, NF-270 membranes also had a CWP twice that of HYDRACoRe-50 despite having lowest MWCO. This difference may be due to the smaller thickness of its active (skin) layer [36], since the CWP is related to pore size, porosity, and membrane thickness [37].

2.5. Filtration setup and experiments

NF tests were performed according to a standardized protocol using a crossflow filtration system as described by Krzeminski et al. [38]. The system was operated in recirculation mode, with both the permeate and the retentate fed back into a 30 L feed tank. Unless specified otherwise, all experiments were carried out at constant feed pressure of 8 bar. The pressure was adjusted to the desired value and when reaching steady state conditions (i.e., relatively constant pressure and flux levels), the filtration experiments were conducted for a predetermined duration (Table 5). The crossflow velocity (CFV) of the system during the filtration was 0.33–0.42 m/s.

Table 3
Amount of stock solutions used to prepare feed water.

Cyanotoxins	Amount of stock solution [L] used per 10 L feed water
MCs	0.3
CYN	0.8
STXs	1.0
ATX	0.4

Fresh membrane sheets with an effective membrane area of 99.4 cm^2 were used in each experiment. Prior to installation, the membrane sheet was wetted in demineralized water for at least 1 h. The membranes were flushed for 30 min with demineralized water and compacted overnight at the highest pressure (10–13 bar) applied during the subsequent membrane performance test (MPT).

The MPTs were done with demineralized water under similar conditions as the filtration tests and carried out for approximately 30 min both before and after each filtration experiment to determine CWP and asses the initial and subsequent loss in hydraulic permeability. After the initial MPT, 10 L feed water spiked with cyanotoxins was transferred to the feed tank.

Three sets of filtration experiments were carried out to assess the performance of each membrane and elucidate the impact of operation time, feed pressure, and pH on rejection of selected cyanotoxins. The operating conditions during the different NF tests are summarized in Table 5.

2.6. Mathematical modelling of fouling

In this study, blocking models were examined to determine the most significant fouling mechanism that may occur during filtration experiments. For this, we opted for the classic blocking laws proposed by Hermia [80] used for filtration at constant pressure. These models, defined for frontal filtration, are also reported to be used in the case of cross-flow filtration from previous studies [14,15,39,81].

They consist of four fouling models (Fig. S3) expressed by Eqs. (1)–(4) below, separately describing four different fouling mechanisms: (1) pore constriction, (2) complete blockage (3) intermediate blockage, and (4) cake formation.

The pore constriction model is based on the membrane pore size decreasing when foulant is adsorbed into the membrane pores by which the particles approaching the membrane are adsorbed and deposited on the internal pore wall, thereby reducing the pore volume. The complete blocking model occurs when the size of foulants is similar to the membrane pore size and assumes complete sealing of the membrane pores when foulants settle on the membrane surface. The intermediate blocking model is based on the probability of a pore being blocked by foulant coming toward the membrane. The cake formation model is the most severe fouling mechanism and assumes the formation of a deposit on the particles that already block the pores of the membrane.

$$J = \frac{4J_0}{\left(k_{pc}J_0 t + 2\right)^2} \tag{1}$$

$$J = J_0 exp(-k_{cb}t) \tag{2}$$

$$J = \frac{J_0}{k_{ib}J_0 t + 1} \tag{3}$$

$$J = \frac{J_0}{\left(2k_{cf}J_0^2 t + 1\right)^{\frac{1}{2}}} \tag{4}$$

where: J is the permeate flux (L/m^2.h); t is the filtration time (min); J0 is the initial permeate flux at $t = 0$; kpc, kcb, kib, and kcf are the model constants.

The degree of model fitness (R2) to the experimental results is used to identify the prevailing fouling mechanisms and the maximal R2 values indicated the best fitting model. To the best of our knowledge, blocking laws have never been used to describe the mechanism of fouling in algal organic matters enriched water. The fitting procedure in this study was performed with the Levenberg–Marquardt algorithm with OriginLab®.

Table 4
Characteristics of the NF membranes used in the study.

Membrane brand name	MWCO	Hydrophobicity	Material	CWP[f] L/m^2.h.bar	Iso electric point (IEP)	Zeta potential (mV)		
						pH 5	pH 7	pH 10
HYDRACoRe-50	1 kDa	Hydrophobic[a]	SPES[c]	6–7	None[g]	−85[g]	−85[g]	−85[g]
HYDRACoRe-10	3 kDa			20–23	None[g]	−85[g]	−85[g]	−85[g]
TRISEP 8040-SBNF-TSA	2 kDa	Hydrophilic[b]	CA[d]	9–11	/	/	/	/
FilmTec™ NF270	0.3 kDa		PA-TFC[e]	16–18	3[h]	−15[h]	−25[h]	−35[h]
					3[i]	−65[i]	−85[i]	−90[i]
					3.5[j]	−20[j]	−30[j]	−40[j]
					4[k]	−10[k]	−20[k]	−30[k]

[a] Information taken from Nair [35].
[b] Information taken from Pettersen [65].
[c] Sulfonated polyethersulfone.
[d] Cellulose acetate.
[e] Polyamide Thin-Film Composite.
[f] Measured in this study.
[g] Information provided by manufacturer.
[h] Data taken from Tu et al. [78] at Electrolyte background of 10 mM KCl.
[i] Data taken from Mouhoumed et al. [77] at Electrolyte background of 1 mM KCl.
[j] Data taken from Tang et al. [76] at Electrolyte background of 10 mM NaCl.
[k] Data taken from Lin et al. [79] at Electrolyte background of 0.001 mM KCl.

Table 5
Operating conditions, duration and time of samples collection during the different NF tests.

Test #	Membranes	Pressure	pH	Test duration	Time of sampling
		[bar]	–	[hours]	[hour]
1	All membranes	8	7	48	0, 2, 6, 24 and 48
2	All membranes	8	5, 7, 10	24	0, 24
3	All membranes	3, 5, 8, 13	7	24	0, 24

2.7. Sampling and in-line measurements

The operating pressure, permeate flux, pH, and conductivity in the permeate were continuously monitored during each test. The pH and conductivity in the feed were measured and recorded continuously throughout each test using a digital multi meter (WTW Multi 3430 set) submerged in the feed tank. Samples for cyanotoxins analyses were collected in duplicates from the feed tank and the permeate at predetermined filtration times as specified in Table 5. Samples were immediately frozen at −20 °C.

2.8. Analytical methods

The concentrations of the different toxins in the collected samples were determined in duplicate using the competitive enzyme-linked immunosorbent assay (ELISA) method using Eurofins Abraxis (CYN, MCs, ATX and STXs) ELISA kits. The samples were analysed according to the manufacturer's instructions and the absorbance of the colour generated at the end of protocol/analysis for each sample was evaluated at 450 nm wavelength using a Thermo Scientific™ Multiskan™ FC Microplate Photometer (Thermo Fisher Scientific, Oslo, Norway). The detection limits for ATX, CYN, MCs and STXs by the ELISA assays are 0.1, 0.04, 0.1 and 0.015 μg/L as, respectively. The concentrations in the samples were determined by fitting to a linear curve according to the manufacturer's instructions.

