Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1160440

57 (2016) 26050–26062
November

Separation of nitrite and nitrate from water in aquaculture by nanofiltration membrane

Carlos Felipe Hurtado[a], Beatriz Cancino-Madariaga[b,*], Cristian Torrejón[a], Paula Pinto Villegas[c]

[a]*School of Marine Sciences, Pontificia Universidad Católica de Valparaíso, Av. Altamirano 1480, Valparaíso, Chile, Tel./Fax: +56 32 2274264; email: felipe.hurtado@pucv.cl (C.F. Hurtado)*
[b]*Mechanical Department, Universidad Técnica Federico Santa María, Av. Santa María 6090, Canal Chacao, Viña del Mar, Chile, Tel. +56 32 2277932; emails: beatriz.cancino@usm.cl, bcancinomadariaga@gmail.com*
[c]*INPROMEM (Research in Membrane Process), Carrera 241, Villa Alemana, Chile, email: paula.pv.84@gmail.com*

Received 19 November 2015; Accepted 25 February 2016

ABSTRACT

Recirculating aquaculture systems (RAS) normally use nitrifying bacteria to control nitrogen compounds. However, some problems from the nitrification process may arise, creating toxic concentrations for the fish. Nanofiltration (NF) could be the answer for this fluctuation, controlling the quality of water in the required level. In this work, we analyze the capacity of NF 270 membrane to reject nitrite and nitrate ions in two different concentrations and using two different water hardness, based on the concentration detecting in RAS in Chile. In the first test, NF membrane was tested at different transmembrane pressures (TMP) in two types of model solutions, formed by nitrite or nitrate dissolved in deionized water, testing two concentrations, high (H) and low (L), according to the concentration that are dangerous for fish in RAS. In this test, NF 270 membrane rejected approximately 75% of nitrite or nitrate, at the best TMP (19 bar). In the second test, the membrane was tested using nitrite, nitrate, and different qualities of water, based on the water hardness produced by different salts, found in RAS in Chile. This water quality was formulated and classified as soft and hard. There, bivalent cations present in the water are rejected in more than 70% and monovalent cations passed easier through the membrane with a rejection between 50 and 80%, depending on N-molecules concentrations and on the water hardness. We can conclude that this phenomenon is related with the hydrated energy and Donnan exclusion. The rejection of the N-molecules in those conditions depends on the concentration and the hardness of the water. For soft water hardness, the rejection was between 40 and 60% for the N-molecules and for hard water quality, this percentage is in the range of 25–40% at 20 bar of TMP. With these results, a membrane process was proposed to separate the nitrite and nitrate from hard water including different steps that should be tested in a prototype.

Keywords: Nitrite removal; Nitrate removal; Nanofiltration; Aquaculture

---

*Corresponding author.

1. Introduction

Water in aquaculture is becoming a scarce resource, especially in recirculating aquaculture systems (RAS). RAS are often designed in terms of fish biomass or stocking density, which determines the amount of feed provided in tank water, or the feeding rate [1]. Increasing stocking density implies more waste from fish and feed provided to tanks, which in turn, tends to increase the concentration of anions and cations involved in nitrogen and carbon cycles [2], as well as dissolved minerals [3]. The main compounds are ammonium (cation), nitrite (anion), and nitrate (anion) [1,4]. RAS normally uses nitrifying bacteria to control ammonium compounds, but some problems appear producing a high degree of fluctuation in the efficiency of the nitrification process [5–7]. One of the problems in biofiltration processes is an uncertain growth of colonies of nitrifying bacteria in the bed biofilters, which can reduce their activity due to sudden changes in water temperature or pH (values less than 7) [8]. The increase in soluble organic matter, or the presence of certain chemicals used in the treatment or control of infectious diseases fish under cultivation, such as formaldehyde [9] and oxytetracycline [10], among others, also affect adversely. If biofilters do not work properly, they could increase the level of ammonia and nitrite, thereby causing the death of fish.

In these systems, two different species of bacteria in two consecutives stages are used. *Nitrosomonas* to convert ammonium (NH_4^+) to nitrite (NO_2^-), and *Nitrobacter* to convert nitrite to nitrate (NO_3^-), [7,11,12]. Nitrification is the oxidation of ammonia to nitrite and nitrite to nitrate by autotrophic bacteria [13] and this fixed-film biological process occurs in biofilters [14,15].

Aquaculture operations often rely on natural colonization of nitrifying bacteria in production systems. This natural method works well for initiating a biofilter, but can take a relatively long time (e.g. 4–8 weeks) to establish a healthy and viable population of both ammonia-oxidizing and nitrite-oxidizing bacteria. Such stresses can inhibit nitrification rates resulting in spikes in either ammonia and/or nitrite. Nitrite-oxidizing bacteria are known to be especially sensitive to stress [16], and in this regard, recovery times of these bacteria can last for several weeks, increasing the concentration of ammonia and nitrite. Then nitrite is an intermediate compound and is toxic because it affects the hemoglobin capacity to transport oxygen and produces an unbalance of electrolytes [17,18]. Nitrite can produce, depending on the concentration in water, different diseases like stress in fish and diminished growing rate, damage the internal organs of the fish or diminish the tolerance to diseases [19,20]. Since nitrate cannot be oxidized, any further via nitrification, nitrate will accumulate in the system. There are two common methods for reducing nitrate, using water exchanges or implementing denitrifying biological reactors [21,22]. Nitrate is the final product and a less toxic compound in the nitrification system. Nitrate concentrations in water between 200 and 500 mg/L are tolerated by fish [23–25]. Nitrate level in RAS are normally maintained with the daily renovation of water [17].

Besides this, biofilters have several problems which include between others, excessive sludge production, unstable performance, and nitrate accumulation [26]. In this scenario, RAS are increasing in the world, and normally only a small percentage of water is treated, less than 1% [1,27]. However, when the water is scarce and there are health problems for the fish using untreated water, the idea to increase the amount of water processed and its recovery became more appealing.

However, the high levels of nitrates in water are not only a problem for RAS, also in drinking water, the high concentration in the reservoir worldwide is very problematic [28]. For drinking water, several processes to remove nitrates from water have been proposed, as biological (biofilter), chemical, catalytic, and membrane process also, as Donnan dialysis, electrodialysis, electrodeionization, reverse osmosis, and ion exchange [28]. Recently, comparison [29] between electrodyalysis and reverses osmosis (RO) for nitrate removal in drinking water indicates that nitrate removal in the RO osmosis was 90% more than that of the electrodialysis system.

Nanofiltration (NF) is a new membrane process comparing with reverse osmosis, and the effect of the ions rejection is a new aspect to consider, besides the lower energy demand, because the lower transmembrane pressure (TMP) necessary for the mass transport phenomena.

Regarding this aspect, we analyzed in previous studies the retention of ammonium for different membranes of NF and RO, concluding the high flux was produced by NF 270 membrane, with no significant differences in retention capacity [2,7]. The ammonia retention was explained due to the ionic force and Donnan effect [30]. However, when different kinds of water i.e. different hardness in the water are used, they could produce an influence over the ionic force or over the surface of the membrane, changing the results. Because of this, in this work are included different qualities of water as well as different levels of nitrite and nitrate concentration that we found in the RAS in Chile (see Table 1).

