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ORIGINAL ARTICLE

Donnan dialysis as membrane process for nitrate removal from drinking water: Membrane structure effect

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Abstract Nitrates are extremely soluble in water and are considered as the renown pollutants of natural water and water table. Removing them through AMX, AM3, and RPA anion exchange membranes has been studied under donnan dialysis conditions as a function of concentration, pH and the nature of the feed phase. It was observed that the AMX membrane gives the highest nitrate transport efficiency and that the optimal concentration in the selected zone was in 6.2 g/L (0.1 M) with 37.9%. It was also observed that the best pH for the concentration of 0.62 g/L is pH 10 with yield of 23%. Results are evaluated by the yield calculated with nitrates concentration detected by molecular absorption spectrometry in 212 nm.

1. Introduction

Nitrate is mainly found in natural water at moderate concentrations but it is often enriched above the contaminant levels from excessive use of fertilizers and uncontrolled discharge of raw water (Peavy et al., 1985; Lin and Wu, 1996; Sihrimali and Singh, 2001). Most important environmental problems caused by nitrate are eutrophication in water supplies and infectious disease (Barber and Stuckey, 2000). Excess nitrate in drinking water may cause blue baby disease called as methemoglobinemia in new born infants as well as other illness (Arden, 1994; Öztürk and Bektas, 2004). In order to protect public health from the adverse effects of high nitrate intake, World Health Organisation (WHO) set the standard as 50 mg/L to regulate the nitrate concentration in drinking water. The conventional processes (coagulation, filtration, and chlorination) applied for water treatment are not useful for nitrate elimination from water. (Knobeloch et al., 2000). Therefore, traditional biological treatment methods (Ergas and Rheinheimer, 2004; Reyes-Avila et al., 2004; Jianping et al., 2003; Rabah and Dahab, 2004) and other methods (adsorption (Cengeloglu et al., 2006), ion exchange, catalytic denitrification (Pintar et al., 2001), reverse osmosis (Schoeman and Steyn, 2003), Donnan dialysis (Schaetzel et al., 2004;

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Wisniewski et al., 2005, 2006), and electrodialysis (Elmidaoui et al., 2001, 2003; Salem et al., 1995)) have to be applied to remove nitrate from water. Reverse osmosis and electrodialysis have better economics, larger automation possibilities, lower level in feed and process parameters control and no need for extensive post treatment are advantages (Schoeman and Steyn, 2003; Elmidaoui et al., 2002). However, the utility of these processes has been limited as they are relatively expensive and merely displace nitrate into concentrated waste brine that may pose a disposal problem (Wasik et al., 2001). The advantage of a catalytic reduction process is the rapid removal of nitrate from water. The disadvantage of this process is also its high capital (Gavagnin et al., 2002; Peel et al., 2003). Moreover, it is difficult to maintain the treatment processes in conventional biological treatment methods.

Donnan dialysis is an ion-exchange membrane process that can be used for the purification and concentration of diluted solutions (Guirao et al., 1995) and is generally applied in analytical fields where the preconcentration of various cations and anions is performed. The process was based on a chemical potential difference between two compartments separated by an ion-exchange membrane. However, Donnan dialysis is not applied in industry mainly because of its slow kinetics although it has some economical and energy efficient advantages. Some potential applications have so far been studied at laboratory scale (Wodzki et al., 1996; Kelly et al., 1986; Cherif et al., 1998; Pyrzynska, 1991). The studies which use donnan dialysis as separation process to remove nitrate ions are rare. Therefore, the objective of this work is to eliminate nitrate ions from water by using anion-exchange membranes. To achieve this purpose, the AM3, AMX and RPA anion exchange membranes were examined with respect to pH of the solutions on the two sides of the cell, the receiver phase concentration, and the effects of mono and bivalences of co-existence anions on the removal of nitrate from aqueous solutions.

