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Drinking Water Denitrification Using A Novel Ion-exchange Membrane Bioreactor

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A novel ion-exchange membrane bioreactor, able to prevent secondary pollution of biologically treated drinking water, was developed and specifically tested for water denitrification. This system combines ion-selective membrane dialysis and biological conversion. The ion-selective membrane facilitates the extraction of the pollutant from the water to the biological compartment, hinders the transfer of organic and inorganic nutrients, and confines the microbial culture involved in the conversion process within the bioreactor. In the study hereby presented the system was used to investigate the removal of nitrate from a synthetic groundwater containing 50 mg−N L^{-1} of nitrate. The treated water obtained was free of inorganic nutrients and ethanol, the carbon source was selected for the biological process, and the surface denitrification rate achieved was 7 g−N m^{-2} day^{-1}. This system proved to be effective in producing a treated water effluent that does not require the extensive posttreatment associated with conventional biological treatment.

Introduction

Nitrate is a common pollutant in ground and surface waters due to growing population density and use of nitrogen rich fertilizers. Pollution of drinking water with nitrate presents a serious health hazard because at concentrations higher than 10 mg−N L^{-1}, sufficient quantities of nitrite can be formed in the intestinal tract of infants and lead to acute asphyxiation, a syndrome known as methemoglobinemia. Other epidemiological studies have linked nitrate to congenital malformations and increased risk of cancer development (*1*).

The two most common technologies used to remove nitrate from drinking water are ion exchange and biological denitrification. Operational and capital costs of treatment for each of these technologies are about the same (*2*), which by themselves fail to explain why is biological denitrification favored in Europe and why is ion-exchange considered to be a better technology in the U.S.A. (*3*). The difference in distribution may be explained by costs related to the risks associated with each of these technologies. Indeed in Europe, where due to higher population density the availability of drinking water is scarcer than in the U.SA., converting nitrate into an innocuous gas product is highly valued against the costs of storing concentrated brines in landfills and possible leachate contamination of groundwater sheds. On the other hand, ion-exchange is the selected choice in the U.S.A. because smaller size water treatment plants price highly the operation simplicity of ion-exchange systems.

Biological treatment requires supply of exogenous organic carbon and nutrients, which are seldom completely consumed. These nutrients remain in the treated water, causing what is known as secondary pollution (*4*), and must be removed by extensive posttreatment. Furthermore, biological treatment of drinking water is still associated with risks of microbial contamination, release of toxins, soluble microbial products, and, after disinfection, with an increase in the formation potential of disinfection byproducts (*5*).

A significant research effort has been devoted to engineering biological systems capable of overcoming microbial contamination and secondary pollution of the treated water. Cross-flow filtration coupled to biological reactors has been claimed a successful design, with a few units installed in Europe (*6*). Filtration systems have high volumetric denitrification capacity (*7*) and are capable of retaining bacteria (*8*), protozoa, and their cysts and reducing virus counts (*9*). However, the treated effluent is the filtered biomedium, and, therefore, it is likely to be polluted with incompletely consumed substrates or microbial soluble metabolites because smaller molecules are not completely retained by ultra- or microfiltration. Membrane-contactor systems were also proposed to overcome secondary pollution and microbial contamination. In these systems, microporous membranes (*10*) or membrane and agar immobilized cell composites (*4*) separate the microbial culture from the water being treated. Unfortunately, bench scale results revealed that microporous-contactors were not sufficient to prevent pollution of the treated water with incompletely degraded substrate (*11, 12*) and that the treated water was contaminated with microorganisms supported by the presence of organic pollutants (*11, 13*). One of the reasons that accounts for the poor performance of these systems is the existence of convective transport which causes mixing of treated water and biomedium.

Inorganic secondary pollution, with nutrients such as phosphate and sulfate, has not been specifically addressed by any of the technologies described above, although it is known that even very low concentrations of phosphate (below 1 μg L^{-1}) can promote extensive microbial growth in drinking water (*14*).

Ion-Exchange Membrane Bioreactor (IEMB)

An advantageous alternative to the above-mentioned systems is the ion-exchange membrane bioreactor, which combines ion-selective membrane dialysis, also known as Donnan dialysis (*15*), and biological remediation.

