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Nitrate removal in a closed marine system through the ion exchange membrane bioreactor

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ABSTRACT

The accumulation of nitrate in closed marine systems presents a problem for both the marine life and the environment. The present study, proposes the application of the ion exchange membrane bioreactor (IEMB) concept for removing nitrate from marine systems, such as aquaculture tanks or marine aquariums.

The results obtained demonstrate that the IEMB was able to remove naturally accumulated nitrate from water taken from a public marine aquarium (Oceanário de Lisboa) and bioconvert it, in an isolated compartment (biocompartment), to molecular nitrogen, thus preventing secondary contamination of the treated water by microbial cells, metabolic by-products and excess of carbon source (ethanol). This system allowed for the removal of nitrate at concentrations of 251 and 380 mg/l down to below 27 mg/l exchanging it for chloride.

Under the studied operating conditions, the IEMB proves to be a selective nitrate removing technology preserving the initial water composition with respect to cations, due to the Donnan exclusion effect from the membrane, and minimizing the counter diffusion of anions other than nitrate and chloride, due to the use of water with the same ionic composition in the biocompartment. This is an advantage of the IEMB concept, since the quality of the water produced would allow for the reutilisation of the treated water in the aquarium, thereby reducing both the wastewater volume and the use of fresh water.

1. Introduction

In closed marine systems, such as marine aquariums, the natural biological processes may induce chemical alterations in the water, which could affect the marine life. The catabolism of reduced nitrogen compounds by aquatic animals is responsible for the release of ammonia. In environments with no significant primary productivity, such as marine aquariums, ammonia is converted by nitrifying organisms into nitrate [1–4]. This process leads to an accumulation of nitrate over time, frequently up to levels which could be toxic to certain fish species leading, at the same time, to an environmental problem related with its discharge. An acceptable level of nitrate for marine populations has been considered to be of less than 20 mg NO_3^-N/l (corresponding to less than 85 mg/l of NO_3^-) [5,6]. The "Water Quality Criteria" [7] recommends that nitrate levels in freshwater systems should not exceed those in the tap water supply, 50 mg/l of NO_3^-. Additionally, since marine species are generally more sensitive to nitrate than the freshwater ones, nitrate should not exceed 40 mg/l in the water supply [7]. Nitrite is even a more toxic anion that results from an incomplete reduction of nitrate. Levels of nitrite ranging from 0.2 mg NO_2^-N/l (0.65 mg/l of NO_2^-) to 12 mg NO_2^-N/l (39 mg/l of NO_2^-) have been referred as safe levels in aquaculture systems [8].

The disposal routes of aquarium wastewaters depend strongly on their location and environmental legislation for wastewater disposal. Many small aquarium facilities usually control nitrate concentrations by performing regular water changes. However, in a large aquarium, this procedure is operationally more difficult, since a significant fraction of water has to be replaced [1]. In the Portuguese public aquariums, saline water is typically not taken directly from the sea but, instead, the water is generally prepared after amendment with different salts, which guarantees its reproducible composition and allows for a better quality control. Therefore, the use of nitrate removing systems that permit the in situ reuse of aquarium water presents numerous advantages. Efforts have been directed to develop technologies for nitrate removal with maximum water recovery. The most commonly used technology for nitrate removal in marine systems is biological denitrification using external [1,2,9,10] or endogenous carbon sources [3,11–14] as well as hydrogen [6]. There are several reports describing the successful application of biological denitrification in large marine aquariums [1,2]. However, these technologies require sub-

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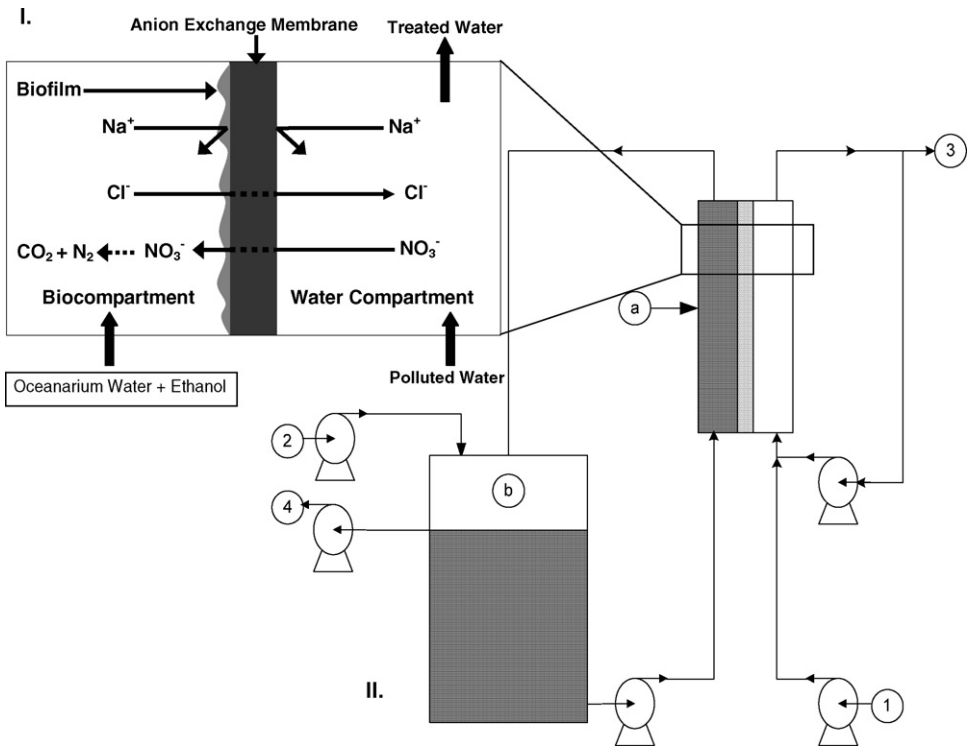