2. Experimental

KNO_3, NaCl, $NaHCO_3$, Na_2SO_4 and Na_3PO_4 were of analytical grade obtained from Aldrich (Germany) and their solutions were prepared without further purification with distilled water. Binary and ternary ion-exchange equilibrium data were obtained for the RHONE POULENC RPA membrane. The matrix of the ion exchange membrane studies consists of a vinyl polychloride network reinforced by a polyester screen, with quaternary and tertiary ammonium as functional groups. The manufacture data were completed by the determination of the humidity percentage and the ion exchange capacity of the membrane. The Neosepta AMX and AM3 anion exchange membranes were produced by a Japanese firm, which were kindly provided by Eurodia. These two membranes have quaternary ammonium groups. The main characteristics of the anion exchange membranes are presented in Table 1. The membrane is supplied in the chloride ion form. Before the membranes were used, they were treated with distilled water at 70 ± 1 °C for 1 h. Then, in order to remove the impurities, they were also treated with 0.1 M HCl and 0.1 M NaOH at 50 ± 1 °C for 1 h, respectively. The treated membranes were finally immersed into the 1 M NaCl solution at 25 ± 1 °C for 24 h to transform the membrane into the chloride form. To transport nitrate ions, a two-compartment cell (made of Plexiglas) was used. The membrane was clamped tightly between two compartments of 25 mL capacity and the surface area of the membrane was 8.12 cm^2. The feed phase solutions were 0.1 M $NaNO_3$ and 0.1 M $NaNO_3$ + NaCl and 0.1 M $NaNO_3$ + Na_2SO4, which correspond to mono- and bivalent anions, while the receiver side solutions were different NaCl solutions (0.1, 0.01 and 0.001 M). Solution sampling was carried out at certain time intervals, and the concentration of residual nitrate ions was determined spectrophotometrically. Both external solutions were stirred at 700 rpm with a magnetic stirrer. All of the measurements were carried out at 25 °C.

Table 1 Properties of the studied membranes.

Membrane Mark	AMX Neosepta	AM3 Neosepta	RPA Rhone Poulenc
Exchange capacity in Cl^- form (mmol/g)	1.3	1.13	1.58
Thickness (mm)	0.13–0.14	0.17	0.18
Water content (%)	26	22	39

3. Results and discussions

3.1. Effect of the concentration

The transport of nitrate ions was examined as a function of NaCl concentration in the receiver phase and some typical curves for nitrate transport toward the NaCl side versus time are shown in Figs. 1–3 for the AM3, AMX and RPA anion exchange membranes. It can be seen that, over time, nitrate concentration in NaCl solutions increases almost linearly. The results from both Figs. 1 and 2 suggest that the flux of nitrate ions through anion exchange membranes increases with increase of NaCl concentration from 0.01 to 0.08 M.

In the Donnan dialysis process, the transport of nitrate ions is balanced by the pumping ion: in this case the Cl^- ion is moving in the counterbalance. In other words, an increase of the NaCl concentration in the receiver phase increased the concentration of chloride (pumping ion). Hence, effective transport of nitrate toward the receiver phase for SB-6407 and Neosepta-AMX membranes was obtained. This finding in the present study is in agreement with that of Tor, which reported the removal of fluoride from water by using anion exchange membrane under Donnan dialysis conditions. It was reported that the flux of fluoride increased with increasing the chloride concentration in the receiver phase. A similar result was also reported by Tor et al. Moreover, neither water nor salt leakage was detected with the AMX membrane. Similar results were also reported by Hichour et al. who studied the fluoride removal by Donnan dialysis with anion-exchange membranes.

3.2. Effect of accompanying ions

The transport of nitrate is expected to depend on other co-existence anions in the feed phase, which is why further work was conducted by using a single nitrate solution and binary equal molar mixtures of nitrate and hydrogenocarbonate, nitrate and sulfate and nitrate and phosphate solutions. As can be seen in Figs. 4–6, a comparison of the influence of the hydrogenocarbonate, sulfate and phosphate for the transport of

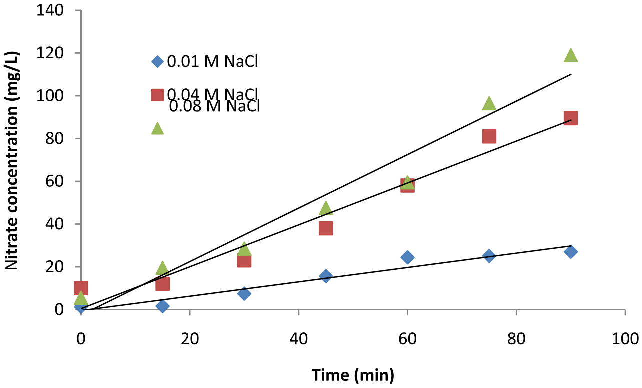

Figure 1 Time dependence of transported nitrate for different concentrations of receiver solution for the AMX membrane (feed phase: 0.1 M NO_3^-).