Compared to previously described systems, the advantage of the ion-exchange membrane bioreactor relies on the use of a nonporous membrane that keeps the water being treated segregated not only from the microbial culture, as in membrane-contactor systems, but also from the biomedium where the culture is suspended. The transfer of species between the water and the bioreactor depends on the characteristics of the membrane, which can thus be selected as to facilitate the extraction of the ionic pollutant from the

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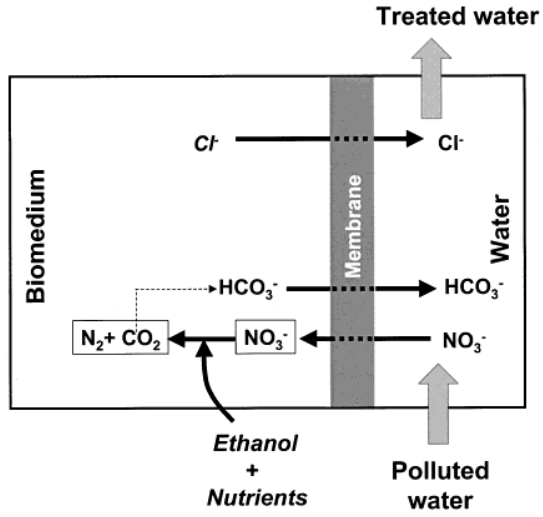

FIGURE 1. Schematic diagram of nitrate transport in the ion-exchange membrane bioreactor.

water and to hinder the transfer of organic and inorganic pollutants present in the biomedium.

The present work proposes this novel system for the first time and discusses its use for nitrate removal from drinking water. For this purpose, an anion-exchange membrane and an anoxic denitrifying bioreactor were selected. As an exchange process, the removal of nitrate from the water is accompanied by the counter transport across the membrane of an equivalent molality of a second ion, hereby named counterion. The transport process through the membrane is diffusive and relies on concentration and charge gradients of the ion species present as driving forces. After being transported, the pollutant can be converted in the bioreactor and is thus kept from diffusing back to the treated water. The principle of the process is illustrated in Figure 1.

Chloride was added to the bioreactor, to be used as the counterion, because it is not regulated by primary water quality standards. Ethanol was chosen as the carbon source and the electron donor of the denitrification process because, unlike organic acids at neutral pH in water, it is not an anion and therefore will not be favorably adsorbed or transported through the anion-exchange membrane. In addition, compared to other nonionizable substrates, ethanol has the advantage of being nonreadily fermentable (*16*), and, therefore, it is less likely to support growth of fermentative organisms and production of organic acids in the anoxic bioreactor.

The objective of this work is to examine the potential benefits of the ion-exchange membrane bioreactor to treat water polluted with nitrate. These benefits include the following: (1) prevention of secondary pollution of the treated water with particulate and dissolved organic and inorganic substances; (2) prevention of microbial contamination with microorganisms from the bioreactor; (3) achievement of a high removal rate of nitrate due to facilitated transport through the membrane; and (4) simplified water treatment by not requiring deoxygenation of the treated water.

To evaluate the behavior of this system, the experimental work performed was organized by first studying the transport process of nitrate, ethanol, and inorganic compounds. Ethanol was used as an indicator of the presence of dissolved secondary organic pollutants, while sulfate and phosphate, the most abundant nutrient anions in the biomedium, were used as models for the permeation of inorganic nutrients and their transport rate related to the concentration of chloride in the biomedium. In a second stage, the denitrification capacity of the system was investigated and related

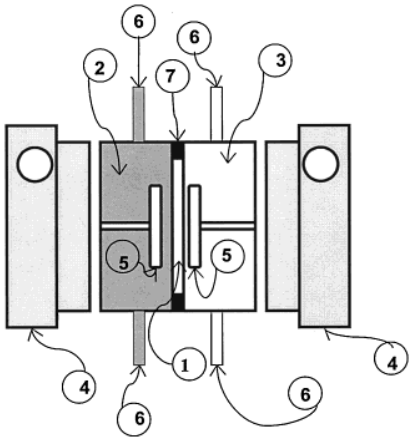

FIGURE 2. Schematic diagram of the dialyzer. Key: 1, ion-exchange membrane; 2, bioreactor flow-cell; 3, water flow cell; 4, magnetic stirrer; 5, magnetic bar; 6, tubing fittings; and 7, rubber O-ring.

to the concentration of chloride and bicarbonate (a counterion produced by the denitrification process).