The hydrophilic dissolved organic compounds (HDOC) of the feed water were characterized using LC-OCD-UV (liquid phase chromatography with an organic carbon detector, an UV254 detector to quantify aromatics and an organic nitrogen detector) providing quantitative measurements of five different fractions; biopolymers humic substances, building blocks and low molecular weight (LMW) acids. The analysis was conducted at DOC-Labor GmbH (Karlsruhe, Germany).

3. Results and discussion

3.1. Feed water characteristics

The physical-chemical properties of the different cyanotoxins as predicted by the modelling tool MarwinSketch are summarized in Table 6.

The final concentrations of the different toxins in the initial feed are shown in Table 7. Since the same cultivation conditions, same toxin extraction protocols and the same apportionment of the toxin stock solutions were applied throughout the study, the final concentrations of MCs, STXs and ATX in the feed waters were relatively stable (5–15 % between min and max). However, the CYN concentrations varied much more, which is believed to be caused by variations in the specific production rate of CYN by the NIVA-CYA 626 strain.

Regarding the pH and conductivity of the feed water over the period of the study, they were in the range of 6.9–7.3 and 254–270 μS/cm, respectively. As for the concentration of dissolved organic carbon (DOC) in the feed water was 3.8 ± 0.62 mg C/L. A more detailed analysis of the DOC using LC-OCD-UV (Table 8) showed that the feed water contained approximately equal amounts (in weight %) of biopolymers, humic substances, LMW neutrals and building blocks (sub-products of humic substances), reflecting the intra- and extracellular remains after cell lysis that were left in the feed water after the GF/C filtration step. The low SUVA (specific UV absorbance) level (SUVA < 3) indicates that the feed water had a typical hydrophilic character [82].

3.2. Rejection of cyanotoxins during nanofiltration

The rejection of the various toxins by NF membranes is likely dependent on the molecular weight cut-off (MWCO) and the surface chemistry of the membrane as well as the relationship between these factors and the size and chemical characteristics (such as polarity, charge, and hydrophilicity) of the toxins.

The rejection rate (%) of cyanotoxins was calculated according to the following Eq. (5):

$$\text{Rejection rate } (\%) = \left(1 - \left(\frac{Cp}{Cf}\right)\right) \times 100 \quad (5)$$

where Cf and Cp are the concentration of cyanotoxins in the feed and

Table 6
Physical-chemical properties and geometrical descriptors of the cyanotoxins as predicted by MarwinSketch (version 22.22; www.chemaxon.com).

Cyanotoxin	$logD_{7.4}$	Charge			Projected diameter		Projected area	
		pH 5	pH 7	pH 10	Min	Max	Min	Max
	–	–	–	–	Å	Å	$Å^2$	$Å^2$
MC-RR	−5.43	0.10	0.00	−0.06	16.5	23.7	147	207
CYN	−2.66	0.00	0.00	−0.57	9.7	16.1	54	100
neoSTX	−3.73	1.98	1.35	−0.12	9.9	13.0	50	71
STX	−5.43	2.00	1.97	0.00	9.6	12.2	49	68
ATX	−0.62	1.00	1.00	0.14	7.7	9.9	35	53

Note: Demethylation is not expected to affect the overall charge state or hydrophilicity of MC-RR.

Table 7
Initial concentration ranges of cyanotoxins in the feed water used.

Cyanotoxins	Initial concentration in feed [μg/L]	Weight % of toxin in final feed
MCs	15.5–16.3	43–52
CYN	3.5–9.7	12–25
STXs	5.5–6.3	16–19
ATX	5.0–6.0	16–34

permeate side, respectively.

3.2.1. Rejection at different time of filtration

The mean rejection ratios of the four cyanotoxins obtained by the four NF membranes during the 48-hour test period are depicted in Fig. 1. The rejection of cyanotoxins by NF-270, TRISEP, HYDRACoRe-10 and HYDRACoRe-50 membranes was found to vary over time and for targeted cyanotoxin. The filtration period is divided into i) initial period of 0–2 h, ii) 2–24 h, and iii) 24–48 h, which are discussed separately for each cyanotoxin and membrane.

Within the first 2 h of filtration, when the NF-270 membrane surface is presumed to be slightly fouled as indicated by around 10 % reduction in flux (Fig. 4), the high initial rejection of MCs (94 %) as shown in Fig. 1a can mainly be attributed to the sieving mechanism. This is because the net charge of the dominant congener of MCs, D-MC-RR (Table 1), is zero at neutral pH (Table 6) and has a higher MW (~1000 Da) compared to the NF-270 membrane MWCO (300 Da). Meanwhile, rejection of MCs in early filtration stages by both loose HYDRACoRe membranes was observed to be above 92 %. However, the TRISEP membrane showed a lower rejection rate of 86 % (Fig. 1a) despite having a lower MWCO compared to the HYDRACoRe-10 membrane. Thus, the high initial rejection shown by HYDRACoRe membranes is presumably due to the existence of an affinity between the MCs and the SPES material. The affinity could be caused by an attraction between the positively protonated arginine cation of MC-RR and the strongly negatively charged sites on the membrane surface [40]. Furthermore, the hydrogen atoms from hydrophilic functional groups that can be present on polyethersulfone (such as sulfone, carboxyl, hydroxyl, and amine functions) can easily bind (create hydrogen bonds) with the electronegative nitrogen and oxygen atoms in the MCs structures. In fact, MC-RR has more nitrogen atoms than any other MCs congeners (3 more N atoms than MC-LR), which may provide more binding sites. On the other hand, the low hydrogen bonding ability of cellulose-based materials [41,42] could explain the lower affinity of the TRISEP toward this congener.

The initial rejection of the CYN by HYDRACoRe-50 was comparable to that given by NF-270 membrane, despite the difference (1000 Da vs. 300 Da) in their MWCO (Fig. 1b). Moreover, the initial CYN removal by HYDRACoRe-10 and TRISEP was around 70 % for both membranes (Fig. 1b). This indicates that the sieving effect was most likely not the dominant mechanism for rejecting this non-charged compound by HYDRACoRe and TRISEP (Table 6) at the onset. Ho et al. [43] reported that CYN exhibited adsorptive behavior similar to MC-RR adsorption by powdered activated carbon (PAC). The mechanism of CYN adsorption on SPES membranes is not well studied, but it may involve both hydrogen and electrostatic interactions. Like MC-RR, CYN is a zwitterion, which means that it has both positive and negative charges on different functional groups. The guanidino group of CYN can make both hydrogen and electrostatic interactions with the sulfonated and hydroxyl groups of SPES membranes.

ATX and STXs are both positively charged (Table 6) and can interact easily with the negatively charged membranes, resulting in high rejection observed in the initial stage, particularly by NF-270 and HYDRACoRe-50 membranes (Fig. 1c, d).