Fig. 1. (I) Schematic diagram of nitrate transport and bioreduction in the ion exchange membrane bioreactor (IEMB). (II) IEMB setup: 1, feed water; 2, biofeed; 3, treated water; 4, biocompartment effluent; a, membrane module with two compartments separated by an anion-exchange membrane; b, bioreactor vessel.

sequent treatment to remove microbial cells and/or a possible excess of carbon source.

Limited information is found in the literature regarding the use of membranes for treating waters from marine systems. A report on the use of reverse osmosis (RO) in aquaculture wastewater treatment [15], demonstrated high nitrate removal rates, which are, however accompanied by the formation of a concentrated brine stream that is collected for further treatment. Additionally, the use of a hybrid system combining a biological reactor with submerged membrane filtration (pore size 0.4 μm) for the treatment of a saline backwash flow from a recirculating aquaculture system [16], showed high nitrate removal efficiencies. Further treatment of the reclaimed water processed by the membrane biological reactor was found necessary for water reuse in a marine fish culture system.

The ion exchange membrane bioreactor (IEMB) concept [17] proposes the integration of membrane separation and biological treatment. In the IEMB process, nitrate is transported through a dense anion-exchange membrane and subsequently converted into molecular nitrogen, by a suitable mixed microbial culture in a separated compartment (biocompartment) (Fig. 1I). The use of a dense, non-porous membrane in the IEMB system, isolates the water stream from the biological compartment, thus allowing for independent adjustment of the hydraulic retention time in the biocompartment without affecting the water production rate. The transport through the membrane is governed by Donnan dialysis principles and it can be enhanced by adding a suitable counter ion (e.g. chloride) to the biological compartment.

The IEMB has been extensively studied for drinking water treatment, especially to remove oxyanion micropollutants, such as nitrate [18–21], perchlorate [22] and bromate [23]. This system has been proven to work efficiently for the removal of these pollutants, avoiding secondary contamination of the treated water by metabolic by-products and excess of carbon source, while preserving the water composition with respect to other ions [22].

As previous demonstrated [20] the transport of anionic pollutants can be enhanced adding a driving counter ion, e.g. chloride, to the biocompartment. In the present application the feed water (contaminated water) has a salinity higher than 18 g/l, in chloride (Section 3.1). Therefore, in order to enhanced the transport of nitrate through the membrane and prevent a high competition between the transport of chloride and nitrate, the concentration of chloride in the biocompartment should be at least, as high as its concentration in the water compartment.

Previous work performed with the IEMB suggests that for nitrate removal from high salinity waters, lower driving forces than those achievable in drinking water applications should be expected, because of the higher chloride concentration in the water compartment. Therefore, this study is focused on evaluating the effect of nitrate and chloride concentrations on the process performance. First, Donnan dialysis experiments were carried out and compared at different chloride and nitrate concentrations. Then, the IEMB performance was evaluated using water from the Lisbon oceanarium containing nitrate. Finally, the applicability of the nitrate transport model (Section 2) was evaluated for the case studied.

2. Transport modelling aspects

A trace counter-ion transport model, previously developed [21], describes with accuracy the performance of the IEMB for removal of trace counter ions from drinking water supplies:

$$J_{NO_3^-} = \frac{(C_{NO_3^-,1}/C_{Cl^-,1}) - (C_{NO_3^-,2}/C_{Cl^-,2})}{(L/(P_{NO_3^-} \times Q)) + (\delta_1/(D_{NO_3^-,w} \times C_{Cl^-,1})) + (\delta_2/(D_{NO_3^-,w} \times C_{Cl^-,2}))}, \quad (1)$$

where $C_{NO_3^-,1}$ and $C_{NO_3^-,2}$ are the concentrations of nitrate in the water and biocompartment, respectively, $C_{Cl^-,1}$ and $C_{Cl^-,2}$ are the major counter-ion (chloride) concentration in each compartment, δ_1 and δ_2 are the thickness of the corresponding boundary lay-