Experimental Section

Flow Cell Dialyzer and Membrane. A stirred dialyzer was used to study kinetics of mass transport through the membrane. The dialyzer, pictured in Figure 2, is constituted by two flow-cells that enclose a flat membrane sandwiched between them. The assembled rig was sealed in a press against two magnetic stirrers on each side. A magnetic bar in each cell provided independent stirring in each of the two chambers. Two dialyzers, with 20 and 80 mL of cell volume and 12.6 and 28.3 cm^2 of membrane area, were used, respectively, in nutrient transport studies and in the denitrification IEMB apparatus. Membrane Neosepta ACS made by Tokuyama Corp. (Japan) was used throughout these studies. The membrane exchange capacity is 1.8−2.0 mequiv g^{-1}(experimentally confirmed), and its thickness is comprised between 0.12 and 0.2 mm. The membrane was stored in a 0.5 M KCl solution.

Kinetics of Mass Transfer. Throughout the description of kinetic studies, the water solution with nitrate is referred as "feed", and the solution without nitrate as "dialysate". The experiments were carried under isothermal (24 °C) and isobaric conditions. The stirring speed in each flow cell was set at 520 rpm. Previous tests conducted with 2.5 mM solutions of KNO_3 and KCl showed that the flux of nitrate was not affected by the stirring speed when it was set at 440, 520, or 650 rpm (data not shown). Dialysate and feed solutions were prepared with deionized water. All anions were added as potassium salts or as acids in order to reduce the number of cationic species in solution.

The cell dialyzer was operated in a batch mode in order to determine the rate of transport of phosphate, sulfate, ethanol, and oxygen. Each flow cell of the dialyzer was connected to a flask, containing the dialysate or the feed solution. The solutions were continuously recycled by gear ZP180 pumps (Ismatec, Switzerland) set at 150 mL min^{-1}, and therefore the volume of the circuit (300 mL) was, on average, renewed in 2 min. The total volume of the dialysate circuit was 700 mL. Samples were taken at regular time intervals (20−60 min), and the volume ratio of feed to dialysate phases was kept constant during each experiment. The total volume of sampling represented 10% of the initial volume. The permeability of the membrane to dissolved ethanol was tested using a dialysate solution containing 25.3 mM of ethanol and 2.5 mM of KCl and a feed solution with 2.5 mM of KNO_3. The permeability of the membrane to phosphate and sulfate was tested using a dialysate solution

TABLE 1. Operational Settings and Average Results in Run 1 and Run 2

	parameter	run 1	run 2
bioreactor feed	flow rate (mL day^{-1})	81	81
	HRT (day)	3.5	3.5
	ethanol (mM)	28	45
	KCl (mM)	6.5	21.0
polluted water	flow rate (mL min^{-1})	0.32 ± 0.02	0.31 ± 0.02
	HRT (h)	4.2	4.4
	NO_3^- (mM)	2.3	3.6
	Cl^- (mM)	0.13	0.13
	HCO_3^- (mM)	1.0	1.0
	sulfate (mM)	0.06	0.06
treated water	flow rate (mL min^{-1})	0.32± 0.02	0.31 ± 0.02
	NO_3^- (mM)	0.65	0.3
	NO_2^- (mM)	0.005	0.001
	Cl^- (mM)	0.80	1.97
	HCO_3^- (mM)	1.82	2.30
	sulfate (mM)	0.06	0.06
	phosphate (mM)	N/d[a]	N/d[a]
	ethanol (mM)	N/d[a]	N/d[a]

[a] N/d, not detected.

containing 1 mM of K_2HPO4, 1 mM of K_2SO_4, and 1 mM of KCl, while the feed solution contained either 2.5 mM of KNO_3 or 2.5 mM of KCl. Conductivity (Orion) and pH (Metler-Toledo) were measured online. When required, pH was adjusted to 8.0 with 1 M KOH.

Polluted Groundwater and Bioreactor Feed. Synthetically concocted groundwater polluted with nitrate was prepared by supplementing deionized water with 10 mg L^{-1} of KCl, 10 mg L^{-1} of K_2SO_4, 100 mg L^{-1} of $KHCO_3$, and variable concentrations of KNO_3. The bioreactor feed was prepared according to a predefined C:N molar ratio, higher than the stoichiometric theoretical value, to avoid carbon limitation in the bioreactor compartment (see Table 1). The concentration of inorganic nutrients in the biofeed was defined by the amount of ethanol added. Per gram of ethanol in the biofeed solution the following nutrients were added: 0.11 g of KH_2PO_4; 6.45 mL of salt solution (26 g L^{-1} NH_4Cl, 2.5 g L^{-1} $MgSO_4.7H_2O$ g L^{-1}, 2.25 g L^{-1}, Na_2SO_4 g L^{-1}, 0.9 g L^{-1} $CaCl_2$·$2H_2O$); 2.42 mL of iron solution (0.77 gL^{-1} $FeCl_2$·$4H_2O$); 0.4 mL of micronutrient solution (0.1 g L^{-1} $ZnSO_4$·$7H_2O$, 0.03 g L^{-1} $MnCl_2$·$4H_2O$, 0.3 g L^{-1} H_3BO_3l, 0.2 g L^{-1} $CoCl_2$·$6H_2O$, 0.01 g L^{-1} $CuCl_2$·$2H_2O$, 0.02 g L^{-1} $NiCl_2$·$6H_2O$, 0.03 g L^{-1} $NaMoO_4$·$2H_2O$). The oxygen dissolved in the bioreactor feed was removed by purging with nitrogen.