After 2 and up to 24 h of filtration, the rejection of MCs appears to be stable or only slightly decreased for NF-270 and both SPES membranes (HYDRACoRe-50 and HYDRACoRe-10), respectively (Fig. 1a). In contrast, the CYN rejection by both SPES membranes was characterized by a steep decrease ranging from 91 % to 63 % and 67 % to 30 % for HYDRACoRe-50 and HYDRACoRe-10 within this period (Fig. 1b), respectively. This decrease indicates an increase of CYN permeation through both membranes, seemingly attributed to saturation and gradual exhaustion of the membrane adsorption capacity for polysulfone based membranes [46,47]. It seems that the adsorption of CYN onto SPES membranes is a temporary effect that occurs in the initial stages of filtration and will not provide long-term removal of the toxin in practice. Moreover, the STXs and ATX rejection was generally found to continuously decrease during the period lasting from 2 or 6 to 24 h when using NF-270 and both SPES membranes (Fig. 1c, d). This decrease in rejection may be explained by the strong electrostatic attraction that occurred on the membrane surface and within the pore walls. This attraction facilitates the passage of STXs and ATX toxins into the permeate side by diffusion as the number of available sorption sites on the membrane surface and within the pores became saturated with the toxins. Generally, a higher membrane charge density decreases the rejection of positively charged solutes because of the suppression of dielectric exclusion due to the elimination of the fixed charges at the

Table 8
DOC level and relative abundance of algal organic matter (AOM) with different molecular size ranges in the used feed water as determined by LC-OCD-UV ($n = 6$).

DOC LC-OCD [mg/L]	Fractions [weight %]					SUVA [L/mg.m]
	Hydrophilic DOC (CDOC)					
	Biopolymers (>20 kDa)	Humic substances (0.5–1 kDa)	Building blocks (0.3–0.5 kDa)	LMW acids (<0.35 kDa)	LMW neutral (<0.35 kDa)	
3.8 ± 0.62	25.6 ± 4.5	23.3 ± 1.3	22.2 ± 2.4	1.5 ± 0.93	18.5 ± 2.3	2.15 ± 0.24

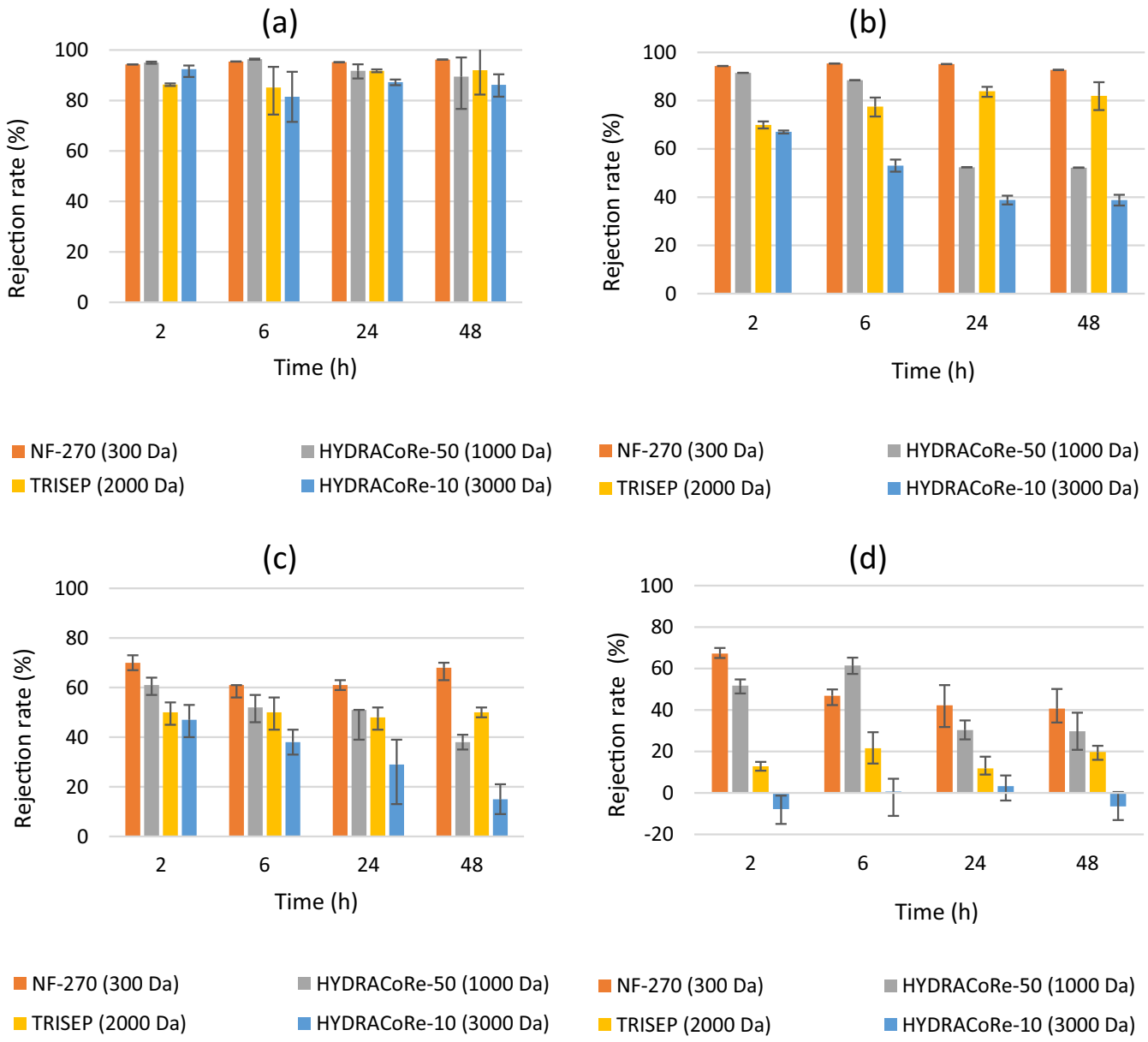

Fig. 1. MCs (1000 Da) (a), CYN (415 Da) (b), STXs (300 Da) (c) and ATX (165 Da) (d) removal rate (%) over the operation time. Error bars represent the upper and lower values of duplicate measurements.

membrane surface and the predominant role of the Donnan effect during the NF process [45].

During the latter phase of filtration (i.e., 24–48 h), the size exclusion through an enhanced cake formation mechanism started to influence the rejection of MCs and CYN by SPES membranes (Fig. 1a, b) and particularly the rejection of the positively charged cyanotoxins (i.e., STXs and ATX) by the NF-270 membrane (Fig. 1c, d). As the porosity reduced, the fouling layer probably became a second filtration medium and contributed to the rejection of the targeted contaminant [50,51]. For instance, the molecular weight of ATX (165 Da) is lower than the MWCO of all the NF membranes used in this study. Ribau and Rosa [52] suggested that ATX may associate with the functional groups of natural organic matters (NOMs) creating complexes, thus enhancing the ATX rejection through a size exclusion effect as can be seen in Fig. 1d. Still, removal rates close to zero along all the filtration periods were observed for HYDRACoRe-10 (Fig. 1d). This can be explained by the very large MWCO of this membrane (3000 Da) compared to the molecular weight of ATX of about 165 Da.