ers next to the membrane surfaces at the water and biomedium sides, respectively ($\delta_1 = \delta_2 = 38\ \mu m$). This thickness is equal to the ratio d_h/Sh where d_h is the hydraulic diameter ($d_h = 0.5$ cm for both channels), Sh is the Sherwood number, calculated using the empirical correlation for membrane modules with parallel flat channels ($Sh = 0.04\ Sc^{0.75}\ Re^{0.33}$), L is the membrane thickness (130 μm); $P_{NO_3^-}$ is the membrane permeability to NO_3^-; Q is the ion exchange capacity of the membrane (1.5 mol/l) and $D_{NO_3^-,w}$ is the diffusion coefficient of counter-ion NO_3^- in water (1.9×10^{-5} cm^2/s) [24].

Eq. (1) demonstrates that the flux of nitrate is proportional to the difference between the ratios of nitrate to the major counter-ion (Cl^-) concentration in the two compartments. This difference is the process driving force. Furthermore, in an IEMB operation, the concentration of nitrate in the bioreactor should be minimal due to its biological reduction to nitrogen. Consequently, the second term in the driving force (in the numerator of Eq. (1)) can be neglected since the ratio between the concentrations of nitrate and chloride in the biocompartment becomes extremely small. The overall transport resistance to nitrate transport is given by three individual resistances in series: a resistance associated with the transport through the membrane, expressed by the first term in the denominator, while the second and the third terms represent the resistances due to the two liquid phase boundary layers at the two membrane surfaces facing the polluted water and the biomedium, respectively.

3. Materials and methods

3.1. Feed water and biomedium

The feed water used in the IEMB studies was collected from the Lisbon oceanarium in two different occasions, containing 251 and 380 mg/l of nitrate, respectively. In marine aquaria and aquaculture systems, nitrate concentrations can reach values of 500 mg NO_3^-N/l [5].

The aqueous solution used as a biomedium was nitrate-free saline water, used to feed the Lisbon oceanarium, with the following ionic composition: 140 mg/l of HCO_3^-, 18,980 mg/l of Cl^-, 2649 mg/l of SO_4^{2-}, 5 mg/l of PO_4^{3-}, 65 mg/l of Br^-, 26 mg/l of $H_2BO_3^-$, 100 mg/l of F^-, 10,556 mg/l of Na^+, 380 mg/l of K^+, 400 mg/l of Ca^{2+}, 1272 mg/l of Mg^{2+}, 13 mg/l of Sr^{2+} and total salinity of 34,580 mg/l. Ethanol, at a concentration of 0.84 g/l, was added as a carbon source. This water contains the essential inorganic nutrients for the microbial culture growth. Therefore, there is no need to add other salts, thus reducing the process complexity.

3.2. Microbial culture

The culture used to inoculate the biocompartment in the IEMB studies was an enriched culture obtained from a primary inoculum grown in aquarium water with nitrate (~300 mg/l, pH 8) and ethanol as the sole carbon source (1 g/l). The enrichment process was conducted in sealed 100 ml flasks containing 50 ml of nitrified oceanarium water with 1 g/l of ethanol, in an incubator at 25 ± 1 °C. When the cultures became visually turbid, they were transferred to new flasks with fresh biomedium. This procedure was repeated three times in order to obtain an enriched culture capable of reducing nitrate under high salinity conditions.

3.3. IEMB studies

The IEMB setup, represented in Fig.1II, was composed by a membrane module (a) with two identical rectangular channels, separated by a mono-anion permselective membrane, Neosepta ACS (manufactured by Tokuyama Soda, Japan), with a working area of 39 cm^2. One of the module channels was connected to an external loop where the aqueous phase was recirculated at a flow rate of 97.2 l/h, corresponding to a Reynolds number of 3000 (Re 3000). This compartment, referred to as water compartment, was continuously fed with oceanarium water (1) containing high concentrations of nitrate. Three different ratios of feed water flow rate per membrane area (F/A) ratios were studied: 0.9, 1.5, 7.7 l/(m^2 h), Table 1 (corresponding to water compartment hydraulic retention times of 28, 17 and 3 h, respectively). The other module channel was connected to a stirred vessel (b) through another recirculation loop (Re 3000). This vessel, inoculated with 100 ml of the enriched microbial culture, obtained as described in Section 3.2, was continuously fed, at a flow rate of 0.0048 l/h, with nitrate-free saline water from the Lisbon oceanarium (2 in Fig. 1II) (Section 3.1), to which 0.84 g/l of ethanol was added as a carbon source. This compartment was operated at a hydraulic retention time (HRT) of 5 days. A relatively high biocompartment HRT was chosen in order to decrease the volume of the effluent produced in the biocompartment of the system. Lower HRTs could be set without affecting the nitrate reduction rates, which would, however, increase the liquid waste volume from the biocompartment, which is undesirable.

Table 1
Experimental conditions of the Donnan dialysis and IEMB studies.