Ion-Exchange Membrane Bioreactor. The layout of the ion-exchange membrane bioreactor used is presented in Figure 3. The dialyzer used in this rig is identical to the largest one previously used for transport studies: cell compartment volume of 80 mL, membrane area of 28.3 cm^2, and similar stirring conditions. A peristaltic pump fed the synthetic polluted groundwater continuously with a flow rate of 0.3 mL min^{-1}, which is equivalent to 4.4 h of hydraulic residence time. The biological reactor was coupled to one of the cells of the dialyzer. The total volume of biomedium (including bioreactor and biological circuit) was 300 mL; the biomedium was recycled between the bioreactor and the dialyzer at a flow rate of 150 mL min^{-1}, equivalent to 2 min recirculation time. The bioreactor was operated as a fed-batch, with 2 min feeding cycles every 4 h and a hydraulic residence time of 3.5 days. Samples of bioreactor effluent were taken daily at the end of a feed cycle. Samples of treated water effluent were collected in refrigerated vials. The temperature was controlled at 24 °C, and the pH and redox potential were measured online. The bioreactor was inoculated with 280 mL of a denitrifying enriched culture. The reactor used for culture enrichment was a steady-state continuously stirred

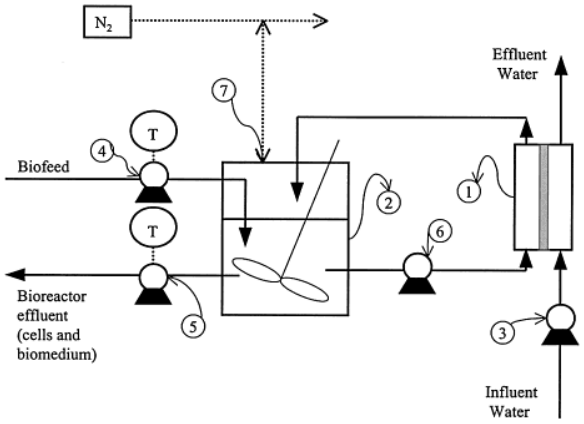

FIGURE 3. Schematic diagram of the ion-exchange membrane bioreactor. Key: 1, flow cell dialyzer; 2, anoxic bioreactor; 3, polluted water pump; 4, timer-switch operated biofeed pump; 5, timer-switch operated bioreactor effluent pump; 6, bioreactor recirculation pump; and 7, nitrogen gas line.

denitrifying reactor that had been inoculated with diluted activated sludge; this reactor was operated with a hydraulic residence time equal to 3.5 days and a volumetric load of 0.3 g-KNO_3 day^{-1} L^{-1}.

Analytical Procedure. Nitrate, nitrite, chloride, phosphate, sulfate, and bicarbonate were determined by HPLC (Shimadzu-Merck) equipped with a column IC-AN-1 (Merck, Germany). The mobile phase (flow rate of 1.2 mL min^{-1}) was a solution of 1.5 mM phthalic acid, 1.38 mM tris(hydroxymethyl)aminomethane, and 300 mM boric acid. A spectophotometric detector was used at 254 nm. Ethanol was analyzed by HPLC with column Shodex SH1011 (Showa Denko K.K, Japan) using a 0.1 M H_2SO_4 solution as the mobile phase (flow rate of 1.0 mL min^{-1}) and a refractive index detector (Merck, Germany). The ethanol detection limit was 1 mg L^{-1}. Ethanol samples and daily prepared standards were refrigerated (4 °C) in sealed vials and analyzed within 1 day after sampling. All other samples were stored at −20 °C and filtered (0.45 μm) before analysis. Subsequently the ethanol concentration in the treated water samples was also confirmed by static headspace gas chromatography (detection limit 1 mg L^{-1}). Oxygen was measured using a dissolved oxygen probe and meter (ColeParmer, U.S.A.).