At the same time, the blockage of pores and/or the formation of a cake layer over the membrane surface could have offset (or counterbalanced) the impact of desorption mechanism to some extent, leading to CYN rejection increase up to 68 % and 51 % for HYDRACoRe-50 and HYDRACoRe-10 membranes (Fig. 1b), respectively. While the rejection pattern of mainly MCs and CYN was observed to vary over time by NF-270 and both SPES membranes as discussed above, the performance of TRISEP membrane in the rejection of these two cyanotoxins was distinct as their rejection was found to progressively improve over the 48 h of filtration (Fig. 1a, b). The increase was from 86 % to 97 %, 70 % to 82 % and from 40 % to 50 % for MCs, CYN and STXs, respectively. The CA material is reported to have only slightly negative surface charge [53,54]. Therefore, the improvement could be due to the formation of a fouling layer as more AOMs deposited on the membrane surface over time. This aspect could minimize the interaction between the TRISEP membrane and the cyanotoxins, resulting in a slow increase of rejection since the start of the filtration due to sieving effect.

Generally, the most effective membrane was NF-270, maintaining a

removal of over 90 % for both MCs and CYN and around 60 % and 40 % for STXs and ATX (Fig. 1), respectively, during the investigated filtration period. On the contrary, the least effective membrane for the cyanotoxins rejection, under the investigated conditions, turned out to be the HYDRACoRe-10. This may be related to its higher porosity. For membranes with higher porosity, the adsorptive sites on the membrane may become quickly saturated, limiting adsorption of compounds with high affinity to this membrane and consequently, leading to rapid breakthrough of compounds [53,55].

3.2.2. *Effect of pH on the rejection of cyanotoxins*

Cyanotoxins rejection was generally constant after 1 day of filtration. As a consequence, sampling of the feed and permeate was limited to 24 h for the purpose of comparing different membranes' rejections as shown in Table 5. Fig. 2, depicting the effect of pH on cyanotoxins rejection, shows that the rejection trends were not similar with changing pH, suggesting that there can be an association of two or more phenomena at the same time. These include steric exclusion, electrical exclusion and an affinity with respect to the target compound/toxin. According to Fig. 2, no significant variation occurred in MCs rejection as the solution pH varied from pH 5 to pH 10 in the case of NF-270 and TRISEP membranes, with an average efficiency of 94 % and 84 %, respectively. Moreover, the CYN rejection was quite stable when varying the pH and ranged between 85 and 88 % for all the membranes except the HYDRACoRe-10 membrane, where the rejection was between 60 and 70 %. This indicates that size effects of CYN and membranes are predominant. Furthermore, the rejection of STXs decreased only slightly from 95 % to 86 % by NF-270 membrane over the studied pH range (Fig. 2c). Therefore, it was assumed that the separation of MCs, CYN and STXs under the above-mentioned conditions occurs exclusively by size exclusion over the studied pH range.

The pH can also cause the dissociation of the functional groups of the solute and the membrane surface, changing their charge and thus influencing the electrostatic repulsion mechanism. The STX congener is reported to be predominantly di-cationic at pH 5 [16]. In addition, the zeta potentials of membranes (particularly for polyamide and cellulose acetate-based membranes) and the protonation of the different functional groups of the AOMs forming the fouling layer generally increase as the pH decreases. Accordingly, the STX rejection dropped gradually from 65 % to 36 %, 59 % to 49 % and 51 % to 25 % between pH 5 and 10, for HYDRACoRe-50, TRISEP and HYDRACoRe-10 membranes respectively. Shi et al. [16] suggested that both dispersive and H-bonding interactions highly dominated the strong adsorption of STXs observed at alkaline pH, indicating the weakening of electrostatic repulsion forces as the pH increases.

The electrostatic repulsion effect is also expected to have an

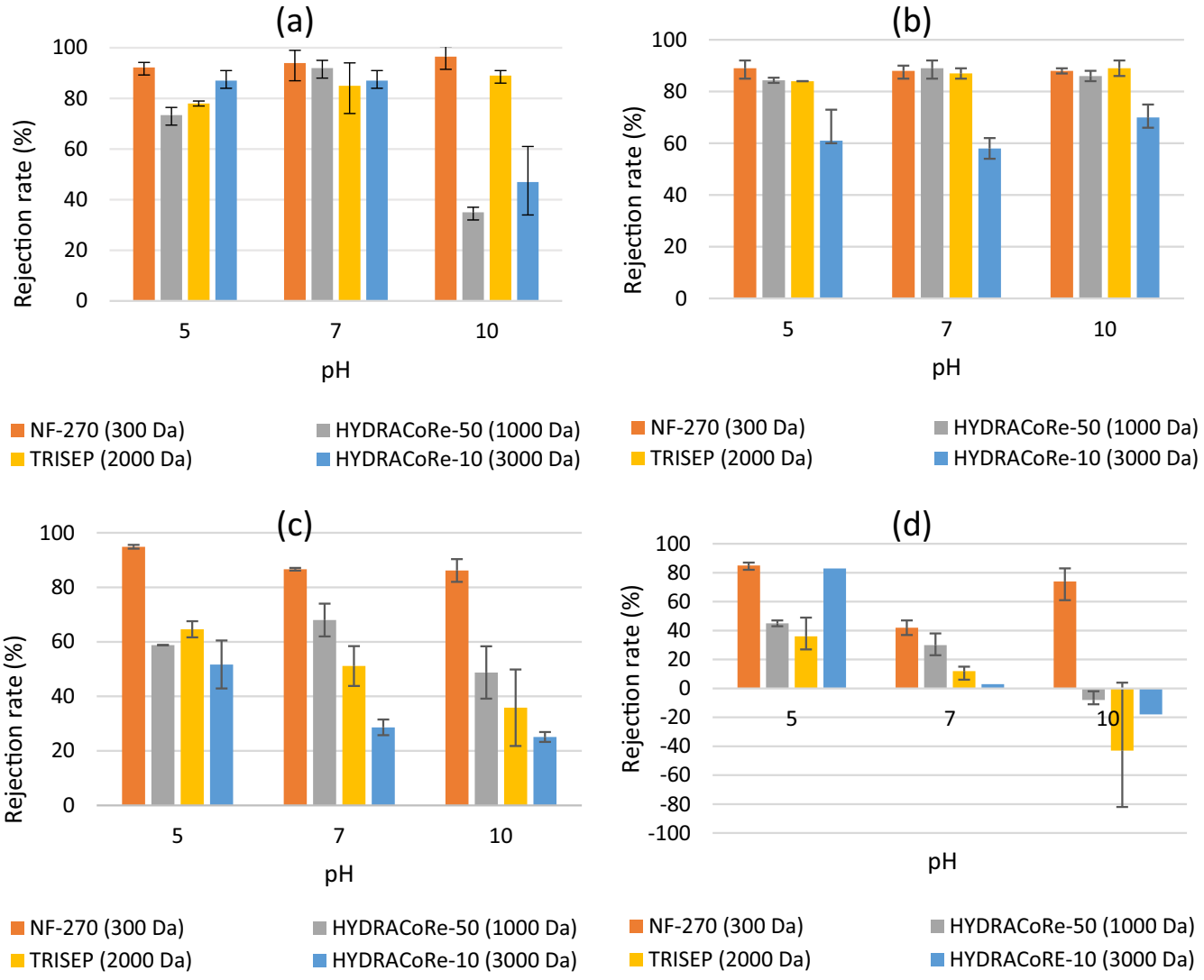

Fig. 2. MCs (1000 Da) (a), CYN (415 Da) (b), STXs (300 Da) (c) and ATX (165 Da) (d) removal rate (%) at different pH. Error bars represent the upper and lower values of duplicate measurements.