Experiment no.	Water flow rate per membrane area, F/A (l/(m^2 h))	Concentrations in the polluted water (g/l)	
		Cl^-	NO_3^-
Donnan dialysis studies			
1	7.7	0.05	0.30
2	7.7	0.90	0.30
3	7.7	1.80	0.30
4	7.7	18.00	0.30
5	7.7	18.00	~0.15
6	7.7	18.00	~0.30
7	7.7	18.00	~0.60
IEMB studies			
8	7.7	18.98	0.38
9	1.5	18.98	0.25
10	0.9	18.98	0.25

All experiments were run for at least 1 week and samples were taken periodically from the water feed, treated water outlet, biomedium and biocompartment for ions, ethanol and cell concentration analyses. All experiments were performed at a temperature of 23 ± 1 °C in an air-conditioned room.

At the end of the IEMB experiments, the membrane was removed from the module and the thickness of the biofilm was calculated by subtracting the thickness of the wet membrane from the thickness measured after biofilm formation on the membrane surface, several measurements were performed in different locations of the membrane in order to obtain an average of the thickness value. Both measurements were performed with a micrometer at a precision of 1 μm.

3.4. Donnan dialysis studies

These studies were performed in the rig described in Section 3.3, except that in this case no microbial culture and carbon source were present. The water compartment was continuously fed with deionized water supplemented with variable concentrations of chloride and nitrate, in the form of their sodium salts according to Table 1. The other compartment, referred to as biocompartment (without microbial culture and carbon source), was fed with an aqueous solution with 18 g/l NaCl.

3.5. Analytical methods

The concentrations of nitrate and nitrite were determined in a segmented flow analyzer (Skalar Analytical, Breda, Netherlands). In

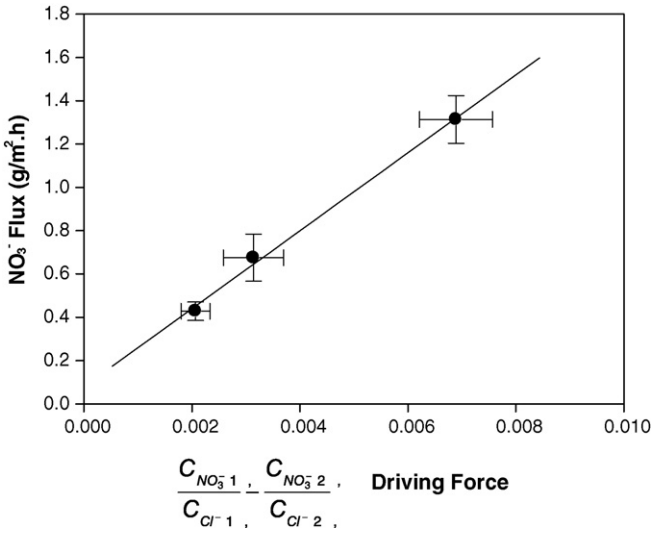

Fig. 2. Influence of the process driving force on the flux of nitrate through the membrane, under Donnan dialysis conditions. Subscripts 1 and 2 refer to concentrations in the water compartment and biocompartment, respectively.

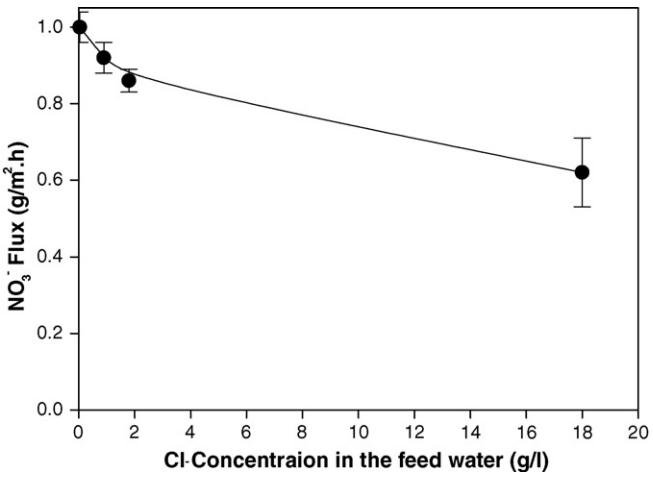

Fig. 3. Influence of the feed water chloride concentration on the flux of nitrate through the membrane, under Donnan dialysis conditions.

this method, nitrate is first reduced to nitrite by hydrazinium sulphate and nitrite concentration (the one originally present and the one formed by reduction of nitrate) is determined by diazotizing with sulphanilamide and coupling with α-naphathylenediamine dihydrochloride to form a highly colored azo dye, which is measured at 540 nm. The detection limits were 1 mg/l for nitrate and 0.1 mg/l for nitrite.