Table 1
Composition and hardness of the water used as hard water and soft water found in the RAS in Chile

Salts and quality parameters of water	Soft water (mg/L)	Hard water (mg/L)
$NaHCO_3$	48	192
$CaSO_4{\cdot}2H_2O$	30	120
$MgSO_4$	30	120
KCl	2	8
pH	7.2–7.6	7.6–8.0
Total hardness	40–48	160–180
Alkalinity expressed in mg $CaCO_3$/L	30–35	110–120

Thus, the aim of this paper is to propose a membrane process to separate nitrate and nitrite from sweet water. For this, it is necessary to know the behavior of the NF 270 membrane in terms of their flux, TMP, and retention or rejection capacity respect to nitrite and nitrate, both dissolved in different types of water quality and with different levels of concentration.

2. Materials and methods

All experiments were carried out in a continuous and non-recirculation mode (Fig. 1), i.e. under non steady-state conditions, using three flat stainless steel high pressure cells. The high-pressure cell arrange was developed and designed by INPROMEM (Research in Membrane Process). To drive the flow, a high-pressure Speck GmbH pump (Germany) working between 0 and 140 bar was included, and to control temperature, a Chiller, Resun, model C-1500 was used [30]. In the non-recirculation mode, the permeate flow is discharged of the system and the concentration of the species or molecules increases through time, i.e. the membrane is used to concentrate the nitrite and nitrate. Permeate flow was determined by direct permeate mass registration over time, using an electronic scale (Radwag 220, Poland). Data acquisition was carried out using a computer.

Each high-pressure cell has a membrane diameter of 5 cm, with a membrane area of 1.65×10^{-3} m^2 and the tank volume is 5 L.

The membrane used in all the experiments was NF 270, commercial nanofiltration membranes from Dow

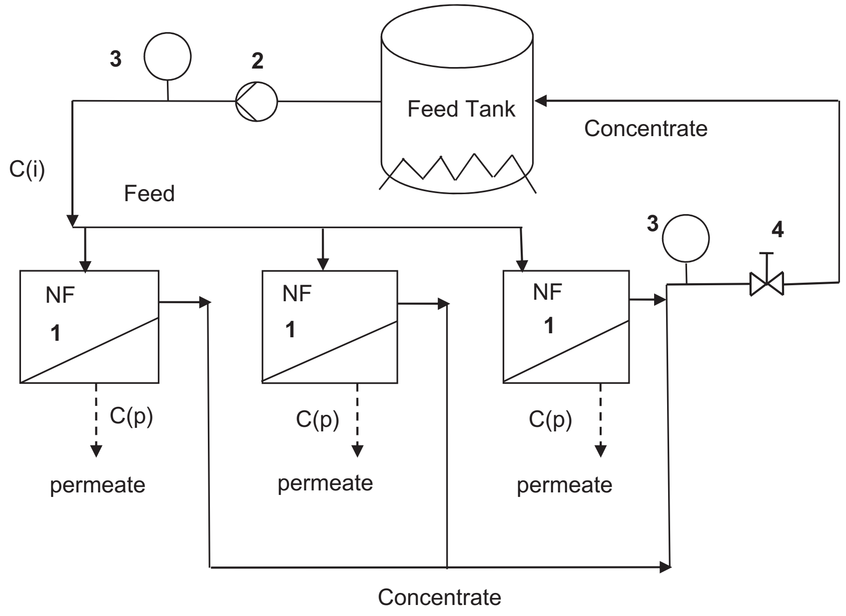

Fig. 1. Schematic representation of the membrane system arrange. *C*(i) is the concentration of the species in the feed of the cell arrange. *C*(c) is the concentration of the species in the retentate and *C*(p) is the concentration of the species in the permeate: (1) high pressure cell, (2) high pressure pump, (3) manometers, and (4) valve.

Table 2
Characteristics of the NF 270 membrane

Cut-off (g/mol)	Contact angle (°)	Zeta potential (mV)	Isoelectric point	% Retention	Refs.
120	N/A	(at pH 10) −35	3	40–60% CaCl2, 97% $MgSO_4$	Gerardo et al. [31]
200–400	N/A	N/A	N/A	>97%	Mohammad et al. [32]
150–200	32.6 ± 1.3	(at pH 9) −41.3	<3; 3.3; 3.5; 5.2	>97% (MgSO4)[a], 56.9 ± 3.8 (NaCl)	Sjömana et al. [33], Tang et al. [34]
N/A	N/A	(at pH 7) −23	3.5	40[c]	Nghiem et al. [35], Nghiem et al. [36]
N/A	30	−6.8; −15.0[b] at pH 7	3.3	N/A	Tanninen et al. [37]

Notes: N/A: not available.
[a] $MgSO_4$ 2,000 mg/L at 4.8 bar.
[b] Measured by streaming potential measurements through pores (first value) and along the surface (second value).
[c] At 3,000 mg/L NaCl and 4.5 bar.

Liquid Separations, USA. Table 2 shows the principal characteristics of the NF 270 membrane, that consists in a semi-aromatic piperazine-based polyamide as active layer with polysulfone as support material, negative charged at the pH range used in this study [30]. Maximum operate pressure is 41 bar [31]. Membrane pre-treatment was described in Cancino Madariaga et al. [30].

The permeate of each cell was evaluated to confirm the reproducibility of the experiment. Following parameters were evaluated in the permeate and concentrate during time at different TMPs as well as the mass flow of the permeate.

Anions of NO_2^- and NO_3^- were obtained from $NaNO_2$ and $NaNO_3$, which are in the form of crystallizing salts. Three kinds of hardness of water were tested, where the composition and the limits of the NO_2^- and NO_3^- concentration were obtained for this study, from different analyses of water quality in RAS in Chile.

(1) deionized water is the so-called “Model water” in this paper,
(2) standard freshwater with low concentration of salts, called “soft water”, (see Table 1 for the composition), and
(3) standard freshwater with high concentration of salts, called “hard water” (see Table 1 for the composition).

The initial volume used for each experiment was 5 l and the conductivity of deionized water used in the experiments was lower than 5 μS/cm.

For each set of measurements described below, samples of 200–300 ml were taken. The permeate volume was accumulated during the process time until completing this sample volume. Each set of measurements considered the following analysis:

Nitrite concentration: was determined in form of NO_2^- through Hach model DR3900 spectrophotometer. Using the program 371N and Hach Method 8507 diazotization.

Nitrate concentration: was determined in form of NO_3^-, this anion was determined using ion selective probe nitrate, model ISENO318101, Hach.

Sulfate concentration: was determined in form of SO_4^{2-} through Hach model DR3900 spectrophotometer. Using the program 680 Sulfate and Hach Sulfaver 4 turbidimetric method.

Sodium concentration: this was determined using cation selective probe sodium ion Na^+, ISENa38101 model, Hach.

Alkalinity: this was determined in form of $CaCO_3$ through the model Hach DR3900 spectrophotometer. Using the program TNT 870 barcode.