influence on the affinity between ATX and the selected membranes as the ATX rejection continuously decreased when pH increased from 5 to 10 (Fig. 2d). Valentine et al. [56] reported that the amine pKa of ATX is 9.4. This means that ATX could become neutral (Table 6) or develop a weak negative charge at pH 10. The rejection of ATX by these membranes at this pH is most likely governed by steric-hindrance since the molecular weight of ATX is much lower than the membranes' cut-off, and thus the global retention is low. The NF-270 membrane pores under alkaline/basic conditions are reported to shrink [73,74]. This may justify the increase in the ATX rejection from 42 % to 72 % noticed between pH 7 and 10 for NF-270 membrane (Fig. 2d).

The removal of MCs by HYDRACoRe membranes was lowest at pH 10 (Fig. 2a). A similar trend using also a SPES based membrane (600–800 Da) for MC-RL removal was observed [50]. The authors speculated that final pH variability in the feedwater between 4.8 and 6.4 might have affected the hydrophobicity of MC-LR in each run and therefore its removal efficiencies. A firm conclusion regarding this trend cannot be made in our case since the octanol-water distribution coefficient (logDow) of MC-RR remains stable between pH 4 and 12 [57].

Likewise, the other three studied cyanotoxins (i.e., CYN, STXs and ATX), considered also as strongly hydrophilic (i.e., LogDow < 1 (Table 6)) and highly soluble in water, are expected to show no change in their hydrophilicity as a function of pH. Given also that such data have not been reported so far, their partitioning behavior is not considered to be important across the studied pH range.

3.2.3. *Effect of pressure on the rejection of cyanotoxins*

The rejection of cyanotoxins by NF treatment under varying feed pressure revealed that the selected membranes reacted differently toward cyanotoxins when pressure was changed. First, the rejection performance of NF-270 remained almost stable at all applied pressures and for every single toxin, with approximate rejections of 94 % and 91 % for CYN and MCs respectively and 75 % for STXs (Fig. 3), meaning that NF-270 was least affected by pressure variation. As the removal of the selected cyanotoxins by NF-270 is controlled by size exclusion, concentrations in the permeate are expected to be independent of pressure. In the case of the TRISEP membrane, the rejection ratio remained relatively stable for MCs (86–98 %) while it increased for the other cyanotoxins with increasing pressure to 13 bar (Fig. 3a). The increase was from 50 to 90 % and 48 to 72 % for CYN and STXs, respectively. It is expected that an increasing pressure resulted in the TRISEP membrane structure becoming more compact, limiting the organic solutes passage through the membrane since the higher pressure would increase solvent permeability more rapidly than that of the solute. This enhances the entrapment of more cyanotoxins over time. On the other hand, it seems that both the SPES based membranes (HYDRACoRe-50 and HYDRACoRe-10) had a distinct behavior when filtering CYN and STXs, where a gradual decrease was observed when the pressure increased (Fig. 3b, c). The CYN rejection decreased from 52 % to 33 % between 8 bar and 13 bar when using HYDRACoRe-50 while it kept steadily going down from 52 % to 14 % in the case of HYDRACoRe-10 when the pressure went up from 3 bar to 13 bar.

In addition, the STXs rejection decreased from 52 % to 23 % and from 48 % to 42 % when increasing the pressure from 3 to 13 bar for HYDRACore-50 and HYDRACoRe-10, respectively (Fig. 3c). As previously discussed in Section 3.2.1, we hypothesized that CYN and STXs might have a tendency to adsorb to SPES membranes (such as HYDRACoRe). The reduction of CYN and STXs retention with increasing

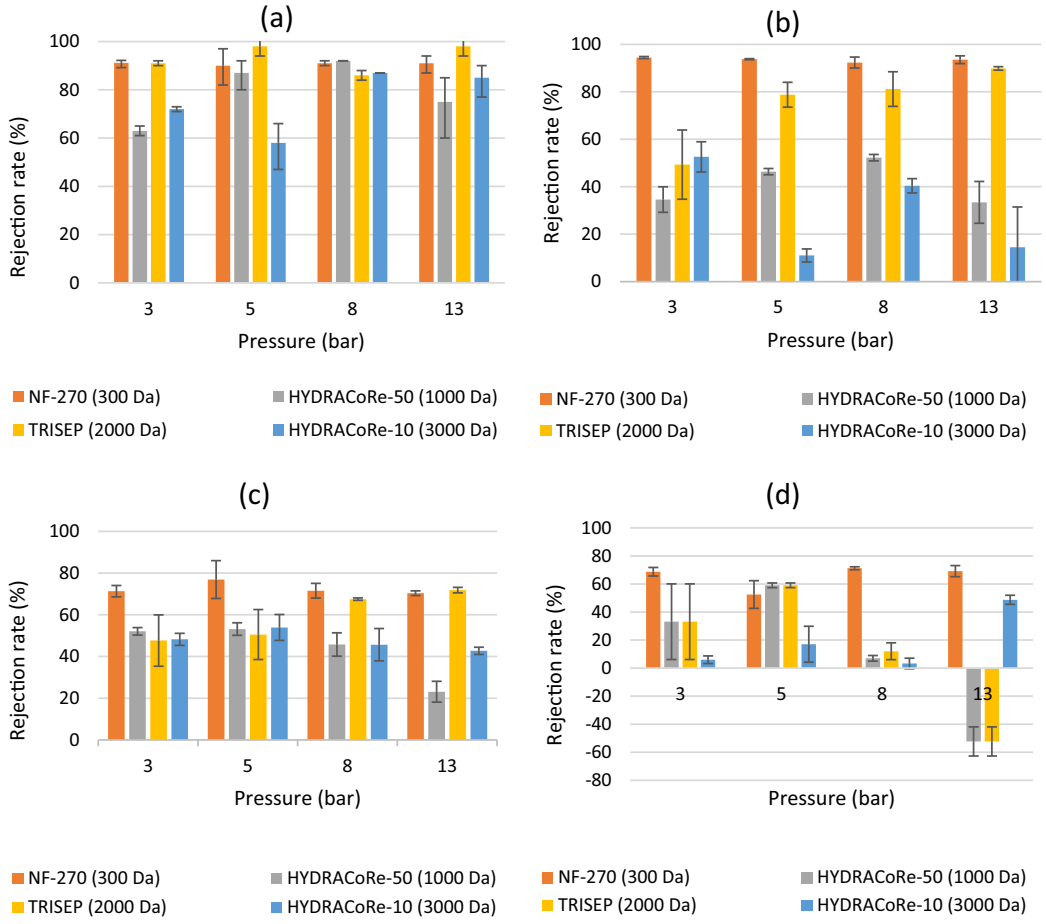

Fig. 3. MCs (1000 Da) (a), CYN (415 Da) (b), STXs (300 Da) (c) and ATX (165 Da) (d) removal (%) at different pressure. Error bars represent the upper and lower values of duplicate measurements.