The ethanol concentration in the IEMB experiments was determined by HPLC using a differential refractometer detector RI-71 and an Aminex HPX-87H column (BioRad, USA). The mobile phase was 0.01N of H_2SO_4 (flow rate 0.5 ml/min). The detection limit for ethanol was 1 mg/l.

4. Results and discussion

4.1. Donnan dialysis studies

The removal of nitrate from saline water was evaluated under Donnan dialysis conditions. Since the feed water had a salinity of 18 g/l as chloride, in all experiments, the minimal concentration of chloride in the biocompartment was set to be at least 18 g/l. The effect of nitrate and chloride in the flux of nitrate was evaluated by varying their concentrations in the feed water.

4.1.1. Effect of nitrate concentration in feed water

The effect of nitrate concentration on its transport through the membrane, under conditions that mimic the marine aquarium water composition, in terms of chloride concentration (~18 g/l of Cl^-), was evaluated. The driving force of the process is dependent on nitrate concentration in water (Eq. (1)). Fig. 2 depicts the results obtained in these experiments. The linear relationship obtained (Fig. 2) is in agreement with the transport model (Eq. (1)), in which the flux is proportional to the driving force, being the constant of proportionality the inverse of the overall transport resistance.

Using the linear slope in Fig. 2 and the denominator of Eq. (1), it is possible to determine the membrane permeability towards nitrate for the present application. The determined value was $P_{m_{NO_3}} = 7.38 \times 10^{-7}$ cm^2/s. Knowing this permeability, Eq. (1) can be used to predict the flux of nitrate through the membrane when treating high salinity water. The membrane permeability (P_m) may be also viewed as a lumped parameter, since it accounts also for any possible effects on the nitrate transport, which are not explicitly recognized by the model, being strongly influenced by the composition of the electrolyte solutions contacting the membrane (e.g. possible effects due to swelling, electrolyte sorption and/or change in the free water content of the membrane).

4.1.2. Effect of chloride concentration in feed water

In order to study the effect, on the nitrate flux, of chloride concentration in the water compartment, four experiments were performed changing the concentration of chloride in the feed water, while the concentration of nitrate was maintained at 300 mg/l.

Fig. 3 depicts the data obtained in Donnan dialysis studies performed at a water flow rate per membrane area (F/A ratio) of 7.7 l/(m^2 h). The results showed that there was a decrease in the flux of nitrate with the increase in the chloride concentration in the water compartment, which is due to the decrease in the driving force (Eq. (1)). However, the observed decrease was not linear, which can be explained by the reduction of the contribution of the water compartment boundary layer resistance (second term in the denominator of Eq. (1)), due to its dependence on the chloride concentration in the water stream. At high chloride concentrations the contribution of this transport resistance was shown to be lower [21].

Experiment 4 (conducted with 300 mg/l of nitrate and F/A = 7.7 l/(m^2 h)) was performed using the same concentration of chloride (18 g/l) in the biocompartment as the one used in the water compartment and similar to the concentration in the oceanarium water. The flux of nitrate in this case was only dependent on the transport through the membrane, because the resistances due to the two boundary layers become negligible at higher salt concentrations (Eq. (1)). The results obtained in experiment 4 demonstrated that the system allowed for the removal of 110 mg/l of nitrate from the feed water. For obtaining higher removal rates, one should either further increase the chloride concentration in the biocompartment, which does not seem practical since the water is already of high salinity, or remove nitrate entering the biocompartment, which can be accomplished using the IEMB concept.

4.2. IEMB studies

The simultaneous transport and bioconversion of nitrate from high salinity water was evaluated in the IEMB by performing three experiments using two water samples collected from the Lisbon oceanarium (Section 3.1) containing approximately 251 and 380 mg/l of nitrate. Nitrate-free saline water (the water fed to the aquarium) supplemented with ethanol was used as the biomedium.

Table 2
Concentration of nitrate and nitrite in the polluted water inlet, in the treated water outlet and in the biocompartment.

F/A (l/(m^2 h))	Ion concentration in the feed water (mg/l)		Ion concentration in the treated water (mg/l)		Ion concentration in the biocompartment (mg/l)	
	NO_3^-	NO_2^-	NO_3^-	NO_2^-	NO_3^-	NO_2^-
0.9	251 ± 29.5	0.23 ± 0.1	26.7 ± 3.6	0.28 ± 0.06	2.15 ± 0.34	0.31 ± 0.05
1.5	251 ± 29.5	0.23 ± 0.1	58.0 ± 3.9	0.27 ± 0.14	2.13 ± 0.30	0.37 ± 0.14
7.7	380 ± 38.0	4.3 ± 0.8	221.9 ± 27.6	3.26 ± 0.07	4.76 ± 1.54	1.38 ± 0.28

In all the three experiments performed, the two IEMB compartments had the same total salinity (of 34 g/l) and composition, except for nitrate. By using this procedure, it was possible to avoid the transport of any other anions, except for nitrate, the only anion that was not initially present in the biocompartment (Section 3.1). This approach guarantees the preservation of the ionic composition of the treated water, which is important for water reuse. The microbial culture used in these experiments was an enriched culture described in Section 3.2.

