

Pollution of nitrate in Moroccan ground water: removal by electro dialysis

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Abstract

Nitrate content in surface water and especially in ground water have increased in Morocco and other areas of the world. Several processes including degradation processes and separation processes can remove nitrate from water. As separating processes, an electro dialysis operation was performed to remove nitrate from a ground water. Preliminary a brief reviews of the nitrate ground water pollution in Morocco was presented. A preselection of several commercial membranes was carried out to determine the best anionic exchange membrane for nitrate removal. The selected membrane transports anions in the following order: $\text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. The results show that a desired product water quality can easily be obtained by electro dialysis. The electro dialysis is a simple process to remove nitrate from ground water.

Keywords: Electro dialysis; Nitrate removal; Ion rejection; Overall rejection; Selectivity

1. Introduction

Pollution of ground and surface water by nitrates becomes a common concern of industrial

and developing countries. In Morocco, the concentration of nitrate in water in some regions exceeds 250 ppm [1,2]. Nitrate contamination is increasingly due to widespread use of fertilisers containing nitrate and from poorly or untreated

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human and animal wastes. Nitrate is also a by-product of many industrial processes, including paper and munitions manufacturing [3].

Deleterious effects of nitrate, especially on infants are well known. Infants are more susceptible to nitrate toxicity than older children or adults and nitrate is a serious potential health threat especially to infants under 6 months of age.

A long consumption of high levels of nitrate can also affect health of adults and older children, causing methaemoglobinaemia or cancer risks due to nitrosamines or nitrosamides. Hence nitrate consumption should be limited and standards have been established. According to international standards, drinking water must contain no more than 50 ppm of nitrate and a guide level of 25 ppm is highly recommended. In Morocco the maximum admissible concentration was fixed at 50 mg NO₃⁻/l.

Wherever the nitrate concentration of the drinking water exceeds the maximum admissible concentration, the nitrate removal becomes a technical challenge. In principle there are biological and chemo-physical technologies available which can be divided into degradation processes including biological or catalytic nitrate reduction and separation processes including distillation, electrodialysis (ED), ion exchange, Donnan dialysis, electrodeionization and reverse osmosis (RO) [3–10].

With regard to the physical processes where the removal of nitrate is returned unchanged to the environment, the biological processes (autotrophic and heterotrophic biological denitrification) have the advantage of the direct degradation of nitrate to molecular nitrogen. Nevertheless, due to the biological activity, these processes are only applicable for full time operation. Moreover the use of micro-organisms in the production of the drinking water poses the risks of the microbial or viral contamination of this drinking water.

The physical processes can easily be started and stopped over longer periods, which makes

them suitable for seasonal operation. Among the physical processes, the distillation is a long-time water treatment method in which water is turned to steam and the condensed steam is collected as treated water. The disadvantage of the ion exchange is the necessity for regeneration chemicals. The bound nitrate ions are released back into the environment and may eventually re-enter the aquifer.

As separating processes, the electrodialysis (ED) and reverse osmosis (RO) have proved their reliability and efficiency in nitrate removal. The advantage of both reverse osmosis and electrodialysis are the low chemical demand in comparison with ion exchange and a reduction of hardness. Nevertheless, in the case of reverse osmosis, the desalination is high and unselective. Only molecules about the size of water are retained; other substances are rejected into a waste stream.

The electrodialysis combines the advantages of selectivity and low chemical demand. The chemical demand is even less than for reverse osmosis and water recovery is greater [4].

The electrodialysis is a widely used electro-membrane process especially for desalination of brackish water and sodium chloride reconcentration from seawater. The removal of ionic components from aqueous solution through ion exchange membranes is carried out under the driving force of an electric field.

The ONEP Co. in Morocco (National Office of Drinking Water) and EURODIA Co. (an affiliate of TOKUYAMA Soda Co. Japan) have an interest in the application of the electrodialysis process to remove nitrate from Moroccan ground water.

The objectives of this work are on one hand a brief presentation of the actual situation of the nitrate ground water pollution in Morocco and on the other hand the demonstration of the performances of the electrodialysis process in nitrate removal from the ground water.