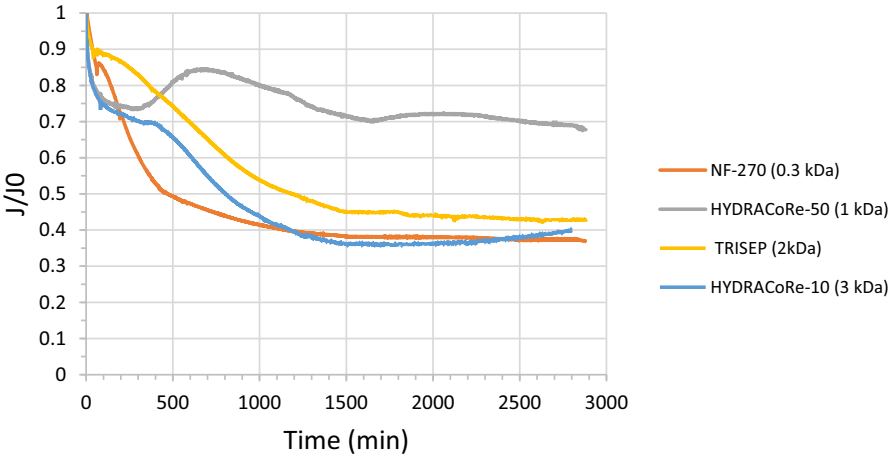

Fig. 4. Flux behavior for NF-270, HYDRACoRe-50, TRISEP and HYDRACoRe-10 membranes for the sample filtration (time evaluated: 2880 min; working pressure: 8 bar).

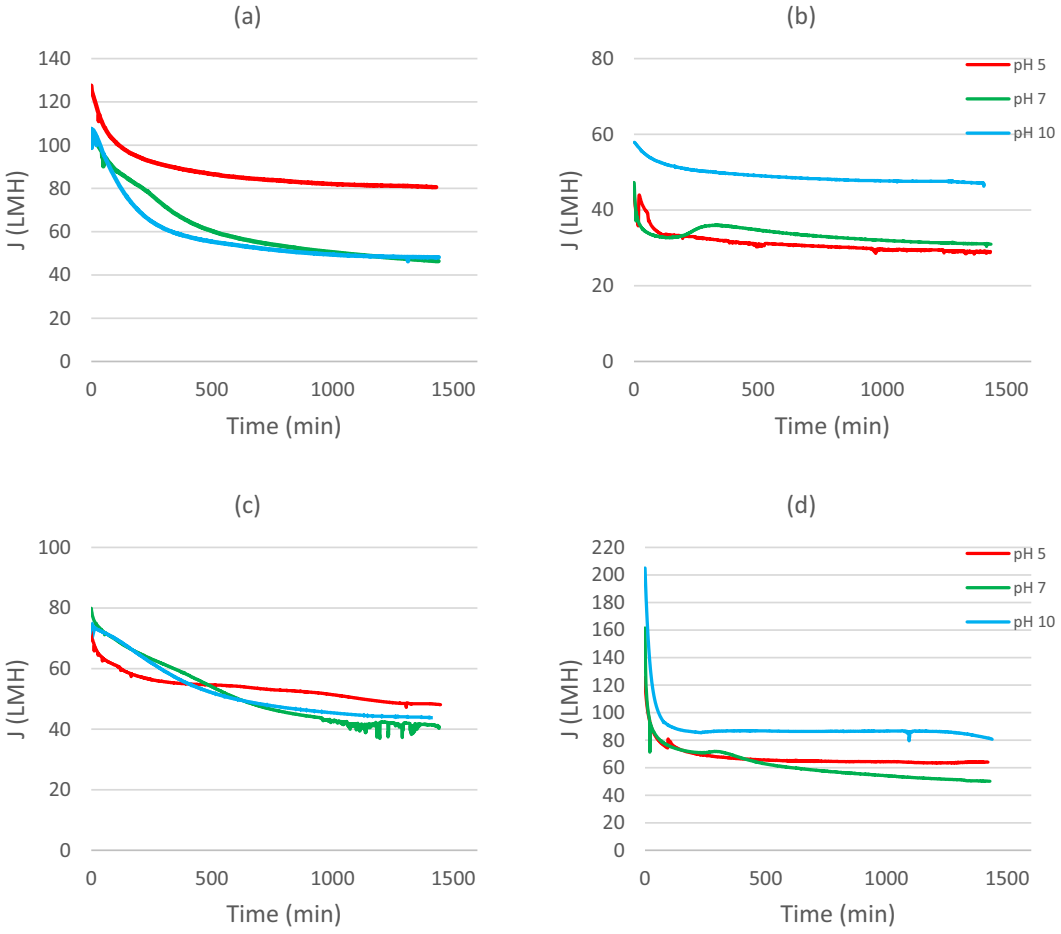

Fig. 5. Flux behavior for sample filtration over time for (a) NF-270, (b) HYDRACoRe-50, (c) TRISEP and (d) HYDRACoRe-10 membranes at different pH (time evaluated: 1440 min; working pressure: 8 bar).

pressure agrees with the hypothesis given by Nghiem et al. [58]. They postulated that the retention of organic solutes that strongly interact with membrane polymers may decrease with pressure.

Semião et al. [59] observed that higher pressure increases concentrations along the pore, thus favoring more adsorption mainly at the pore centre and exit. They suggested that this trend is a consequence of the higher concentration polarization produced by high pressures. As the rejection values of ATX fluctuated sharply, no clear trend can be observed regarding the impact of pressure on rejection of ATX (Fig. 3d).

3.3. Cyanotoxin concentration in the permeate

The NF-270 membrane provided the highest rejection rates and lowest concentrations of cyanotoxins in the permeate (Tables S2 and

S3). This was expected as the NF-270 membrane has the lowest MWCO (0.3 kDa) compared to the other membranes. On the other hand, the HYDRACoRe-50 membrane (1 kDa) was less efficient compared to the TRISEP membrane (2 kDa). This could be related to the inherent high adsorption capacity of this SPES-made NF membrane, eventually increasing the likelihood of diffusing these toxins to the permeate.

As MCs are the most widespread class of cyanobacterial toxins, of which MC-LR is the one of the most toxic and frequently detected congeners, they attracted the utmost care, and their removal is of high interest. However, none of the membranes evaluated in this study were able to eliminate the MCs below the WHO guideline value of 1 μg equivalent MC-LR/L [5]. The WHO guidelines were only fulfilled for NF-270 at an alkaline pH of 10 where a concentration of 0.56 ± 0.1 μg MC-LR eq/L was obtained.