Total hardness and calcium hardness: were determined in form of $CaCO_3$ through titration method, included in the HA-DT mark the Hach kit. The method 8213 and 8204 for calcium hardness was used for total hardness, both using EDTA solution.

pH and temperature: determined by the pH meter and temperature probe, connected to desktop Spercientific 860031.

Conductivity: this was determined by the conductivity probe connected to the meter desktop Spercientific 860031.

2.2. Description of the experiments

The study was separated into three phases (Table 3), where different feed solutions were formulated to analyze the behavior using the NF 270 membrane at different operating conditions.

Phase I tests corresponded to NO_2^- or NO_3^- (depending on the test), dissolved in deionized water. The concentration of the N-compounds were selected to represent two extreme concentrations named low and high concentration.

High and low concentration of NO_2^- and NO_3^- were based on a compilation of the main field RAS currently in operation in Chile (obtained for this study). The lowest and highest concentration of NO_2^- were 0.5 and 3.5 mg/L respectively and for NO_3^- is 5.0 and 150 mg/L respectively.

Phase II, corresponds to NO_2^- and NO_3^- dissolved both at low concentration and similar experiences dissolved at their high concentrations, in soft water (see Table 3), i.e. the high concentration of NO_2^- is dissolved together with the high concentration of NO_3^-, and the same for the low concentration.

And Phase III, corresponds to NO_2^- and NO_3^- dissolved both at low concentration and similar experiences dissolved at their high concentrations, in hard water (see Table 3), i.e. the high concentration of NO_2^- is dissolved together with the high concentration of NO_3^-, and the same for the low concentration.

For all experiments, temperature and pH were 15 ± 1°C and 7, respectively, as these parameters are the most common for salmon in RAS in Chile [12], and as they are also considered standard conditions [38].

The NO_3^- or NO_2^- rejection percentage (R) was calculated using Eq. (1):

$$R = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100 \tag{1}$$

where C_p and C_f represent the NO_3^- or NO_2^- concentrations (mg/L) in the permeate and concentrate, respectively.

The characteristics of the membrane and the behavior of the membrane at different solutions and operation conditions can be described by Eqs. (2) and (3) [30]:

$$J = \frac{\text{TMP}}{\mu(R_M + R_{FT})} \tag{2}$$

where J is the flux, TMP is the transmembrane pressure, R_M is the membrane resistance, R_{FT} is the total fouling resistance including the concentration–polarization resistance, and μ is the viscosity.

$$R_T = R_M + R_{FT} \tag{3}$$

R_T is the total membrane resistances.

When the solution is pure water, or deionized water, R_{FT} is zero, and only R_M exists. In this case, R_M can be obtained directly using the slope of the J vs. PTM curve, as shown in Eq. (3):

$$R_M = \frac{1}{\mu \times m} \tag{4}$$

Table 3
Description of the experimental phases, concentration of NO_2^- and NO_3^-, TMP and ionic strength for nitrate and nitrite in these solutions

Phase	Water type	Concentration (mg/L) in solution		Concentration level of N-compounds[a]	TPM (bar)	$I^{b,c}$ (mmol/kg)
		NO_2^-	NO_3^-			
I	Model	0.5	0	L	6–19–30	0.011
		3.5	0	H		0.076
		0	5.0	L		0.081
		0	150.0	H		2.421
II	Soft	0.5	5.0	L		2.386
		3.5	150.0	H		4.791
III	Hard	0.5	5.0	L	17–19–20–30	9.268
		3.5	150.0	H		11.674

[a] L: low concentration, H: high concentration.

[b] Calculated using Eq. (5).

[c] Including Na^+ effect for model water type.

With m as the slope of the curve J vs. PTM, μ is the viscosity of water at 15°C, that is 0.001 (Pa s).

R_{FT} can be calculated with the R_M value and performing different tests for the solutions of interest using the slope of the J vs. PTM curve, and solving Eqs. (2) and (3).

To obtain the data necessary to solve Eqs. (3) or (2), the flux (J) vs. time for each experiment was determined at different TMPs [30]. All the analyses were made in triplicate and the results were processed statistically using the commercial software centurion Statgraphics Centurion XVI. The statistical analysis was made using ANOVA or Kruskal–Wallis analysis according to the distribution of the data [39].

Eq. (5), describe the ionic strength (I), according to Atkins and De Paula [40]:

$$I = \frac{1}{2}\sum m_A (Z_A)^2 \qquad (5)$$

where m_A is the molality of the molecule A and Z is the ion charge.

3. Results and discussion

3.1. Results for Phase I: model solution

Fig. 2 shows the results for the flux during the time at different TMPs at low and high concentration of NO_3^- and NO_2^- in deionized water. For 19 and 30 bar, the flux is constant during the time without significant differences (p-value ≥ 0.05), using ANOVA analysis, and for 6 bar is the same but using the Kruskal–Wallis analysis. At 6 bar, there is not a normal distribution and in this case, ANOVA cannot be used and is used Kruskal–Wallis. However, there are statistical differences in the flux at different TMPs, according to the statistical Tukey HSD with 95% of confidence.

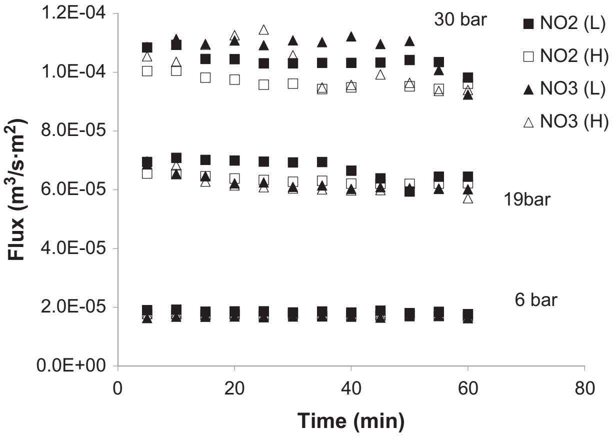

Fig. 2. Permeate flux during the time for low (L) and high (H) concentration of NO_3^- and NO_2^- in model solution at different TMPs.

Fig. 3 shows the slope for the flux vs. TMP obtained using Eq. (3) and the comparison for pure water and the NH_4^+ results obtained in previous works [30]. Table 3 shows the results for the R_T, R_{FT} and the coefficient of determination (R-square) obtained from the slope of the J vs. PTM curve. R_M was obtained for these experiments and there is a very small difference with the value given in a previous work [30]. In Table 4, the percentage of fouling corresponds to the ratio between R_{FT} and R_M, multiplied per 100 to obtain the percentage. In the table, we can appreciate that the higher fouling is produced by NO_3^- (H), followed by NO_2^- (H), that means high concentrations of ions give more fouling resistances, and low concentration of ions produce lower fouling, that is predictable because there are bigger numbers of molecules in solution. However, the high concentration is considerable different for both molecules (150 mg/L for NO_3^- and 3.5 mg/L for NO_2^-). NH_4^+ (with 6.5 mg/L) is in the same range and similar value than in lower concentrations.

