ELECTRODIALYSIS – AN INTERESTING SOLUTION TO THE “NITRATE PROBLEM” IN DRINKING WATER

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Abstract

Although nitrogen is indispensable for life, nitrogen compounds are classified as the primary pollutants of the Earth’s ecosystems. Ground- and surface water pollution with nitrates (NO_3) has already become a global problem, mainly because of an inappropriate and excessive use of fertilizers, discharge of nitrates-containing wastewater, and the increasing deposition of air-borne NO_x. Excessive concentration of nitrate in drinking water is responsible for the incidence of methemoglobinemia (especially in children) and gastric disorder. Among the available methods of nitrate removal from potable water, electrodialysis shows great promise for the future. This paper brings a short introduction to the idea of electrodialysis, specifies its advantages over other methods and presents the results of our experiments. We carried out electrodialysis of water solutions containing excessive amounts of nitrate and various concentrations of other ions (Cl^-, SO_4^{2-}, HCO_3^-). The performances of two anion-exchange membranes, a standard and a mono-anion-selective one, were compared. Depending on the water composition and on the process conditions applied, electrodialysis yielded a nitrate removal of 99%, thus decreasing the concentration of nitrates to values below the admissible levels for potable water.

Introduction

The problem of how to cope with the excess nitrate concentrations found in surface and groundwater resources has taken on a sense of urgency. As reported by the European Environment Agency, in one-third of Europe’s groundwater reservoirs (the main source of drinking water for 50% of the population) nitrate concentrations have exceeded the admissible value of 50 $mgNO_3/dm^3$ (1). Excess nitrate concentrations in potable water are responsible for the incidence of methemoglobinemia, and they also raise the risk of bladder cancer. Excess nitrate concentrations in surface waters produce eutrophication, another serious environmental nuisance which calls for immediate preventive measures.

Most of the water pollution with nitrates comes from agriculture. As a result of unreasonable and excessive use of manure and mineral fertilizers in the past, 87% of Europe’s arable land show groundwater concentrations of nitrates higher than the recommended value of 25 $mgNO_3/dm^3$, and 22% display nitrate concentrations exceeding the admissible level of 50 $mgNO_3/dm^3$ (2). The other contributors to the “nitrate problem” are insufficiently treated municipal and industrial wastewaters, leachates from landfills, and atmospheric emissions.

Unfortunately, despite the legal measures (e.g., the EU Nitrates Directive) taken to abate the nitrate problem, real improvements will not be perceived until after many years. Presently, nitrates are removed from water with the following methods: biological denitrification, ion exchange, reverse osmosis and electrodialysis. However, none of them is perfect, and attempts are made to develop and implement new techniques (Donnan dialysis, catalytic reduction, membrane bioreactors) or modify the available ones (by new designs of relevant equipment or new membrane types).

Compared to other methods, electrodialysis is amongst the most promising approaches to nitrate removal. It is easy to handle, very moderate in the demand for chemicals, enables a high extent of water recovery, and displays (according to the type of the membrane used) a very high selectivity for nitrates. The denitrification of water by electrodialysis is also cost-effective – with an 85% nitrate removal efficiency the operating costs do not exceed 0.1 $/m^3$ (3).

The electrodialysis process involves ion flow across anion-exchange and cation-exchange membranes in a constant electric field. The scheme of the process is shown in Fig.1.