Mody [24] and Dixon et al. [25] were both able to achieve the WHO guideline value of 1 μg MC-LR eq/L at different conditions when tested the polyamide NF-270 membranes to investigate the removal of MCs from surface water spiked with an MCs concentration of 10 μg MC-LR eq/L. The somewhat high concentrations obtained herein could be due to several factors. First, we observed a significant variability in the results of the samples collected at the same time as indicated by error bars representing the difference between the upper and lower values of duplicate ELISA measurements. Similarly, the average coefficient of variance for repeated independent analyses of the same sample was 29 % [60], in comparison with <5 % obtained with HPLC when analyzing MCs. Birbeck et al. [61] reported that cross-reactivity between different variants of MCs was the reason for the notable high concentrations of MCs compared to those obtained by high performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS). Another limitation of the ELISA technique includes overestimation, especially at low concentrations, where concentrations given by ELISA were 3 to 8 times higher than those measured by LC-MS/MS [62].

Using a water source with low content of NOM (DOC = 3 mg C/L), like in our study, an average removal above 90 % of CYN (16 μg/L) by NF-270 membrane was reported [25]. However, the rejection rates correspond to CYN concentrations in the permeate of 0.8 to 1.28 μg/L, above the WHO guideline value of 0.7 μg/L. At a feed concentration of app. 9.7 ± 0.7 μg/L, only NF-270 was able to produce a permeate with a CYN concentration below the WHO guideline value in this study. Upon lowering the initial feed concentration to 3 μg/L in test 2 compared to 9.7 μg/L and 7.4 μg/L used in test 1 and 3, respectively, a general improvement in the rejection of CYN was observed for all membranes and the concentrations in the permeate were below the guideline value of 0.7 μg/L for all membranes except HYDRACoRe-10 (Table S2). A lower feed concentration may reduce solute diffusion and subsequently induce a low solute penetration across the membrane.

Unlike other cyanotoxins, the guideline value of 3 μg/L recommended by the WHO for STXs in drinking water applies to acute exposure and should not be exceeded even for a short time [5]. Interestingly, in this study, the loose TRISEP membrane was able to just reach this threshold at higher pressures of 8 and 13 bar and at acidic as well as at neutral pH with STXs concentrations ranging between 2.5 μg and 3 μg STX eq/L. Applying initial concentrations of 3.45 and 6.81 μg STX eq/L for STX and neoSTX respectively and working under a pressure of 8 bar, Coral et al. [26] observed a decreasing STXs rejection trend when using a NF-270. This was likely related to the formation of a concentration polarization layer and a concentration of 3 and 6 μg equivalent STX/L was obtained in the permeate at the end of the filtration (i.e., after 180 min) for STX and neoSTX congeners, respectively. Having a lower molecular weight (200 Da) and a higher hydrophobicity, the NF-90 membrane turned to be more effective as a complete removal (100 %) of STXs was obtained throughout the filtration period.

ATX targets the nervous system and at very high levels of exposure can induce paralysis and death by respiratory failure [63]. While no official guideline is set for drinking water as there are no studies of chronic ATX exposure [5], a guideline of 3 μg/L has been suggested [64]. Nevertheless, none of the four membranes investigated could meet this value as shown in Tables S2 and S3. Using tap water spiked with 5 μg/L of ATX and a mixture of some MCs congeners, a very low concentration of 0.17 μg/L in the permeate after 48 h of filtration with tight (200 Da) Trisep TS80 4040 polyamide membrane was obtained [21]. After 72 h of filtration, no ATX presence was detected in the permeate.

Table 9 below summarizes the corresponding pH and pressure for test 2 and 3 respectively at which the concentrations of cyanotoxins in the permeate after 24 h of filtration were below or equal to the WHO limits.

3.4. Evolution of flux decline during cyanobacterial metabolite filtration

3.4.1. Flux evolution during the rejection test

The evolution of flux over time at unadjusted pH of 7 and pressure 8 bar (Fig. 5), revealed that the HYDRACoRe-50 membrane suffered less from fouling and had lower flux decrease (30 %) over the 48-h filtration period compared to the other membranes. Actually, the hydrophilic character of both NF-270 and TRISEP membranes and their interaction to the hydrophilic AOMs could be responsible for the 55–60 % flux decrease observed [26]. Moreover, the charge on the surface of the HYDRACoRe-50 membranes is strongly negative due to the presence of sulfonic groups, and it is expected that the strong negative charge of the membrane surface will increase the repulsion of the negatively charged organic compounds and reduce fouling. Another important characteristic of the HYDRACoRe-50 membrane is its smooth surface due to the incorporation of sulfonic groups in the top layer of the membrane [65,66]. The smooth surface can reduce the number of sites for the deposition of large organic macromolecules facilitating their back diffusion resulting in limited blockage of valleys, reduced potential for colloidal fouling, and less severe reduction in flux [67,68].

Although the two HYDRACoRe membranes used in this study have similar membrane material, charge, hydrophobicity and functional groups, a worse fouling expressed by 60 % in flux reduction was observed for HYDRACoRe-10 suggesting that physico-chemical surface properties of the membrane only play a minor role. From the evolution of flux J/J0 ratio (Fig. 5) we can deduce that membranes with higher CWP exhibited higher flux decline. This agrees with the findings from previous studies suggesting that membranes with high permeability generally display more severe fouling during filtration [67,69]. As more contaminants are brought to accumulate on the membrane surface, clogging of the membrane pores by particles that are similar to or smaller than the average pore diameter is believed to be faster. This effect was found to be more prominent for the more porous membranes [70,71].

3.4.2. Flux evolution during pH test

Fig. 5b and c show that the lowest flux decline during filtration with both NF-270 and TRISEP membranes was observed at an acidic pH indicating lower fouling tendency at low pH. Conversely, the two HYDRACoRe membranes manifested the highest initial and steady flux at pH 10 (Fig. 5a). The contradictory fouling tendency observed indicates that the removal mechanisms by hydrophobic interactions are more obvious and dominant at low pH for both NF-270 and TRISEP membranes.

Increasing charge effects (more negative zeta potentials) with increasing solution pH were found generally to enhance the removal of organic compounds and reduce fouling (flux decline), most likely through greater membrane surface repulsion as both organic compounds and membrane have higher negative charge density. The streaming potential measurements depicted in Table 4 showed the anionic HYDRACoRe membranes to have a constant surface zeta potential of −85 mV over a wide range of pH, meaning that the change of characteristics of the organic matters present in the solution was the main reason for the different fouling behavior observed. Therefore, lower flux decline obtained at higher pH can be probably attributed to

Table 9
Optimum pressure and pH conditions found in this study for producing nanofiltration permeates with cyanotoxins concentrations below the WHO limits.

Membrane	Test 2				Test 3			
	MCs	CYN	STXs	ATX	MCs	CYN	STXs	ATX
NF-270	10	5–10	5–10	5	None	3–13	3–13	None
TRISEP	None	5–10	5–10	None	None	None	8–13	None
HYDRACoRe-50	None	5–10	5	None	None	None	None	None
HYDRACoRe-10	None	None	None	None	None	None	None	None

Test 2: Pressure = 3–13 bar; pH = 7; Test 3: Pressure = 8 bar; pH = 5–10. WHO guidelines values for cyanotoxins in drinking water: MCs: 1 μg/L; CYN: 0.7 μg/L; STX: 3 μg/L; ATX: 3 μg/L.

deprotonation of the organic functional groups (e.g., sulfated functional groups of the AOMs polysaccharides), in which the macromolecules are more negatively charged and electrostatic repulsion with membrane surface is higher.