Fig. 4 shows the R% of NO_2^- and NO_3^- in the membrane at different TMPs. We can observe for NO_3^- there is no direct relationship between the concentration and the R%. Instead for NO_2^-, the rejection is higher at high concentration. That could be explained by the ionic strength (see Table 3), i.e. the rejection percentage increase as salt concentration is lower, because the ionic strength is higher. Ionics strength was calculated according Eq. (5). Similar behavior was observed by Abidi et al. [41]. High concentration of salts, for a negative charged membrane, means there are enough counter ions (Na^+) on the surface of the

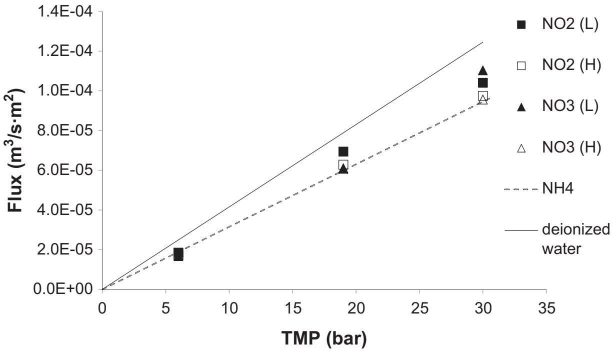

Fig. 3. Permeate flux vs. TMP for low (L) and high (H) concentration of NO_3^- and NO_2^- in model solution, comparison with NH_4 solution in pure water and pure water flux.

Table 4
Results for R_T, R_{FT}, R_M, and the coefficient of determination obtained for the solution of NO_3^- and NO_2^- in deionized water, and NH_4^+ in pure water

N-molecules	R^- square	R_T (m^{-1})	R_{FT} (m^{-1})	% Fouling
NO_3^- (H)	0.9991	3.1531E+13	7.4355E+12	30.86
NO_3^- (L)	0.9837	2.8320E+13	4.2252E+12	17.54
NO_2^- (H)	0.9975	3.0925E+13	6.8304E+12	28.35
NO_2^- (L)	0.9946	2.8654E+13	4.5586E+12	18.92
NH_4^+ ([a])	0.9940	3.0359E+13	4.5588E+12	17.67
Deionized water (or R_M)	0.9969	2.41E+13	0	–

[a] Results for NH_4^+ were obtained using their respective R_M of 2.580E+13 m^{-1}, from Cancino-Madariaga et al. [30] with a concentration of 6.5 mg/L.

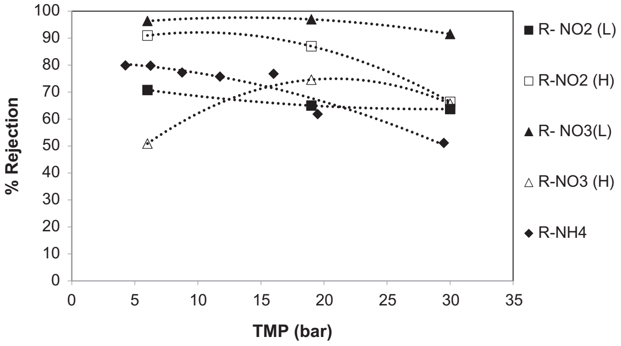

Fig. 4. Rejection percentage of the NF 270 membrane vs. TMP for low (L) and high (H) concentration of NO_3^- and NO_2^- in model solution, comparison with NH_4 solution in pure water.

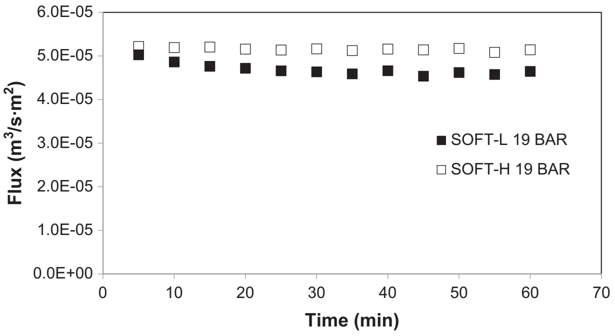

Fig. 5. Permeate flux during the time at 19 bar, for the NO_3^- and NO_2^- solution at low (L) and high (H) concentration in soft water.

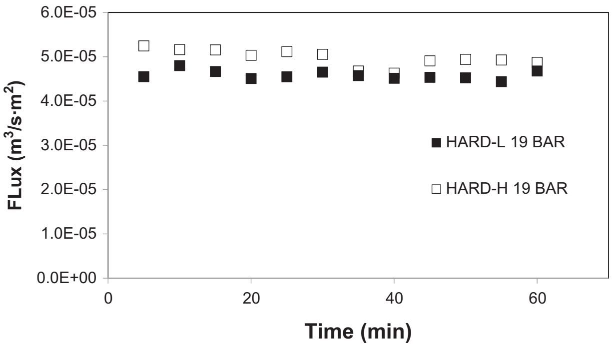

Fig. 6. Permeate flux during the time at 19 bar, for the NO_3^- and NO_2^- solution at low (L) and high (H) concentration in hard water.

membrane, neutralizing the membrane-charged surface, reducing the retention by repulsion of negative ions. As was explained in Cancino-Madariaga et al. [30], the NF membrane separation is produced by negative-charged membrane and because the ions and contra ions are in equilibrium, when the effect is neutralized or the critical TMP is achieved, the ions can move across the membrane governed by the other mechanisms involved [30]. That could explain the behavior for NO_3^- with the high concentration (150 mg/L). For the $NaNO_2$, this phenomenon is different because the high concentration (5 mg/L) is lower compared to the $NaNO_3$ (150 mg/L), and probably is not enough to neutralize all the negative charge on the membrane surface.

3.2. Results for Phase II and Phase III: soft and hard water test

Figs. 5 and 6 shows the Flux during the time for NO_3^- and NO_2^- solutions in soft water respectively at 19 bar of TMP. Similar behavior (not shown) were observed for the others TMP of Table 3. With the data of flux for each TMP according to the procedure explained in the previous section for model solution, Figs. 7 and 8 were obtained. In the soft and hard water, the highest flux are produced in solution with the high concentration of N-molecules.

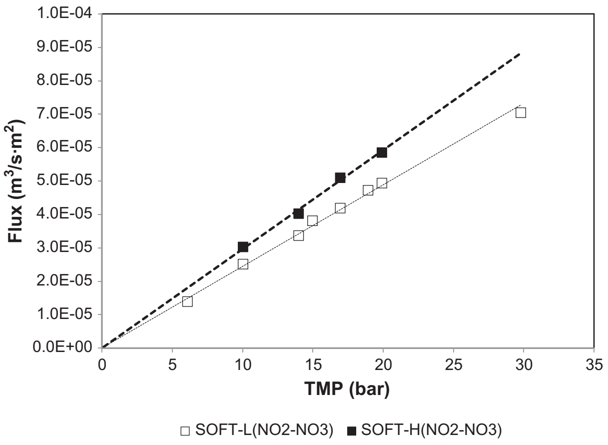

Fig. 7. Flux of the NF 270 membrane vs. TMP for the solution of low (L) and high (H) concentration of NO_3^- and NO_2^- in soft water.