Results and Discussion

Studies of Ethanol and Inorganic Nutrient Transport. The permeability of the membrane to ethanol is a crucial parameter because the carbon source added has been a major contributor to secondary pollution in biological denitrification processes (*4*). Based on this fact, the membrane Neosepta ACS was selected among eight different anion-exchange membranes because it had the lowest permeability to ethanol. In quantitative terms, the transport flux of ethanol (N_i) through the membrane dialyzer can be equationed as the product of the mass transfer coefficient (K_i), the membrane area (A), and the difference between the concentration of ethanol in the dialysate ($C_{i,D}$) and in the feed ($C_{i,F}$). Combining the mass transfer equation and the mass balances for both compartments leads to

$$N_i = K_i \times A \times (C_{i,D} - C_{i,F}) = \frac{dC_{i,F}}{dt} \times V_F = \frac{dC_{i,D}}{dt} \times V_D \quad (1)$$

where K_i represents the overall mass transfer coefficient for ethanol transport from the dialysate to the feed compartment. For the operating conditions used in this study, the overall mass transfer coefficient can be assumed to equal the

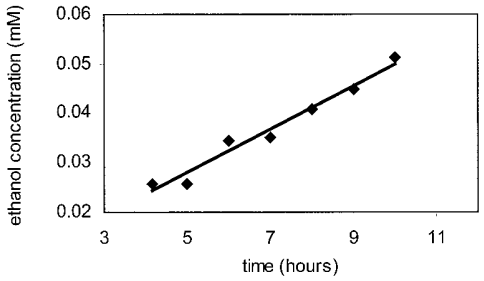

FIGURE 4. Evolution of ethanol concentration in the dialysate compartment during mass transfer studies for determination of the apparent diffusion coefficient of ethanol across the ion-exchange membrane.

diffusion coefficient through the membrane divided by the diffusion length because, as mentioned in the Experimental Section, for a stirring speed above 440 rpm the resistance of both liquid boundary layers was found to be negligible. An apparent diffusion coefficient (Da_i) can thus be defined based on the overall transfer coefficient and the thickness of the membrane (δ_m), as

$$K_i = \frac{Da_i}{\delta_m} \qquad (2)$$

By combining the two previous equations, the apparent diffusion coefficient of ethanol through the membrane was estimated to be 1.8×10^{-8} cm^2 s^{-1} (at 24 °C), from the experimental results plotted in Figure 4. This value is almost 3 orders of magnitude lower than 1.28×10^{-5} cm^2 s^{-1}, which is the effective diffusion coefficient of ethanol in water at 20 °C (*17*). Since the estimated coefficient accounts for the intrinsic membrane resistance to transport, it may be concluded that the overall mass transfer coefficient of ethanol in a dialyzer with a Neosepta ACS membrane will always be equal or lower (if the liquid boundary layers were not negligible) than the calculated value of 1.8×10^{-8} cm^2 s^{-1} (at 24 °C).

Hence, the diffusion value estimated for the Neosepta ACS membrane can be compared with other apparent diffusion coefficients previously reported for membrane-contactors. Lemoine et al. (*4*) determined that the diffusion coefficient for acetate through the agar-membrane in their prototype was 1.9×10^{-6} cm^2 s^{-1} (25 °C), which is about 200 times higher that the value we hereby report. Since the prototype described by Lemoine et al. (*4*) was the only system that claimed to produce treated water that was always free of carbon source, it can be conclude that the ion-exchange membrane bioreactor configuration allows for a significant improvement regarding prevention of secondary pollution.

Most inorganic nutrients in the biomedium are in solution as anions or cations. In general, the diffusion of cations through anion-exchange membranes is very low compared to that of inorganic anions (*15*). Consequently, the pool of potential inorganic pollutants in the ion-exchange membrane bioreactor is reduced to anionic compounds in solution. Sulfate and phosphate were used as models to study the permeation of inorganic nutrients because they are the most abundant ions in the bioreactor medium. The results obtained showed that sulfate does not permeate through the membrane during the 20 h of experiment, which can be attributed to the affinity of Neosepta ACS for monovalent anions (*18*). Based on the minimum detection level of sulfate (0.01 mM) and on the mass transfer equation, similar to the one used to relate ethanol concentrations and mass flux, an apparent diffusion coefficient was estimated for sulfate and found to be equal or less than 2.3×10^{-8} cm^2 s^{-1}.