2. Experimental

The electro dialysis operation was carried out on one hand on a electro dialysis cell to select the best anion exchange membrane for nitrate removal and on the other hand on a electro dialysis pilot to study the nitrate removal by electro dialysis.

The already described electro dialysis cell was manufactured in the laboratory [11]. It is composed of a stack of narrow cells separated alternatively by cationic and anionic exchange membrane. The electro dialysis TS-2-10 pilot was supplied by Eurodia Co. The stack design characteristics of the electro dialysis cell and of the electro dialysis pilot are given in Table 1.

In Fig. 1 the principle of the nitrate removal is given. Under the influence of direct current, nitrates present in the untreated water migrates towards the anode. They leave the diluate compartment, move through the anion exchange membrane and stopped by the cation exchange membrane in the concentrate compartment.

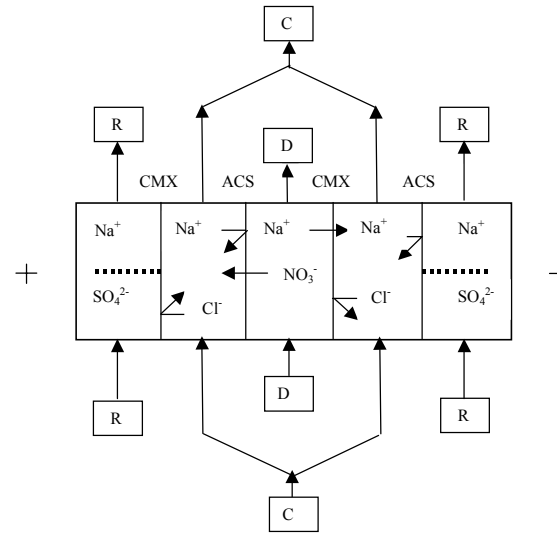


Fig. 1. Principle of the denitrification by electro dialysis. R: Rinse solution; D: Diluted solution; C: Concentrated solution.

Table 1
Stacks design characteristics

Description of equipment	Pilot	Cell
Membrane active area, cm ²	200	36
Number of cell pairs	10	1
Separator frame		
Gasket	EPDM	—
Separator and distributor	PE+PP	—
Electrode		
Anode	DES	Platinum-coated titanium
Cathode	DES	Platinum-coated titanium
Parameters of functioning		
Diluted compartment, l/h	180–200	128
Concentrated compartment, l/h	180–200	116
Electrode compartment, l/h		
Anode	150	76
Cathode	150	76
Current max, A	9	—
Voltage max, V/cell	1.5	—

The circulation of the water to be treated through the diluate and the concentrate compartments was assured by pumps. To prevent a modification of the water composition which could be caused by electrode reactions, the two electrodes compartments were separated from the others with a 0.1 M Na₂SO₄ solution.

To prevent scaling and fouling of the membranes, the polarity of the direct current was reversed at the end of each test and the stack was flushed periodically with an acidic solution in order to remove eventual precipitation of salts.

During the tests, water samples are taken periodically from diluate and concentrate streams and the ion concentrations were determined analytically. The concentration of nitrates and chlorides were determined by specific Ion Method using Orion nitrate, chloride and reference electrodes, and specific Ion Meter. Cations were estimated by Atomic Absorption Spectroscopy (UNICAM 926 AA spectrometer) and the other parameters (pH, TDS, HCO₃⁻, SO₄²⁻) were determined following standard methods.

3. Results and discussion

Morocco is characterised by a Mediterranean semiarid climate and by a limited water resources especially ground water resources. The observed increase these last decades in the nitrate concentrations in water resources especially in ground water resources aggravates the situation.

The pollution of the ground water by nitrates affects nearly all the Moroccan territory. 6% of water resources are estimated to have a nitrate contents more than 50 mg/l. A survey conducted between 1995 and 1998 on the ground water exploited by the National Office of Drinking Water in Morocco (ONEP Co.) showed that 1% of these resources have nitrate more than 100 ppm, 8% more than 50 ppm, 22% between 25 and 50 ppm, 41% between 10 and 25 ppm and 28% lower than 10 ppm. For the surface water

the survey showed that the nitrate contents not exceed 10 ppm. Actually to avoid the nitrate risks, the ONEP Co. proceeds to a systematic dilution of the contaminated water resources.