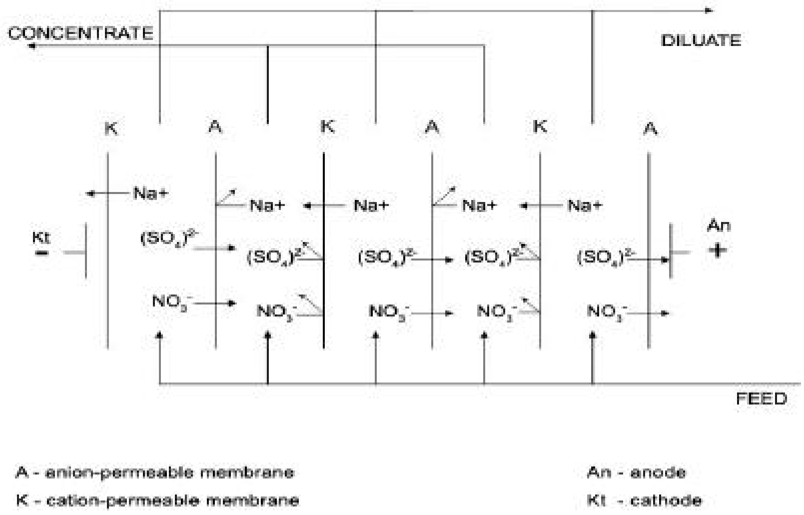


Fig.1. Scheme of a conventional electrodialysis process.

Thus, in the electric field, cations are attracted by the cathode, pass across the cation-exchange membrane and are retained by the anion-exchange membrane; anions flow towards the anode across the anion-exchange membrane and are retained by the cation-exchange membrane. As a result, there is a drop of ion concentration in every other cell of the electrodialyzer (diluate cells). All the fluxes leaving the diluate cells combine to form a desalinated solution (diluate), whereas those leaving the concentrate cells form a concentrated solution and are often referred to as brine. The use of mono-anion-selective membranes offers additional possibilities of nitrate removal by enabling preferential flow of monovalent anions. Selective transport of anions is provided when a thin, strongly crosslinked layer is formed on the membrane surface, which poses no limits to the transport of monovalent anions but prevents polyvalent anion transport. An alternative method consists in producing (on the membrane surface) a thin layer having a negative charge (4).

A major parameter governing the course and cost of the electrodialysis process is current density – the greater it is, the smaller surface area of the membrane is needed. However, it is advisable not to let the current density exceed the limiting value (characteristic for the given concentration of the solution), as otherwise some undesired phenomena may be induced in the course of the process (increased energy demand, pH variations, etc.).

Electrodialysis has a wide spectrum of applications. It is widely used to denitrify water for drinking purposes (Austria, Italy, the Netherlands, France, Switzerland) (5), to produce table salt from sea water (especially in Japan) (6), to demineralize whey (7), to desalinate brackish water (6), to refine fruit juice, as well as to recover salts and acids from industrial effluents, etc. (7).

Methods

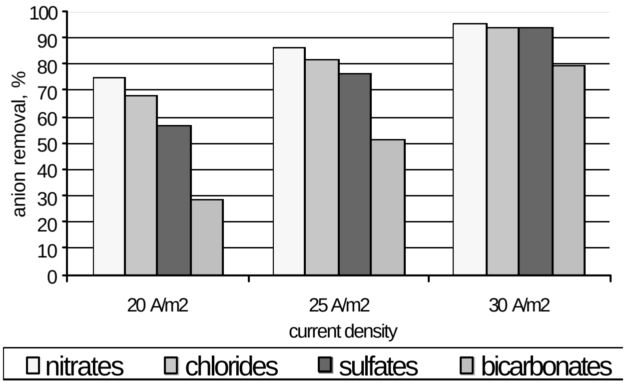
The denitrification process was carried out using a Geomasep 136 laboratory setup for electrodialysis, which involved 10 pairs of cells with a 360 cm^2 effective surface of membranes of the same sign. Use was made of Neosepta CMX cation-exchange membranes and two types of anion-exchange membranes: standard Neosepta AMX and mono-anion-selective Neosepta ACS (all manufactured by Tokuyama Corp., Japan).

The samples used in the experiments contained four-component solutions ($NaNO_3$, NaCl, Na_2SO_4, $NaHCO_3$) of a composition similar to that of natural water and were analyzed for ion concentrations in the diluate; chlorides and bicarbonates were determined by the titrimetric method, and sulphates and nitrates by spectrophotometry, using a DREL 2000 device.