The hydrophilic polyamide membrane may have slightly negative net charge at acidic pH (Table 4). Hence, there might have been charge attraction rather than repulsion between the membrane surface and contaminants that led to more pronounced fouling of the membrane. The same is expected to occur for the hydrophilic cellulose acetate membrane. The protonation of the different functional groups of AOMs leads to lower water solubility and an increase in the feed hydrophobicity enhancing possibly the decline in the amount and proportion of strongly hydrophobic organic matter in the NF permeate when using hydrophilic membranes such as NF-270 and TRISEP [72]. Hence, the improved flux decline at pH 5 in the case of NF-270 and TRISEP membranes could mainly be related to the higher hydrophilic nature of their surface compared to the HYDRACoRe membranes. In others work, NF-270 displayed a decreasing trend of CWP with the increase of solution pH [73,74]. The authors assumed that acidic hydrolysis caused the increase of the number of hydrophilic sites on the NF-270 membrane surface under acidic conditions, which caused a significant increase of CWP. Under alkaline/basic conditions (i.e., high pH), hydration swelling of the membrane skin layer occurred resulting in shrinking (narrowing) of membrane pore size, and thus, reduced the permeation.

3.4.3. Flux evolution during pressure test

The membrane flux variations at various pressures are presented in Fig. S2. For all tests, an increased operating pressure clearly increased the initial flux of each membrane. However, a higher pressure applied often induced a more serious flux decline over the experiment duration, regardless of the membrane. This phenomenon stems from the fact that the filtered volume is greater at high flux, and therefore there are more clogging substances which are sent toward and deep inside the membrane pores, thus increasing the concentration polarization (and hence the boundary layer thickness, solute concentration and compaction). At high flux values, the convective driving force (permeation drag) can overcome the electrostatic repulsive force between the membrane and organic compounds (both negatively charged around neutral pH) and therefore enhance their attachment to the surface of the membrane. Conversely, when the convective driving force is weaker than the electrostatic repulsive force this may prevent attachment to the membrane surface, and this could explain why there is little or no clogging at very low permeation flux [67].

In addition, the NF-270 membrane was most affected by the variation of pressure (Fig. S2a). At pressures of 8 and 13 bar, this membrane experienced a pronounced flux decay during the first 6 h which was possibly caused by an extensive fouling layer formation on the membrane surface or within the pores. In the period of 6–24 h, the membrane flux began to alleviate and reached a stationary state indicating that the cake layer attains its equilibrium state. This happens when the permeate flux is compensated by the diffusive flux of the solutes from the membrane [75].

3.5. Fouling mechanisms during the pressure and pH tests

Tables S4 and S5 show how well the experimental results fit Hermia's models for different pH and pressure levels, respectively. The R2 values in Table S4 indicate that the four-blocking model had similar fit at each pH level studied when using HYDRACoRe-50 membrane. This suggests that multiple fouling mechanisms may occur simultaneously with this membrane. Likewise, no dominant mechanism was observed at pH 5 and pH 7 for HYDRACoRe-10 membrane. However, the cake formation model seemed to be slightly more influential at pH 10. On the other hand, the cake formation model fitted best at neutral and alkaline conditions for the two hydrophilic membranes (i.e., NF-270 and TRISEP).

The possible shrinking of the membrane pores under alkaline/basic conditions of these two hydrophilic membranes, especially for NF-270, as discussed earlier in Section 3.4.2, might have limited the pore plugging and the penetration of low molecular weight organics inside the pores, making the fouling mechanisms dominated mainly by a cake layer.

As shown by the R2 values in Table S5, the pressure variation within the studied range did not seem to affect the fouling mechanisms of HYDRACoRe-50 and TRISEP membranes. In contrast, for the two membranes with higher permeability (i.e., NF-270 and HYDRACoRe-10), there was a shift of mechanisms from a combination of blocking models at low pressures (3 and 5 bar) to cake formation model at high pressures (8 and 13 bar). These results imply that the different pressure levels applied did not have any significant effect on the fouling of HYDRACoRe-50 and TRISEP membranes. However, the high influx of foulants to the polyamide membrane (NF-270) and the SPES membrane (HYDRACoRe-10) caused more rapid accumulation of foulants on the surface, leading to pronounced flux decline, especially at high pressures. Nevertheless, the fitting results of the four pore blocking models were very poor ($R2 < 0.1$) for NF-270 and HYDRACoRe-50 membranes at pressures of 3 bar and 5 bar respectively.

4. Conclusion

This study investigated the removal of CYN, MCs, STXs and ATX present in mixture using four NF membranes commonly applied in the Norwegian drinking water facilities and other studies. The following conclusions are drawn:

- The NF-270 membrane turned to be the most effective of the tested membranes, achieving above 90 % rejection rates of studied cyanotoxins primarily due to sieving effect, while the primary mechanism of the cyanotoxins removal with the loose TRISEP membrane over the course of filtration is believed to be fouling development.
- HYDRACoRe-10 and HYDRACoRe-50 membranes were generally least efficient in rejection of cyanotoxins other than MCs and the >90 % CYN rejection observed at the beginning of filtration process by HYDRACoRe-50 was only a temporary effect most likely due to the existence of affinity. Afterward, a decrease of the corresponding retentions was observed once reaching saturation of the membrane.

- The degree of flux decline over a long filtration period followed the order of HYDRACoRe-10 > NF-270 > TRISEP > HYDRACoRe-50 and was found to be proportional to the initial clean water permeability of the membranes.
- The effect of pH on the ability of NF-270 and TRISEP membranes to reject MCs and CYN was insignificant, while working under acidic pH enhanced the flux and removal of positively charged cyanotoxins (i.e., STXs and ATX). Increasing the pH to 10 improved the flux decline for SPES membranes, but also resulted in the lowest MCs, STXs and ATX removal.
- Increasing the feed pressure from 3 bar to 13 bar resulted in higher flux decline over the experiment duration, regardless of the membrane and simultaneously enhanced the rejection of cyanotoxins in the case of the TRISEP membrane while no improvement was noticed for the NF-270 membrane. Nevertheless, an opposite removal trend was noticed for CYNs and STXs when working with the SPES membranes. This was linked to the existence of strong adsorption to the membrane polymer.
- The evaluated membranes were unable to produce permeates with cyanotoxin concentrations below the WHO guidelines for drinking water. Using tighter NF membranes with MWCO equal or below 200 kDa appears to be more suitable for simultaneous removal of multiple toxins. Otherwise, a hybrid membrane system, which incorporates a pretreatment, would be recommended.
- ELISA is a fast and cost-effective tool for cyanotoxins quantification, but the method reliability remains an issue.

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.

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.jwpe.2023.104694.

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