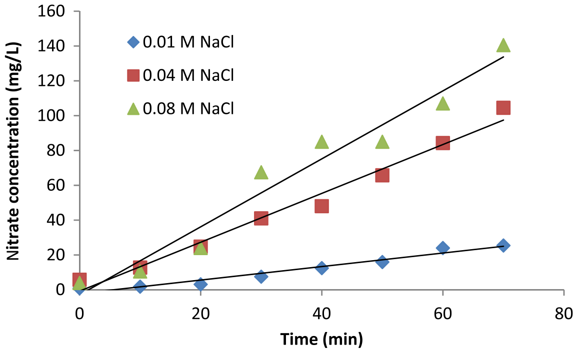

Figure 2 Time dependence of transported nitrate for different concentrations of receiver solution for the AM3 membrane (feed phase: 0.1 M NO_3^-).

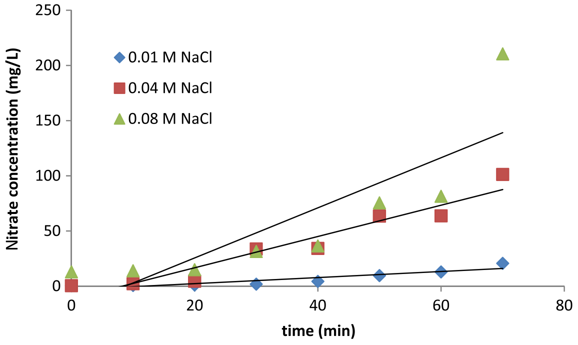

Figure 3 Time dependence of transported nitrate for different concentrations of receiver solution for the RPA membrane (feed phase: 0.1 M NO_3^-).

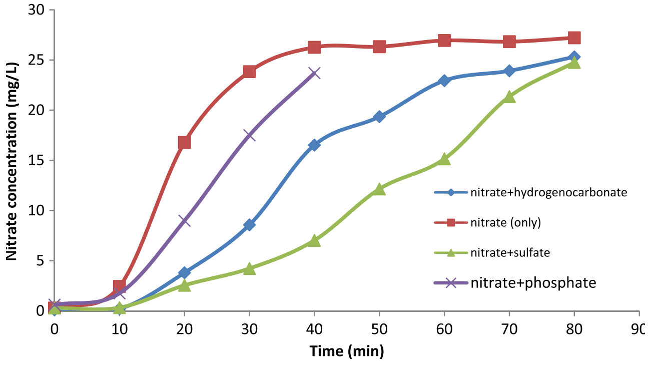

Figure 4 Time dependence of transport of nitrate in contact with different accompanying anions for the AMX membrane (receiver phase: 0.1 M NaCl).

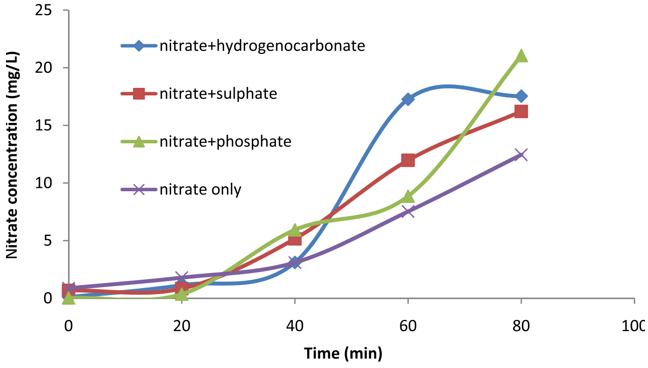

Figure 5 Time dependence of transport of nitrate in contact with different accompanying anions for the AM3 membrane (receiver phase: 0.1 M NaCl).