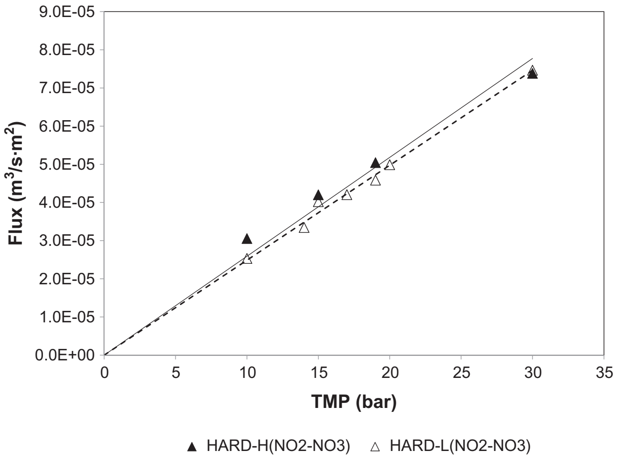

Fig. 8. Flux of the NF 270 membrane vs. TMP for the solution of low (L) and high (H) concentration of NO_3^- and NO_2^- in hard water.

These behaviors could be attributed to the ionic strength which were the high concentration of counter ions produced at high concentration of salts, results in a higher ionic strength. The difference between high and low concentration is lower in hard water solution when compared with the soft water solution, which could be produced by the effect of the salts and ions concentration in the solutions (hardness). In high concentration of salts (hard water), the concentration of $NaNO_3$ does not have a more relevant effect in the flux, comparing with the soft water. In the statistical analysis showed, there are no significant differences (p-value ≥ 0.05), according the ANOVA test or Kruskal–Wallis. Similarly to the model solution, there are statistical differences in the flux at different TMPs, according with the statistical Tukey HSD with 95% of confidence.

Different mechanisms are involved in the NF process, related with the membrane self and with the solution to treat. These mechanisms include size exclusion, charge effect (Donnan and dielectric exclusion), and different diffusivity and solubility of the ions in the solution [30,36,42]. When ions are present in the solution, several effects occurs involving electrostatic interaction [43]. Ions properties like molecular weight, stoke and hydrated radii, hydrated energy, ion valence are relevant to analyze the process. In the case of one or two types of molecule in solution, there are some models to calculate their properties [40]. However, when the solution is more complex, as is shown in Table 1, the real behavior and the thermodynamic of this mixture will be completely different with respect to pure ions in the solution and also depends on the concentration of them [44]. This difference can be appreciated, for example, comparing the calculated ionic strength for NO_2^- in Table 3 and in Table 5 for 0.5 mg/L, that is 0.011 and 0.006, respectively. Table 5 was calculated for the pure ion in water (NO_2^-) not considering the Na^+ ion added with the salt $NaNO_2$ and Table 3 was taking account of this Na^+. In addition, when more molecules are present in water, higher value of ionic strength is obtained (see Table 3). There, the soft and the hard solution present 2.386 and 9.268 mmol/kg, respectively.

For NF process, especially for NF 270 that is a loose membrane [36], pores and ions in water solution present interactions that govern the mass transport through the membrane. The ions are hydrated by a shell of dipolar water molecules, affecting the mobility because the hydrated radii is bigger than the stoke radii [43]. The hydration energy is correlated with these effects. According to Richards et al. [43], high hydration energy is present in ions with smaller ionic radii which have larger hydrated radii with slow transport through the membrane. However, other authors show differences respect to this rule [42] (see Table 5); indeed, higher hydration energy is present in divalent ions. Table 5 shows the stoke radii for Ca^{2+} is ca. 1.6 times than for Na^+ and the relation between the hydrated energy is ca. 3.9 times. Moreover, Figs. 9–12 show higher R% for Ca^{2+} comparing with Na^+. Therefore, the charge of the ion is important also in the hydration energy.

Figs. 9 and 10 show the retention percentage of N-molecules at different TMPs for low and high concentration, respectively, and the R% for the other ions present, in soft water. In this water, Mg^{2+} and Ca^{2+} ions have the higher R%, but the R% is decreased for

Table 5
Molecular weight, stoke and hydrated radii, hydrated energy, and ionic strength of different molecules in solution of deionized water

Ion	MW (Da)	Stokes radii [32] (nm)	Hydrated radii [32] (nm)	$I^{a,b}$ (mmol/kg)	Hydrated energy [42,45] (kJ/mol)
Na^+	22.99	0.184	0.358	N/A	406, 407
CO_3^{2-}	59.98	0.266	0.394	N/A	N/A
K^+	39.10	0.125	0.331	N/A	N/A
Cl^-	35.45	0.121	0.332	N/A	378, 376
Mg^{2+}	24.30	0.347	0.428	N/A	N/A
SO_4^{2-}	96.02	0.230	0.379	N/A	1,047, 1,138
Ca^{2+}	40.08	0.310	0.412	N/A	1,584
NO_3^-	61.97	0.129	0.335		317, 329
5 mg/L				0.041	
150 mg/L				1.21	
NO_2^-	45.98	0.114	0.330		331[c]
0.5 mg/L				0.006	
3.5 mg/L				0.038	
NH_4^+	18.00	0.125	0.331	0.181	307

Notes: N/A: not available.

[a] Calculated using Eq. (5).

[b] Without Na^+ effect for NO_2^- and NO_3^-.

[c] Simulated value given by Richards et al. [43].

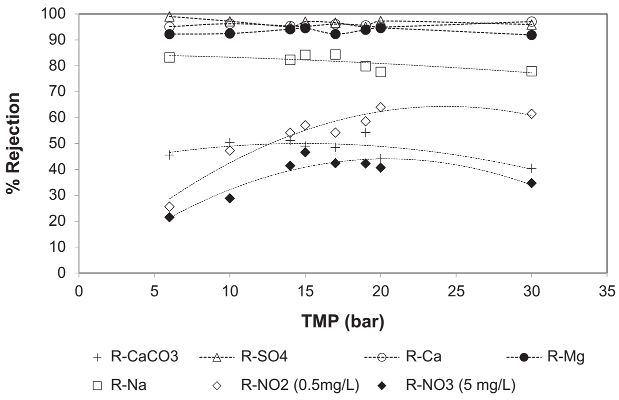

Fig. 9. Rejection percentage of the NF 270 membrane vs. TMP for low (L) concentration of NO_3^- and NO_2^- in soft water.

high concentration of the N-molecules. However, the SO_4^{2-} is always with a high R%. Mehdipour et al. [42] obtained similar effect for SO_4^{2-}, where the rejection for SO_4^{2-} by the membrane is always high, that can be explained by their high hydration energy (see Table 5).

For the N-molecules, the rejection depends on their concentration and the TMP. The R% increase with TMP until 20 bar approximately (see Fig. 10). That means for soft water at 20 bar approximately, the better R% is between 40 and 60% independent of the concentration of nitrite and nitrate.