Results presented in Table 2, Figs. 4 and 5 show that the system was able to remove nitrate from the feed water to values considered acceptable for the Lisbon oceanarium (<40 mg/l NO_3^-). For the experiments performed at the lowest water feed flow rate per membrane area ratio (F/A = 0.9 l/(m^2 h)), it was possible to achieve a nitrate removal rate of 90%, removal of nitrate from 251.0 ± 29.5 to 26.7 ± 3.6 mg/l in the water compartment. Nitrate was transported from the water compartment to the biocompartment where it was reduced by the culture to a residual concentration of 2.15 ± 0.34 mg/l (see Table 2). In the biocompartment, no nitrite accumulation was observed at steady state, meaning that nitrate reduction was complete. In all experiments, the treated water presented practically the same pH (7.99 ± 0.03) and conductivity (43 ± 3 mS/cm) as the fresh feed saline water (pH 8.00 ± 0.1 and conductivity = 42 ± 4 mS/cm).

Nitrite, which is an intermediate product of nitrate bioreduction, is a highly toxic compound; the results obtained showed that, for the water treated with the IEMB system, the concentration of nitrite was always below the lower reference level considered to be safe for marine systems (see Section 1).

Previous studies [20] demonstrated that in an IEMB operation, the presence of higher concentrations of chloride in the biocompartment allows for the transport of ions (such as nitrate) against their concentration gradient. In the present case, the concentration of chloride was high and equal in both compartments. Therefore, nitrate accumulation in the biocompartment, due to a possible failure in its bioconversion, may result in the back transport of that

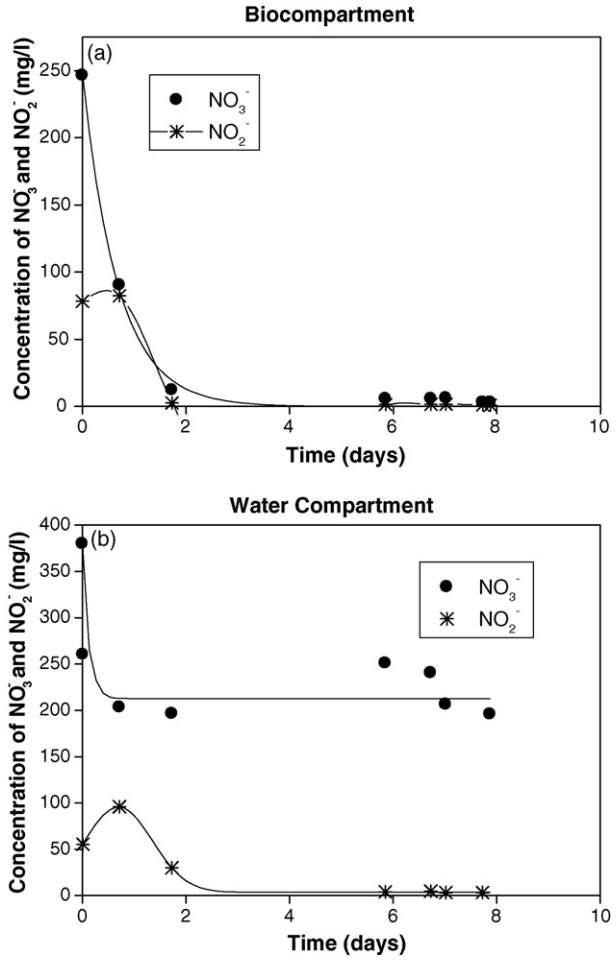

Fig. 4. Time course of nitrate and nitrite concentration in the biocompartment (a) and in the water compartment (b), for the experiment performed with oceanarium water contaminated with 380 mg/l of nitrate at an F/A ratio of 7.7 l/(m^2 h).