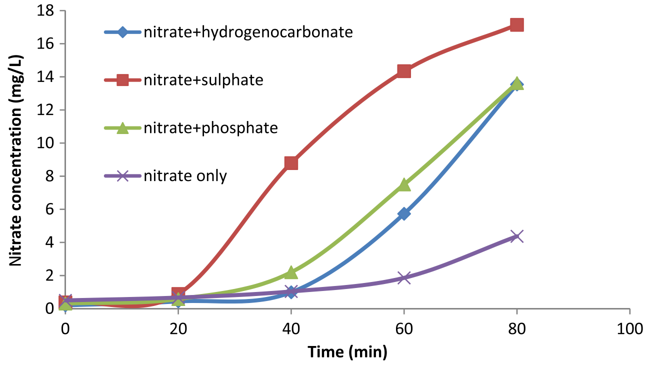

Figure 6 Time dependence of transport of nitrate in contact with different accompanying anions for the RPA membrane (receiver phase: 0.1 M NaCl).

nitrate through the AM3, AMX and RPA anion exchange membranes gave many sequences which depend of membrane nature and ionizable groups. In the case of the AMX Neosepta anion exchange membrane, the removal efficiency of the nitrate from a single nitrate solution is higher than its removal from the equal molar mixtures of nitrate and hydrogenocarbonate, nitrate and sulfate and nitrate and phosphate.

As can be seen from the Fig. 4, a comparison of the influence of the hydrogenocarbonate, sulfate and phosphate through the AMX membrane gave the sequence nitrate-only > nitrate + phosphate > nitrate + bicarbonate > nitrate + sulfate. For the AM3 and RPA exchange membranes the influence of accompanying ions on the transport of nitrates is given by the relative sequences nitrate + bicarbonate > nitrate + sulfate > nitrate + phosphate > nitrate-only and nitrate + sulfate > nitrate + phosphate > nitrate + bicarbonate > nitrate-only. This main difference in the influence of nitrate transport is probably due to the structure of the membrane. In fact, there are many species in the ion exchange membrane which affect the mobility of the ions through the membrane.

The mobility of the mono- and bivalent ions in an ion exchange membrane was investigated by Miyoshi, who reported that a monovalent ion makes an ion pair with a fixed ion in the membrane and it is transferred step by step between neighboring fixed ions. In case of bivalent ions, two fixed ions were used by bivalent ions for transport. Namely, monovalent ion needs only one fixed charged ion that is corresponding of a half-set of a bivalent ion. The results obtained from the present study were in agreement with this explanation. However, we can advance that for the trivalent ions, three fixed ions are used by trivalent ions for nitrate transport. Tor et al. who studied the transport of chromium through cation-exchange membranes by Donnan dialysis in the presence of some metals of different valences reported that the recovery factor (RF) values decreased with increasing the metal valence (Tor et al., 2004).

3.3. Effect of initial pH

At first, the optimum pH of the feed phase was determined under Donnan dialysis condition. The effect of pH of the feed phase on the flux of nitrate through the anion exchange membrane is shown in Fig. 7, which indicated that the transport of nitrate was maximum at pH 10. At a pH above 6 and 10, a decrease in nitrate transport was observed because of a competition between nitrate and hydroxide ions to reach the receiver phase. Moreover, less nitrate transport was also found at pH below 6 and 10. This may be as a result of the formation of weakly ionized nitric acid. Durmaz et al. reported that the influence of pH of the feed phase on the flux of fluoride through the AHA anion exchange membrane is negligible. However, many workers reported that maximum transport of fluoride from water by using Donnan dialysis technique with different anion exchange membranes such as ACM and poly (2-chloroaniline) anion exchange membranes was obtained at pH 6, which supported the results in this study in the acid part.

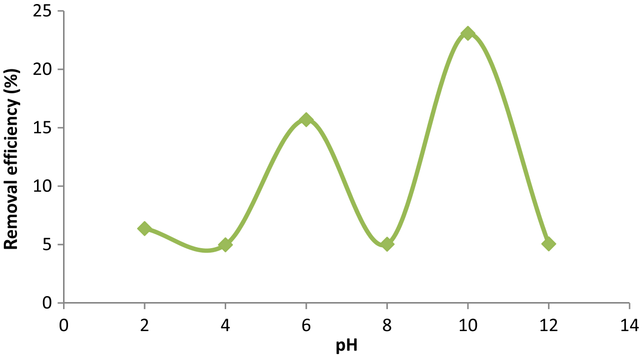

Figure 7 The effect of initial pH of feed phase on nitrate transport (feed phase: 0.1 M $NaNO_3$, receiver phase: 0.1 M NaCl, pH of receiver phase: 6).