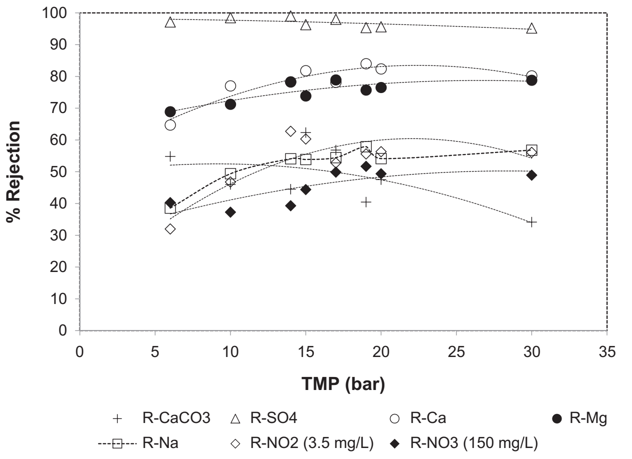

Fig. 10. Rejection percentage of the NF 270 membrane vs. TMP for high (H) concentration of NO_3^- and NO_2^- in soft water.

Commercial NF membranes are normally characterized by the retention capacity of $MgSO_4$ in water at one TMP. NF 270 membrane tested by the manufacturer (Dow Chemical, datasheet information), reports a retention of 99.3% at 2,000 mg/L of $MgSO_4$ for 3.5 bar. For NF 270 membrane at really high concentration of $MgSO_4$ between 5,000 and 15,000 mg/L, the value reported by Al-Zoubi et al. [46] was close to 100% of rejection between 2 and 9 bar. However,

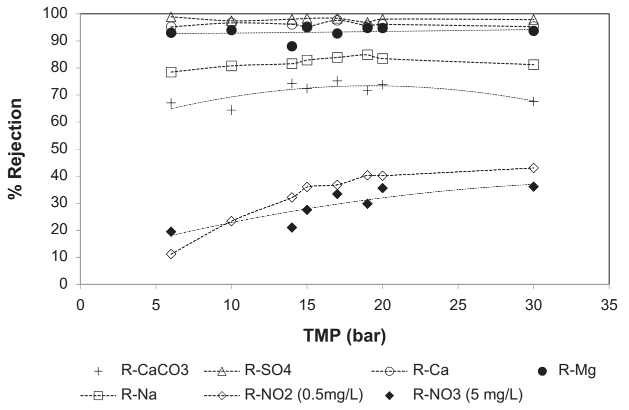

Fig. 11. Rejection percentage of the NF 270 membrane vs. TMP for low (L) concentration of NO_3^- and NO_2^- in hard water.

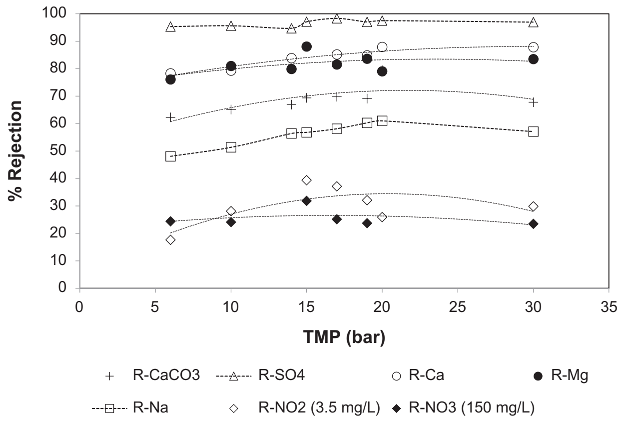

Fig. 12. Rejection percentage of the NF 270 membrane vs. TMP for high (H) concentration of NO_3^- and NO_2^- in hard water.

according to Figs. 10 and 12, at the concentration as were presented in Table 1 (30 and 120 mg/L), the behavior is different. Here, the effect of the high concentration of N-molecules produces a lower *R*% of Mg^{2+} between 70 and 80% depending on water hardness. SO_4^{2-} presents a high *R*%, similar for all the experiences and according to the references. That means the behavior of the *R*% of the membrane for $MgSO_4$, cannot be predicted for all the ranges of concentration using data at very different scales. Also the other salts contribute to obtain these differences between the behavior with the NF membrane. This result implies that the NF behavior must be tested before the system is designed, especially if the range of different salts and N-molecules are important in the process.

The *R*% of the N-molecules for hard water can be appreciated at different TMPs in Figs. 11 and 12, for low concentration and high concentration of the N-molecules, respectively. In addition, Fig. 12 can represent what could happen if the process is going on and the concentration increases from low level (soft) until the water solution in the concentrated flow is achieved at the level of hard water. In Figs. 11 and 12, we can observe that 20 bar could be also the best TMP, because more pressure means more energy and high cost and the *R*% also does not increase significantly. The *R*% change between low concentration of N-molecules and high concentration, between 30 and 40% for low concentration until 25% approximately, that is remarkable. This low retention of NO_2^- and NO_3^- ions, in hard water means the most part of the molecules are in the permeate, and could be separated with other kinds of membrane or processes, where the water has low concentration of Mg^{2+} and Ca^{2+} ions, and also low concentration of SO_4^{2-} because they have a high *R*% with this membrane. Also if we use the data obtained for soft water as a reference about what could happen when the Ca^{2+} and Mg^{2+} ions are separated from the water, we can predict that the *R*% of the NO_2^- and NO_3^- molecules could be increased, specially looking at the high concentration of those molecules in soft water (Fig. 10), i.e. could be possible to treat the permeate of the first NF process with a second NF process, increasing the *R*% since 25% until 50% approximately, and in a third step of NF, could be also better, going to the behavior of Fig. 4, the model solution without salts. Fig. 13 shows this proposed NF membrane process.

The concentrate in Fig. 13 could be processed in different configurations, using NF or reverse osmosis membranes. However, the proposed process here, is for the concentrate of NF 1, with low NO_2^- and low NO_3^-, high Mg^{2+} and Ca^{2+}, and high SO_4^{2-}, again uses the NF to concentrate more the bivalent ions and separate the N-molecules. With this permeate of the proposed NF 1-1 (see Fig. 13) that could be processed together with other permeates because the bivalents cations, are lower, closed to the model solution of Fig. 4.

The same procedure could be followed for the other concentrate of the NF 2, and NF 3 if the *R*% is low (named NF 2-1, NF 3-1, in Fig. 13). However, when the *R*% increases higher than 70%, it could be interesting to follow the other methods to treat this flow, as membrane contactor or to pump the concentrated flow to the normal biofilters. To develop this configuration, it is necessary to obtain more results in future tests specially with a prototype test with this configuration.