Results

The investigated solutions contained equivalent concentrations (2.5 eq/m^3) of $NaNO_3$ (corresponding to a nitrate concentration of 155 gNO_3/m^3), NaCl, Na_2SO_4 and $NaHCO_3$. Electrodialysis was carried out with three current densities, 20; 25 and 30 A/m^2, in order to establish the most advantageous process conditions in terms of nitrate removal efficiency and energy demand. The limiting value of the current density, 29 A/m^2, was determined in a preliminary test for a salt concentration of 1.5 eq/m^3, i.e. a salt removal efficiency of 85%. The volume of the diluate and concentrate amounted to 10 dm^3 and 1.8 dm^3, respectively, which provided an over 84% recovery of water. The process was discontinued when the concentration of nitrates fell below the admissible level for drinking water (50 gNO_3/m^3). The standard AMX and monoselective ACS anion-exchange membranes were tested with the same process parameters.

Figure 2 relates the removal efficiencies of particular ions to current density in conventional (with Neosepta AMX membranes) and monoselective (with ACS membranes) electrodialysis after 2 hours of the process. Concentration variations for particular components of the solution are plotted in Fig.3a (conventional electrodialysis) and 3b (monoselective electrodialysis).



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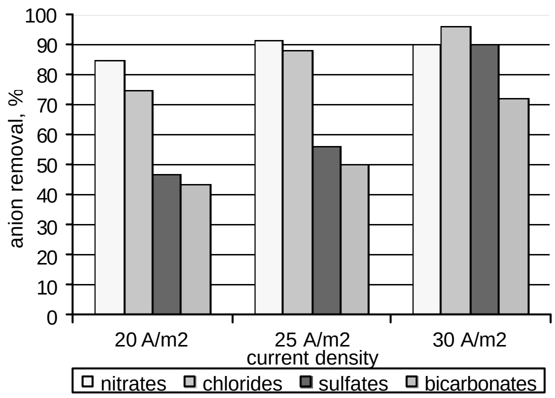
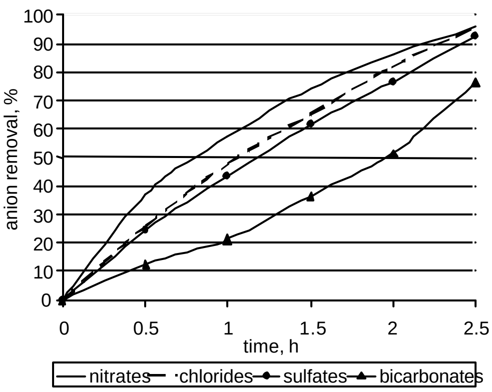


b

Fig.2. Effect of current density on ion removal from a four-component solution by conventional (a) and monoselective (b) electrodialysis after 2 hours of the process (initial concentration of each component, 2.5 eq/m^3).



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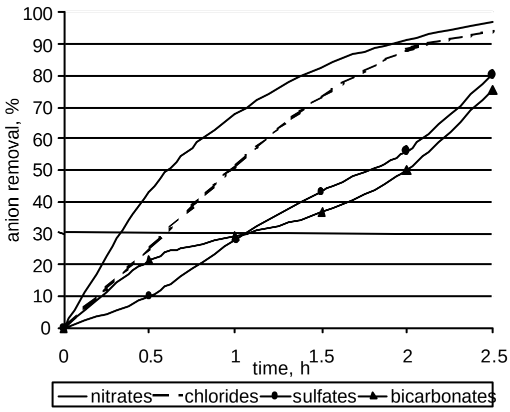

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Fig.3. Concentration variations for particular ions in the diluate during conventional (a) and monoselective(b) electrodialysis (initial concentration of each component, 2.5 eq/m^3; i = 25 A/m^2).