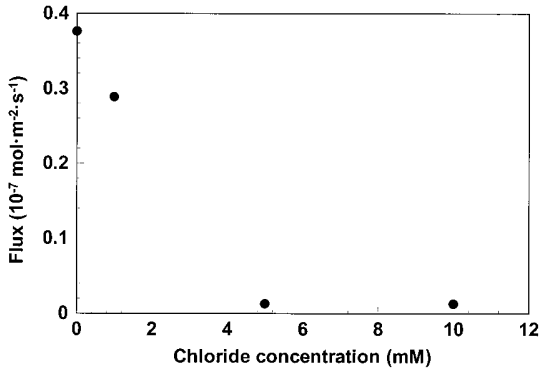

FIGURE 5. Flux of phosphate through the membrane at different concentrations of potassium chloride in the dialysate solution. The concentration of phosphate in the feed was constant and equal to 3 mM.

Regarding phosphate, although the concentrations detected were near detection level (0.01 mM), it was observed that, under the same set of conditions, there was a detectable transport of phosphate through the membrane. This higher permeability may be explained by the existence of monovalent phosphate, $H_2PO_4^-$, which represents approximately 20% of the total phosphate in solution at pH 8. Increasing the pH of the biomedium would reduce the fraction of monovalent phosphate, but an increase in pH would also affect the biological activity. Hence, it was decided to maintain pH and investigate the influence of chloride molarity in the biomedium upon the transport of phosphate. The concentration of phosphate in the dialysate was set at 3 mM, and the flux of phosphate was measured with increasing concentrations of chloride in the dialysate, while the feed solution contained 2.5 mM of KCl. The results are shown in Figure 5, where it is clear that the permeability of phosphate decreases and becomes undetectable when the concentration of chloride is 5 and 10 mM. The decrease in phosphate flux can be explained by the increased competition between the two anions, chloride and monovalent phosphate, for a limited number of complexation sites (membrane carriers) in the membrane matrix.

Denitrification in the Ion-Exchange Membrane Bioreactor. A bench scale ion-exchange membrane bioreactor was used to treat synthetically concocted polluted water saturated with oxygen at room temperature. Table 1 summarizes the operational settings and results obtained for two different experiments: run 1, operated for 12 days, and run 2, operated for 16 days. The main objective of the two experiments was to compare the denitrification rate of the ion exchange bioreactor when operated with different concentrations of chloride in the biomedium, respectively 6.5 and 21 mM.

Ethanol and phosphate were not detected in the treated water during the course of the experiments, and the concentration of sulfate in the effluent was equal to its original concentration in the polluted water. These results reinstate what was discussed above about the kinetics of ethanol and nutrient transport through the membrane. They also confirm that the water treated in the ion exchange membrane bioreactor does not contain the most common secondary pollutants present in water after biological treatment.

Figures 6 and 7 show the time course concentration of nitrate, chloride, and bicarbonate in the treated effluent for run 1 and run 2. The concentrations of bicarbonate and chloride in the treated water (effluent) were higher than in the polluted water (influent). The difference corresponds very closely (98−100%) to the amount of nitrate removed by ion-exchange. The pH of the treated water and the polluted influent water were equal, and the conductivity readings for

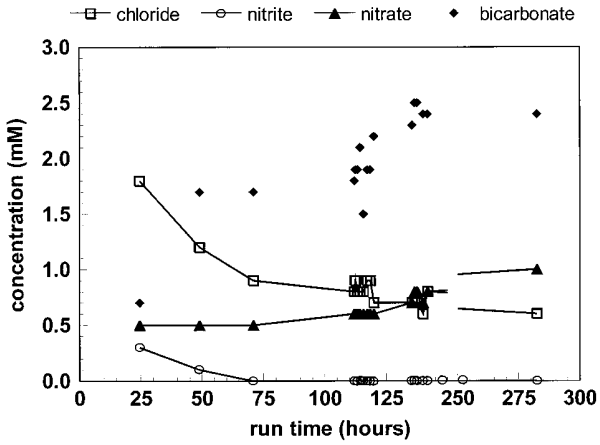

FIGURE 6. Concentration profiles of nitrate, nitrite, chloride, and bicarbonate in the water effluent of the ion-exchange membrane bioreactor in run 1. Concentration of nitrate in the influent: 2.3 mM.