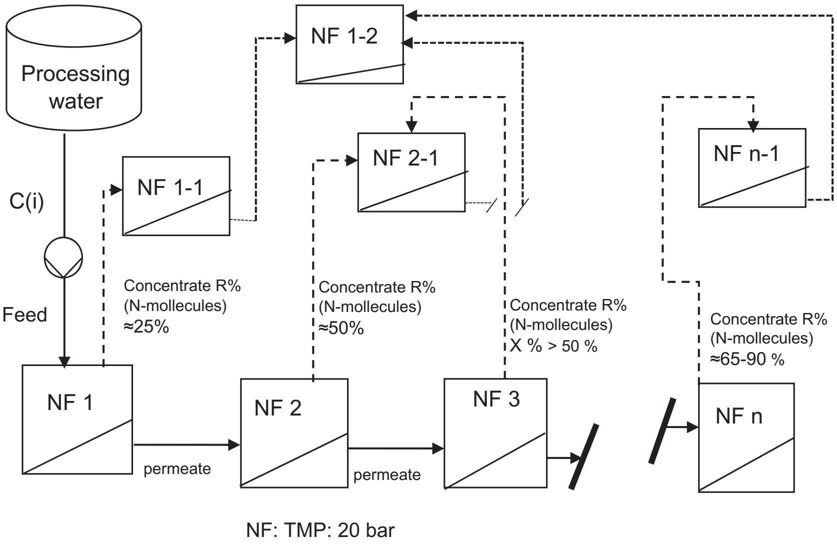

Fig. 13. Proposed NF membrane process for the retention of NO_3^- and NO_2^- ions in solution.

Moreover, the impact of the treatment of N-molecules in concentration lower than 200 mg/L, is not only useful for RAS systems. Paugam et al. [47], mentioned the problems with nitrates in water especially in drinking water, where the limit for drinking water must be of 50 mg/L. However, some places in the world, present concentrations of 200 mg/L, with potential damage for the human health. Epsztein et al. [48] recently showed the problems Israel is facing because of the intensive application of fertilizers, exceeding the concentration levels of 70 mg/L. In fact, they also proposed two-membrane process to analyze the behavior to the treatment of drinking water. These systems are similar to our proposal in Fig. 13. They obtained an *R*% of 10% for nitrate using NF 270 membrane at constant 8 bar. At similar TMP (Figs. 11 and 12), the *R*% for our tests were 20%, that could be because the temperature is different, 24°C for Epsztein et al. [48] and 15°C in our tests. The higher temperature could produce less retention because the viscosity changes and also the properties of the membrane, change. Epsztein et al. [48] do not include nitrite, probably because it was not present in the water they processed; however, this molecule is also more dangerous than nitrate. Thinking by doing the same extrapolation of the process and considering similar levels for the nitrite as the nitrate retention (see Figs. 11 and 12), the results using the process presented in Fig. 13 could be successful. The TMP to use in the final process, must be studied depending on the cost of the membrane process proposed, where the cost of the energy, the cost of the investment in membranes, and the cost of the cleaning and its frequency must be included. With these parameters, the values to prevent the osmotic pressure and the fouling of the membrane could be obtained.

4. Conclusions

The rejection percentage for NO_2^- and NO_3^- using NF 270 membrane was tested for different qualities of water normally found in the RAS systems. For model solution where the water was deionized, the NF 270 membrane rejected approximately the 75%, for 19 bar of TMP and the behavior of the membrane during the time was stable. In RAS, the N-molecules are between two ranges of concentrations, and for those there are some differences between the water hardness expressed as soft and hard water quality.

The bivalent cation molecules presented in the water presented an *R*% over 70% and monovalent cations pass through the membrane easier with an *R*% between 50 and 80% depending on the concentration of N-molecules and the water hardness. We can conclude that this phenomenon is related principally with Donnan exclusion and the hydrated energy. On the other hand, the N-molecules in the RAS water formulated are rejected for different mechanisms, where the quality of water influences the behavior of the *R*% in the membrane strongly. We could also obtain the range of the *R*% in a different qualities of water, necessary to propose the membrane process to treat this water. For soft water quality, i.e. with low hardness, the rejection is between 40 and 60% for N-molecules and for hard water quality, this percentage is in the range of 25–40% at 20 bar of TMP. We can conclude that the rejection for N-molecules depends on their concentration in water and also as was mentioned before, of the water quality. Finally, the treatment proposed consists in serial and parallel configurations of NF membrane processes, which must be thoroughly looked into at pilot level to obtain the process parameters necessary for their economic evaluation.

Acknowledgment

The author thanks the Grant FONDECYT No 11121375.

References

[1] M.B. Timmons, J.M. Ebeling, F.W. Wheaton, S.T. Summerfelt, B.J. Vinci, Recirculating Aquaculture Systems, second ed., Cayuga Aqua Ventures, Ithaca, 2002.

[2] D.E. Seawright, R.R. Stickney, R.B. Walker, Nutrient dynamics in integrated aquaculture-hydroponics systems, Aquaculture 160 (1998) 215–237.

[3] C. Martins, M. Pistrin, S. Ende, Ep.H. Eding, J. Verreth, The accumulation of substances in recirculating aquaculture systems (RAS) affects embryonic and larval development in common carp *Cyprinus carpio*, Aquaculture 291 (2009) 65–73.

[4] P.J. Walsh, P.A. Wright, Nitrogen Metabolism and Excretion, CRC Press, Florida, FL, 1995.

[5] R.F. Malone, T.J. Pfeiffer, Rating fixed-film nitrifying biofilters used in recirculating aquaculture systems, Aquacult. Eng. 34 (2006) 389–402.

[6] D.W. Graham, C.W. Knapp, E.S. Van Vleck, K. Bloor, T.B. Lane, C.E. Graham, Experimental demonstration of chaotic instability in biological nitrification, ISME J. 1 (2007) 385–393.

[7] C.F. Hurtado, B. Cancino-Madariaga, Ammonia retention capacity of nanofiltration and reverse osmosis membranes in a non steady state system, to be use in recirculation aquaculture systems (RAS), Aquacult. Eng. 58 (2014) 29–34.

[8] J.E. Alleman, K. Preston, Behavior and physiology of nitrifying bacteria, in: Proceedings of the Second Annual Conference on Commercial Aquaculture, CES 240/IL-IN-SG-E-91-8, Illinois-Indiana Sea Grant Program, Bloomington, 1991, 1–13.

[9] J.M. Heinen, J.A. Hankins, A.L. Weber, A semiclosed recirculating-water system for high-density culture of rainbow trout, Prog. Fish-Cult. 58(1) (1996) 11–22.

[10] A.L. Klaver, R.A. Matthews, Effects of oxytetracycline on nitrification in a model aquatic system, Aquaculture 123 (1994) 234–247.

[11] S. Chen, J. Ling, J.P. Blancheton, Nitrification kinetics of biofilm as affected by water quality factors, Aquacult. Eng. 34 (2006) 179–197.

[12] E.J.M. Emparanza, Problems affecting nitrification in commercial RAS with fixed-bed biofilters for salmonids in Chile, Aquacult. Eng. 41 (2009) 91–96.

[13] J.M. Ebeling, M.B. Timmons, J.J. Bisogni, Engineering analysis of the stoichiometry of photoautotrophic, autotrophic, and heterotrophic removal of ammonia-nitrogen in aquaculture systems, Aquaculture 257 (2006) 346–358.

[14] S.I. Sandu, G.D. Boardman, B.J. Watten, B.L. Brazil, Factors influencing the nitrification efficiency of fluidized bed filter with a plastic bead medium, Aquacult. Eng. 26 (2002) 41–59.