Discussion

Both conventional electrodialysis (with standard AMX anion-exchange membranes) and monoselective electrodialysis (with mono-anion-selective Neosepta ACS membranes) yielded a very high removal of nitrates, which varied from 75 to 99%, according to the current density applied.

Of the ions tested, nitrates were removed with the highest efficiency. The removal efficiency for the other ions, ranked in descending order, was as follows: chlorides, sulphates and bicarbonates (Fig.2). In conventional electrodialysis, the difference in removal efficiency between nitrates and chlorides was insignificant (up to 8%), and so was that between nitrates and bivalent sulphates (up to 18% with the lowest investigated current density). The use of mono-anion-selective membranes increased noticeably the retention of sulphates and consequently the efficiency of nitrate removal. In monoselective electrodialysis, the difference in removal efficiency between nitrates and sulphates amounted to 40%. With the same current density, the removal of nitrates in the monoselective process was approximately by 10% higher than in the conventional process. Of all the ions tested, bicarbonates were removed with the poorest efficiency (markedly poorer than that of sulphates), regardless of whether by conventional or monoselective electrodialysis.

Current density was found to be a major contributor to the course and final effect of the electrodialysis process. When current density increased, so did the extent of desalination. This is due to the rise in the intensity of the current flowing through the electrodialyzer, with ions being the charge carriers. It should, however, be noted that any rise in current density raises the costs of the process (increased energy demand for ion transport). It is also worth remembering that the increase in current density decreases the difference in removal efficiency between individual components of the solution – particularly distinct in the monoselective process. Thus, sulphates, which at low current densities were removed with an efficiency by 40% lower than that of nitrates, showed the same removal efficiency as did the latter, when current density took the highest investigated value. Hence, if current density approaches the limiting value, the monoselective properties of the membranes deteriorate, enabling the transport of both monovalent and polyvalent ions. This implies that monoselective electrodialysis should be performed with a current density far below the limiting value.

Figure 3 relates the removal of particular ions to the duration of the process, with a current density of 25 A/m^2 (which can be regarded as the optimal value for our experiments). As shown by these plots, the difference in removal efficiency between particular ions decreases with time both in conventional and monoselective electrodialysis. The difference in the removal of nitrates and bicarbonates, very distinct at the beginning, became much smaller after two hours. From Fig.3 it can also be seen that at the final stages of the two electrodialysis processes, with current densities of 20 and 25 A/m^2, there is a rise mainly in the removal efficiencies of chloride ions, sulphate ions and bicarbonate ions present in the solution. Summing up, if electrodialysis is carried out with the aim to reduce the nitrate content below the admissible value, it is not necessary to extend the duration of the process to more than 2 hours (irrespective of the current density applied), especially when a co-removal of other ions is an undesired effect.

Conclusions

- Electrodialysis provides a high removal of nitrates from aqueous solutions. Under appropriately defined conditions (current density, duration of the process, number of cell pairs) and with appropriately selected membranes (standard or mono-anion-selective, according to the composition of the water to be treated), removal efficiencies ranging between 75 and 99% can be achieved. Applied to natural waters taken in for municipal supply, electrodialysis makes them comply – in terms of nitrate content – with the demands made on potable water.

- The use of mono-anion-selective membranes is advantageous when electrodialysis involves lower current densities (20-25 A/m^2). Under such conditions, monoselective electrodialysis yields a higher (by 5 to 10%) removal of nitrates than does the conventional process, with a concomitant markedly higher retention of sulphates (the difference in sulphate retention between the two processes amounts to 20%) and an effective retention of bicarbonates.

- Besides a lower energy demand, electrodialysis involving low current densities provides a greater "selectivity of desalination", i.e. particular components of the solution are removed with various efficiency. With the highest investigated current density, the monoselectivity effect of the membranes disappears – the removal of sulphates from the four-component solution increases to the level of nitrate removal. When the highest investigated current density is applied to the conventional electrodialysis process, the difference in the removal efficiency between particular components also disappears.

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