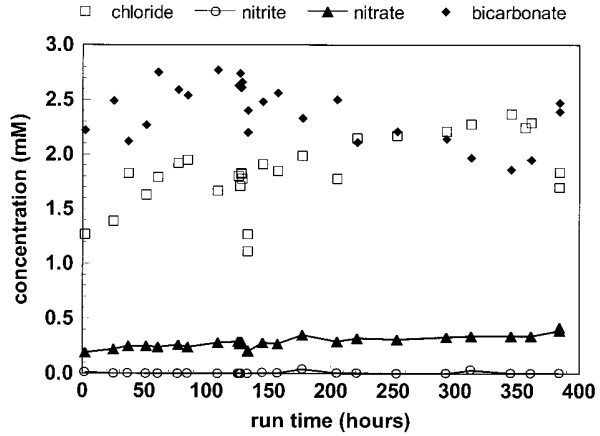

FIGURE 7. Concentration profiles of nitrate, nitrite, chloride, and bicarbonate in the water effluent of the ion-exchange membrane bioreactor in run 2. Concentration of nitrate in the influent: 3.6 mM.

both circuits were constant throughout the course of these experiments. These results support the assumption that anion exchange is the dominant mechanism of mass transport through the ACS Neosepta membrane and demonstrate that chloride and bicarbonate are the most important elements in the mechanism of nitrate extraction. Chloride was added to the system as potassium chloride dissolved in the bioreactor feed.

As opposed to chloride, bicarbonate was "indirectly" added to the bioreactor because bicarbonate is formed from carbon dioxide, which is a product of ethanol oxidation during the biological denitrification process. High concentration of dissolved carbon dioxide and bicarbonate in the biomedium was expected because the bioreactor was not air-purged, and, hence, the biomedium was in equilibrium with the mixture of gases produced by denitrification, mostly nitrogen and carbon dioxide, produced at an approximate molar ratio of 0.63 (*19*). Under these conditions, the pH determines the exact concentration of bicarbonate in the biomedium for a given saturation concentration of dissolved carbon dioxide. The pH of the bioreactor was found to stabilize at 7.2 and the concentration of bicarbonate in the biomedium fluctuated between 9 and 11 mM. For these values, the theoretical partial pressure of carbon dioxide in the headspace was estimated to be 10−13% (*20*).

The anoxic bioreactor was inoculated immediately before the start-up of the system. As expected, the concentration of nitrate in runs 1 and 2 stabilized within hours after start

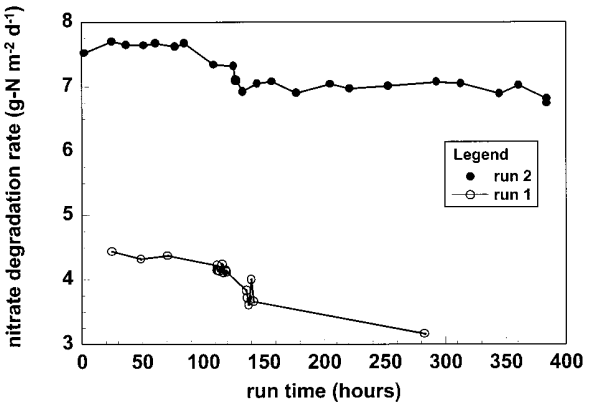

FIGURE 8. Denitrification rate per unit area of membrane in the ion-exchange membrane bioreactor in run 1 and run 2.

up. However, during run 1, a concentration of 0.26 mM of nitrite was detected after 25 h, decreased to 0.08 mM at 50 h, and became nondetectable after 71 h of operation. The occurrence of nitrite was coincident with higher redox potential readings in the system (redox potential increased from −500 to −200) and might have been caused by ethanol limitation because during the start-up period oxygen could have been introduced in the bioreactor. To reduce the stabilization period, the bioreactor of run 2 was spiked with 10 mM of ethanol (460 mg L^{-1}) immediately after start-up. As a result, the concentration of nitrite in the treated water during run 2 was in fact lower, 0.006 mM after 2 h, and bellow detection level after 25 h. These results demonstrate that, with the exception of the start-up period, the quality of the treated water was in compliance with the relevant standards for drinking water (*21*).