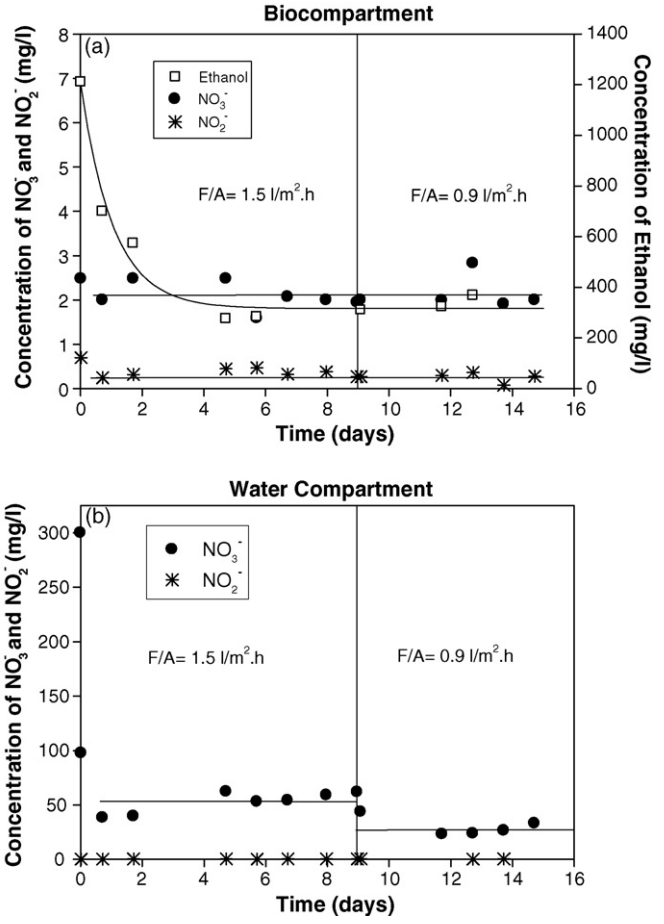

Fig. 5. Time course of nitrate, nitrite and ethanol concentrations in the biocompartment (a) and in the water compartment (b), for the experiment performed with oceanarium water contaminated with 251 mg/l of nitrate. The ethanol concentration in the water compartment was always found to be below the detection limit of 1 mg/l.

pollutant to the treated water stream. Fig. 4 shows the results of an experiment performed with an F/A ratio of 7.7 l/m^2 h and 380 mg/l of nitrate. This figure shows that the nitrate concentration in the treated water was reduced to 221.9 ± 27.6 mg/l in a short period of time (<3 h) and was then maintained stable during the experimental run duration of 8 days. Fig. 4 demonstrates that an incomplete reduction of nitrate, during the first 2 days of the experiment (before reaching steady state), caused accumulation of nitrite in the biocompartment to a maximum of 79 mg/l (Fig. 4a) and, consequently, nitrite was transported to the treated water compartment (Fig. 4b), achieving a concentration of 99 mg/l in the first day of operation. The use of the IEMB for saline water treatment, under the studied conditions, requires a strict control of the nitrate reduction, in order to avoid the back transport of nitrate and/or nitrite to the treated water stream.

Fig. 5 presents the evolution of the concentrations of nitrate, nitrite and ethanol in both water and biocompartment for experiments performed using two different water flow rate per membrane area ratios (F/A). This figure shows that the nitrate concentration in the treated water for the water flow rate per membrane area (F/A) ratio of 1.5 l/(m^2 h) was reduced to 58.0 ± 3.9 mg/l in less than 17 h and was maintained stable thereafter before changing the F/A ratio to 0.9 l/(m^2 h) leading to a lower nitrate concentration (26.7 ± 3.6 mg/l) in the treated water, which maintained stable for the rest of the run.

The results showed that the decrease in the F/A ratio from 1.5 to 0.9 l/(m^2 h) allowed for the removal of nitrate to levels below the acceptable limit for closed marine systems (<40 mg/l), although this change had no influence on the performance of the mixed microbial culture. These results, demonstrate that the concentration of nitrate in the treated water can be controlled by the F/A ratio parameter in the IEMB operation.

Results also proved that the high salinity of the biomedium did not reduce the activity of the microbial culture. This fact can be explained by the enrichment and acclimation procedure applied to the culture used to inoculate the bioreactor (Section 3.2). Studies performed by other authors [10] on acclimation of an immobilized freshwater denitrifier to high saline conditions, suggested that preliminary enrichment of the culture reduced the time necessary to achieve a steady state nitrate removal in the bioreactor.

Similarly to what was observed in previous studies [22], in the present experiments, a biofilm developed on the membrane surface contacting the biocompartment. The average thickness of these biofilms (0.076 ± 0.021 mm) was higher than the ones (typically 0.017 ± 0.006 mm) developed in the studies performed with contaminated drinking water [22]. This result may be attributed to the higher flux of nitrate, transported through the membrane from the water compartment to the biocompartment, compared to the drinking water application (300 ppm of NO_3^- in the saline water), thus creating near the membrane surface conditions for the development of a thicker reactive zone biofilm. This biofilm had no detrimental effect on the performance of the IEMB or on the nitrate flux, which remained constant at each steady-state values (0.2–1.2 g/(m^2 h) for the experiments performed at F/A = 0.9–7.7 l/(m^2 h)) during 16 days of operation. The biofilm can be considered as a nitrate reducing reaction zone, advantageous from a mass transfer viewpoint for a given time period, after which an additional resistance to nitrate mass transport due to the biofilm overgrowth could be encountered. The reason why the biofilm does not represent an additional transport resistance for a relatively long operation times, could be mainly attributed to the maintenance of anoxic (instead of aerobic) conditions in the biocompartment, which result in the development of a relatively thin biofilm.