[15] T.C. Guerdat, T.M. Losordo, J.J. Classen, J.A. Osborne, D.P. DeLong, An evaluation of commercially available biological filters for recirculating aquaculture systems, Aquacult. Eng. 42 (2010) 38–49.

[16] S. Singh, J. Ebeling, F. Wheaton, Water quality trials in four recirculating aquacultural system configurations, Aquacult. Eng. 20 (1999) 75–84.

[17] M.B. Timmons, J.M. Ebeling. Recirculating Aquaculture Systems, second ed., Cayuga Aqua Ventures, Ithaca, New York, NY, 2010.

[18] Q. Jiang, A. Dilixiati, W. Zhang, W. Li, Q. Wang, Y. Zhao, J. Yang, Z. Li, Effect of nitrite exposure on metabolic response in the freshwater prawn Macrobrachium nipponense, Cent. Eur. J. Biol. 9 (2014) 86–91.

[19] J.A. Camargo, Á. Alonso, Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment, Environ. Int. 32 (2006) 831–849.

[20] N. Romano, C. Zeng, Subchronic exposure to nitrite, potassium and their combination on survival, growth, total haemocyte count and gill structure of juvenile blue swimmer crabs, *Portunus pelagicus*, Ecotoxicol. Environ. Saf. 72 (2009) 1287–1295.

[21] J. van Rijn, Y. Tal, H.J. Schreier, Denitrification in recirculating systems: Theory and applications, Aquacult. Eng. 34 (2006) 364–376.

[22] M.J. Sharrer, Y. Tal, D. Ferrier, J.A. Hankins, S.T. Summerfelt, Membrane biological reactor treatment of a saline backwash flow from a recirculating aquaculture system, Aquacult. Eng. 36 (2007) 159–176.

[23] J.E. Huguenin, J. Colt, Design and Operating Guide for Aquaculture Seawater Systems, Elsevier Science Publishing Company, New York, NY, 1989.

[24] G.A. Wedemeyer, Physiology of Fish in Intensive Culture Systems, Chapman and Hall, New York, NY, 1996.

[25] J. Colt, Water quality requirements for reuse systems, Aquacult. Eng. 34 (2006) 143–156.

[26] N. Ali, N.A. Hanid, A. Jusoh, The potential of a polysulfone (PSF) nanofiltration membrane as the end stage treatment technology of aquaculture wastewater, Desalin. Water Treat. 32 (2011) 242–247.

[27] J. Orellana, U. Waller, B. Wecker, Culture of yellowtail kingfish (*Seriola lalandi*) in a marine recirculating aquaculture system (RAS) with artificial seawater, Aquacult. Eng. 58 (2014) 20–28.

[28] S. Bensaadia, M. Amara, O. Arousa, H. Kerdjoudj, Transfer of nitrate ions using a polymeric-surfactant membrane, Desalin. Water Treat. 57 (2016) 5981–5987.

[29] M. Pirsaheb, T. Khosravi, K. Sharafic, M. Mouradic, Comparing operational cost and performance evaluation of electrodialysis and reverse osmosis systems in nitrate removal from drinking water in Golshahr, Mashhad, Desalin. Water Treat. 57 (2016) 5391–5397.

[30] B. Cancino-Madariaga, C.F. Hurtado, R. Ruby, Effect of pressure and pH in ammonium retention for nanofiltration and reverse osmosis membranes to be used in recirculation aquaculture systems (RAS), Aquacult. Eng. 45 (2011) 103–108.

[31] M.L. Gerardo, N.H.M. Aljohani, D.L. Oatley-Radcliffe, R.W. Lovitt, Moving towards sustainable resources: Recovery and fractionation of nutrients from dairy manure digestate using membranes, Water Res. 80 (2015) 80–89.

[32] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review: Recent advances and future prospects, Desalination 356 (2015) 226–254.

[33] E. Sjoman, M. Manttari, M. Nystrom, H. Koivikko, H. Heikkila, Separation of xylose from glucose by nanofiltration from concentrated monosaccharide solutions, J. Membr. Sci. 292 (2007) 106–115.

[34] C.Y. Tang, Y.N. Kwon, J.O. Leckie, Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes, Desalination 242 (2009) 149–167.

[35] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Removal of natural hormones by nanofiltration membranes: Measurement, modeling, and mechanisms, Environ. Sci. Technol. 38 (2004) 1888–1896.

[36] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Pharmaceutical retention mechanisms by nanofiltration membranes, Environ. Sci. Technol. 39 (2005) 7698–7705.

[37] J. Tanninen, S. Platt, A. Weiss, M. Nyström, Long-term acid resistance and selectivity of NF membranes in very acidic conditions, J. Membr. Sci. 240 (2004) 11–18.

[38] US EPA, Science Advisory Board Review of the Technical Basis for ListingAmmonia on the Toxics Release, EPA-SAB-EPAC-LTR-95-001, US EPA, Washington, DC, 1995.

[39] D.C. Montgomery, Design and Analysis of Experiments, fifth ed., John Wiley, New York, NY, 2001.

[40] P. Atkins, J. de Paula, Physical Chemistry, eighth ed., W.H. Freeman and Company, New York, NY, 2006.

[41] A. Abidi, N. Gherraf, S. Ladje, M. Rabiller-Baudry, T. Bouchami, Effect of operating parameters on the selectivity of nanofiltration phosphates transfer through a Nanomax-50 membrane, Arabian J. Chem. (2011), doi: 10.1016/j.arabjc.2011.04.014.

[42] S. Mehdipour, V. Vatanpour, H.-R. Kariminia, Influence of ion interaction on lead removal by a polyamide nanofiltration membrane, Desalination 362 (2015) 84–92.

[43] L.A. Richards, A. Schäfer, B. Richards, B. Corry, The importance of dehydration in determining ion transport in narrow pores, Small 8(11) (2012) 1701–1709.

[44] A. Santafé-Moros, J.M. Gozálvez-Zafrilla, J. Lora-García, Nitrate removal from ternary ionic solutions by a tight nanofiltration membrane, Desalination 204 (2007) 63–71.

[45] L. Paugam, S. Taha, G. Dorange, F. Quemeneur, Influence of ionic composition on nitrate retention by nanofiltration, Trans IChemE 81, Part A (2003) 1199–1205.

[46] H. Al-Zoubi, N. Hilal, N.A. Darwish, A.W. Mohammad, Rejection and modelling of sulphate and potassium salts by nanofiltration membranes: Neural network and Spiegler-Kedem model, Desalination 206 (2007) 42–60.

[47] L. Paugam, C.K. Diawara, J.P. Schlumpf, P. Jaouen, F. Quéméneur, Transfer of monovalent anions and nitrates especially through nanofiltration membranes in brackish water conditions, Sep. Purif. Technol. 40 (2004) 237–242.

[48] R. Epsztein, O. Nir, O. Lahav, M. Green, Selective nitrate removal from groundwater using a hybrid nanofiltration–reverse osmosis filtration scheme, Chem. Eng. J. 279 (2015) 372–378.