The membrane surface rate of denitrification was calculated for run 1 and run 2 based on the rate of conversion of nitrate and nitrite and is plotted in Figure 8. The rates in run 1 and 2 are rather different in magnitude. The initial value for run 1 was 4.4 g−N m^{-2} day^{-1} and decreased progressively to reach a final value of 3.2 g−N m^{-2} day^{-1} after 12 days. On the other hand, during run 2, the rate of denitrification only decreased slightly during the first 3 days, after which it leveled at 7 g−N m^{-2} day^{-1} for the remaining 13 days. The difference in magnitude can be better explained based on the kinetics of ion exchange, than on the bioreactor efficiency, because the microbial start-up culture and the nutrient concentration of the biomedium were the same for both runs. An important difference between runs 1 and 2 is the concentration of chloride which, as mentioned earlier, was intentionally increased and was more than four times higher in run 2 than in run 1 (Table 1). Since the diffusion coefficient of chloride in the Neosepta ACS is reported to be higher than the diffusion of bicarbonate (*22*), an increase in the concentration of chloride available to be exchanged for nitrate can account for the increase in the kinetics of nitrate extraction. The differences between the diffusion of chloride and bicarbonate through the membrane reinforce the option of adding chloride as a counterion in order to improve the transport rate of nitrate and, hence, the overall denitrification capacity of the system. Nevertheless, despite the reduction of nitrate removal rate induced by an excess of bicarbonate, the bicarbonate-nitrate exchange may be advantageous when treating waters with a molar ratio of chloride to bicarbonate that is near or higher than 1.4 because beyond this threshold number, the dezincification potential of treated water may enhance the dissolution of zinc from brass fittings in the distribution system (*2*). This problem did not arise during these two runs because the chloride-to-alkalinity ratio was within 0.5−1.1 during run 2 and always bellow 0.2 during run 1, except during start-up when it was 0.6.

Another trait observed in the denitrification rate plot is its initial decrease, registered in both experiments. Theoretically, this decrease can either suggest that the membrane was in transient-state during the first 3 days after start-up or that an additional form of resistance to transport increased slowly during that period of time. The first hypothesis seems rather unlikely because previous transport studies with this membrane showed that steady-state was reached within 4 h. On the other hand, the second hypothesis is more easily tenable because the growth of biofilms on membrane bioreactors is known to increase the resistance to the transport of solutes within the first days of operation (*23*). Indeed, 2 days after start-up, a biofilm was visually detected on the membrane surface in contact with the denitrifying culture: it was observed that the membrane surface changed from an initially light yellow color to dark orange. The presence of a biofilm on the dialyzer membrane in run 1 and run 2 was further confirmed when the system was discontinued. Development of a biofilm was never observed on the membrane surface exposed to the feedwater.

The formation of a biofilm hinders the transport of nitrate from the water to the biological compartment and the diffusion of ethanol and other essential nutrients from the bulk of the biomedium, leading to a decrease of the overall nitrate degradation rate. Nevertheless, this additional resistance to ethanol diffusion contributes to the low ethanol content in the treated water (bellow 1 mg L^{-1}). This performance was achieved even when the ethanol bulk concentration in the bioreactor was as high as 300 mg L^{-1}. The fact that no ethanol was detected in the water circuit may explain why it was not observed development of a biofilm on the corresponding side of the membrane surface.

The ion-exchange membrane bioreactor proved to have a good potential as a biological treatment technology because it prevents secondary contamination of the drinking water with the most common substances, which are exogenous carbon source and inorganic nutrients. Moreover, the surface denitrification rate achieved, 7 g−N m^{-2} day^{-1} in the ion-exchange membrane bioreactor, is higher than the values reported for membrane-contactor systems which ranged between 0.27 and 4 g−N m^{-2} day^{-1} (*10*−*13*). Finally, in contrast to all other biological denitrification systems, the system was operated without being necessary to eliminate oxygen that is naturally dissolved in the polluted or in the treated water, because the permeability of the membrane to oxygen was found to be negligible.

However, the hydraulic residence time of the water stream (HRT = 4.4 h) is high when compared with other biological treatment processes. This value may be reduced by increasing the membrane area to bioreactor volume ratio or by improving the membrane transport properties toward nitrate. This problem has to be addressed in further process development studies for large scale application. Also, the effect of biofilm development on the biomedium side of the membrane has to be investigated for long-term operation, to clarify its impact on the nitrate degradation rate and the transmission of ethanol to the water stream.

The studies hereby presented tested the application of the IEMB system to remove nitrate in order to produce a treated effluent that meets all the relevant criteria for drinking water. Nevertheless, the application of the IEMB (either using anion-exchange or cation-exchange membranes) extends far beyond nitrate removal since it can be potentially used to treat several other ionic pollutants where effective biological cultures are available, such as bromate, heavy metals, and sulfate, among others. For each new application, the operating conditions of the IEMB have to be defined as to optimize the final result, whether it means to enhance removal rates, shelter the biological process from metabolic inhibitors, or segregate biological products from the treated effluent. Overall, the critical issues will be the same as in the application hereby described, i.e. ion-exchange process, biological conversion, and, perhaps most importantly, the confinement of undesirable pollutants and microbial contaminants.

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