An important issue for all biological denitrification systems is the possible risk of secondary contamination of the treated water, by excess of carbon source (ethanol in the present study). No permeation of ethanol into the water compartment was observed during the IEMB studies. Even with an excess of ethanol of about 1 g/l in the biocompartment, the concentration of ethanol in the treated water stream was always below the detection limit of 1 mg/l. This result may be attributed to the low permeability of ethanol through the membrane used (3.58×10^{-8} cm^2/s, [25]) and, additionally, to the formation of a biofilm at the surface of the membrane, contacting the biocompartment, which serves as an additional reactive barrier against the transport of ethanol.

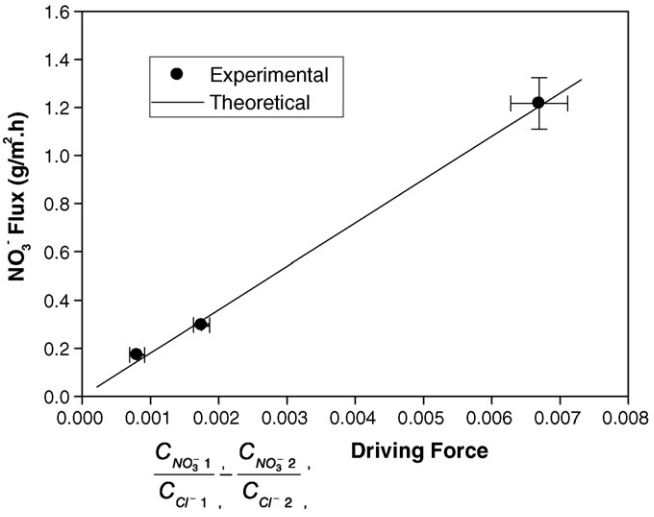

Fig. 6. Comparison between the experimentally determined nitrate fluxes with the theoretically predicted ones by the transport model (Eq. (1)). Subscripts 1 and 2 refer to concentrations in the water compartment and biocompartment, respectively.

4.2.1. Model validation

In order to verify the accuracy of the model (Eq. (1)) the experimental results obtained were compared with the nitrate flux predictions of the model. Fig. 6 demonstrates that the predicted fluxes, calculated using Eq. (1) and the membrane permeability value determined in Section 4.1.1, matches well the experimental fluxes for all IEMB experiments. Therefore, it can be concluded that for several applications of the IEMB (treating high or low saline waters), the model can be used to predict the behavior of the system, if the permeability parameter is previously determined under the same operating conditions (Section 4.1.1).

4.3. Comparison of the IEMB performance with other systems for nitrate removal from saline waters

The main advantage of the IEMB, in comparison with traditional biological nitrate removal systems using an external carbon source, is the possibility of removing nitrate from the polluted water and simultaneously bioreducing it to nitrogen in a separate compartment. This complete isolation of the microbial culture from the water stream is possible due to the use of a dense anion-exchange membrane. The IEMB also prevents the need of a strict control of carbon source dosing or additional treatment units to remove an incompletely degraded carbon source, microorganisms and metabolic by-products from the treated water, because they are retained in the biocompartment. As a result, the IEMB represents a simple and more compact solution than traditional technologies used for the removal of nitrate in closed marine systems.

Comparing the IEMB system with other membrane treatment technologies, such as, e.g. reverse osmosis [15], the IEMB system allows for a conversion of nitrate into harmless nitrogen, while in the RO system the nitrate removed from the contaminated water is accumulated in a brine stream, which frequently needs further

treatment. Additionally, since RO is not a selective membrane process, demineralised water is obtained and the required salts have to be added to the treated water to allow its reuse. In contrast, the IEMB, if operated as described, is a selective NO_3^- removing process, preserving the original water composition with respect to other ions. This is an advantage of the IEMB for the studied application, allowing for the reuse of the treated water.

5. Conclusions

The applicability of the IEMB system for the removal of nitrate from a close marine system was demonstrated. The results obtained showed that high concentration of chloride in the water compartment decreases the transport of nitrate through the membrane. However, even under saline conditions, the IEMB can efficiently remove nitrate down to values acceptable for the oceanarium.

The use of the IEMB system, previously limited to drinking water treatment, can be extended to the removal of pollutants from high saline water. Therefore, the IEMB system proved to be a possible alternative for the treatment of aquarium or aquaculture waters. Additionally, it has the potential to be applied for the removal of pollutants, from highly concentrated saline solutions used in the regeneration of ion exchange resins. These concentrated regeneration solutions represent an environmental problem and are limiting the wider use of ion exchange technology.

The proposed model can be used to predict the behavior of the system for any application of the IEMB (with high or low saline waters). Therefore, it could be applied as a tool for process design and scale up.

Considering the potential application of the IEMB on a large scale, process optimization in order to reduce its capital and operational costs is imperative. The membrane cost has the most significant impact on the overall process cost. Therefore, further investigation and process validation at a pilot scale will be performed with different membranes, different system configurations and spacers in the water compartment with the objective of improving the system cost efficiency.

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