At highly acidic pH the nitrate molecules of feed side and chloride molecules of the receiver side are surrounded by H^+ ions and their charges are masked and are then transported through membrane with difficulty.

For an alkaline pH, the nitrates and chloride ions are free and then diffuse quickly in the membrane. For this reason at pH 10 the nitrate removal efficiency attempts its maximum.

For a strong alkaline pH, the membrane containing alkyl ammonium groups is stabilized by the hydroxide and then the nitrate transport will be more and more difficult. As a result the removal efficiency decreases for a pH greater than 10.

3.4. Effect of the membrane structure

To study the effect of membrane structure on the ions transport through anion exchange membrane, Ktari et al. studied the potassium and hydrogen transport ($C = 10^{-3}$ M) and reported that only the diffusion boundary layer controls the ions transfer.

In this study we will be interested in the nitrate concentration domain (0.01 M; 0.1 M) and then we try to define the phenomenon which controls the nitrate transport from the feed side to the permeate side under the donnan dialysis conditions.

As shown inFig. 8, we can separate the domain of concentration in three domains: the domain A (10^{-2} M; 4.10^{-2} M), the domain B (4.10^{-2} M; 8.10^{-2} M) and the domain C (8.10^{-2} M; 0,1 M).

For the zone A, the nitrate removal efficiency decreases between 0.01 M and 0.02 M and then stays constant up to

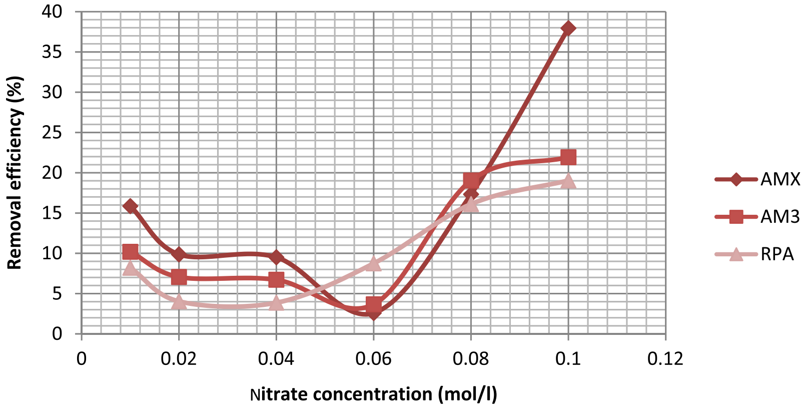

Figure 8 Contribution of the membrane structure on the nitrate transport in the range 0.01 M to 0.1 M of nitrate for AMX AM3 and RPA anion-exchange membranes.

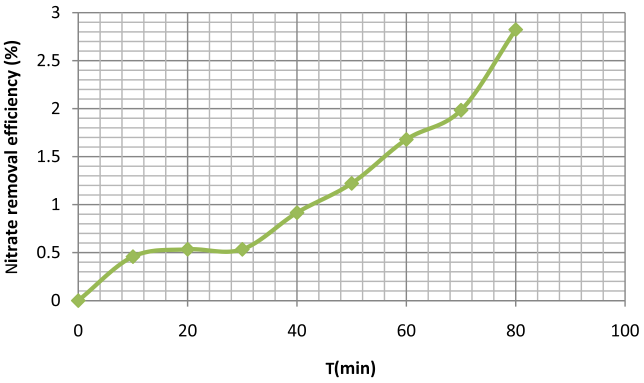

Figure 9 Nitrate removal efficiency versus time under donnan dialysis conditions for $C = 0.03$ M.

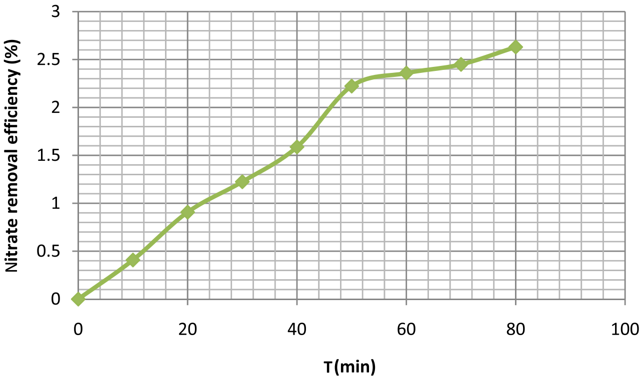

Figure 10 Nitrate removal efficiency versus time under donnan dialysis conditions for $C = 0.06$ M.

0.04 M. This behavior is observed for the three anion exchange membranes. As a result we can affirm that in this zone (A) the membrane has not any effect on the nitrate transport and consequently the nitrate transport is controlled by the diffusion boundary layer.

For the zone B, we remark that each membrane admits a different effect. On the other hand the membranes AMX and AM3 have a similar effect contrarily to the RPA membrane. Wherefrom we can advance that in the zone B the membrane controls the ionic transport.

In the zone C, the nitrate transport is probably controlled by the membrane.

To verify the last hypothesis, we will choose one concentration from each domain: 0.03 M for the domain A, 0.06 M for the domain B and 0.09 M for the domain C and then we will modify the parameters controlling the ionic transport. For this purpose we will use the AMX membrane quite there keeping the flux at 180 ml/h and $T = 35$ °C and for an agitation rate of 300 rd/min.

The change of the parameters led to a decrease of the removal efficiency which was 10% under donnan dialysis conditions (Fig. 8) and becomes 2.82% (Fig. 9). This indicates that the nitrate transport is controlled only by diffusion boundary layer.

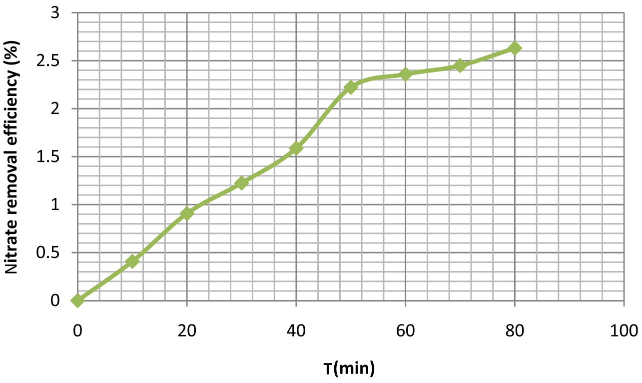

Figure 11 Nitrate removal efficiency versus time under donnan dialysis conditions for $C = 0.09$ M.

In the zone B, the curve shows that the nitrate removal is not influenced by the donnan dialysis conditions. In fact, the removal efficiency was 2.63% (Fig. 8) and becomes 2.59% (Fig. 10). This confirms that between 0.04 M and 0.08 M the ionic flux is controlled completely by the membrane.

In the domain C and for the same applied temperature and agitation the removal efficiency attempts only 1.52% (Fig. 11) in the place of 27% (Fig. 8). This last result brings to light the effect of the applied parameters on the nitrate removal. Then both membrane structure and the diffusion boundary layer affect the nitrate transport for nitrate concentration comprised between 0.08 M and 0.1 M.

4. Conclusion

The results showed that transport of nitrate through anion exchange membranes AMX, AM3 and RPA by Donnan dialysis in the domain 0.01 M; 0.1 M is viable and the transport depends on membrane structure for the concentration between 0.04 M and 0.08 M, the concentration of the receiver phase as well as co-existence anions (bicarbonate, sulfate and phosphate) in the feed phase. It was observed that the nitrate transport capacity of AMX is higher than that of the AM3 and RPA membrane. In these conditions the best nitrate removal efficiency is of 37% with AMX membrane. The pH of the feed phase has an important effect on nitrate transport through anion exchange membranes. The best removal efficiency was obtained at pH = 10 (25%) for the alkaline zone and at pH = 6 (17%).

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