3.1. Selection of the best anionic exchange membrane

A preselection of several commercial membranes was carried out to designate the best anionic exchange membrane for the nitrate removal. Five types of anion exchange membranes (AFN, ACS, AMX, ADP and ADS) and one type of a standard cation exchange membrane (CMX membrane) have been used. AFN, ACS, AMX and CMX membranes are made by Tokuyama Co.; ADP and ADS by Morgane Co. The properties of the tested membranes are listed in Table 2.

Table 2
Properties of tested membranes

Membranes	Exchange capacity, meq/g	Electric resistance, Wcm ^{2a}
AFN	2.60	1.25
ACS	1.55	2.40
AMX	1.60	2.75
ADP	1.40	5.85
ADS	1.20	1.63
CMX	1.50	2.69

^aMembrane equilibrated with 0.5 M NaCl solution at 20°C

The laboratory tests were carried out on a ground water of the north of Morocco (Ain Sbit in the region of Rabat) having the composition of the Table 3. The used current density for the preselection operation was 10 mA/cm².

The preselection operation was carried out by following the evolution of three parameters: specific ion rejection, overall rejection and voltage on both ends of the stack. The specific ion rejection (SR) and the overall rejection (OR) are expressed by the following relation:

Table 3
Mean composition of the untreated water

Parameters	Untreated water
TDS, mg/l	1107
NO ₃ ⁻ , mg/l	133
SO ₄ ²⁻ , mg/l	67
Cl ⁻ , mg/l	317
Na ⁺ + K ⁺ , mg/l	101.29
Ca ²⁺ , mg/l	140
Hardness, meq/l	9.76
Temperature, °C	20
pH	7.40

$$SR\% = \frac{[Ion]_{t=0} - [Ion]_t}{[Ion]_{t=0}} \times 100$$

$$OR\% = \frac{[TDS]_{t=0} - [TDS]_t}{[TDS]_t} \times 100$$

The ion concentrations and total dissolved salinity (TDS) were determined in the diluate compartment. Determination of specific ion rejections and overall rejection is necessary to control the nitrate removal and the selectivity of the tested membrane. The voltage gives an idea of the energetic cost.

The best results correspond to minimum variations of TDS, maximum nitrate removal, minimum sulfate removal and to minimum energy cost. In others words the best anionic

exchange membrane must enable a lower desalination and a higher selectivity toward nitrates. The electro dialysis of drinkable water with a non-selective membrane not only removes the nitrates but also the other anions which is not really suitable for drinking purposes. It is therefore necessary to selectively eliminate nitrates and preserve the initial characteristics of the treated water.

Moreover, in electro dialysis, a precipitation of carbonate or sulfate salt in the concentrate compartment limits the performances of the operation by decreasing the recovery rate of water and the overall rejection of ions and by causing scaling and fouling of the membranes. To minimise these risks, usually, acid and antiscalant were used. The best anionic exchange membrane must also enable a good blockade of the bivalent anions especially sulfate in the diluate compartment.

In Table 4 the analytical results of the treated water after 1 h of the electro dialysis operation for various couples of membranes are collected. The values of the different parameters are comparable for the various anionic exchange membranes. The higher overall rejection was obtained with ADS membrane (75.40%). The lower value with ACS membrane (68.47%). After one hour, the nitrate content was around 30 mg/l for all the tested membranes. The best nitrate rejection was obtained with AFN membrane (80.50%); the lower with AMX membrane (75%). The lower

Table 4
Analytical results of treated water after 1 h of electro dialysis operation for various couples of membranes

Mem-branes	ddp, V		pH		Hardness, meq/l		NO ₃ ⁻ , mg/l		Cl ⁻ , mg/l		SO ₄ ²⁻ , mg/l		TDS, mg/l	
	1 h	Δddp	1 h	ΔpH	1 h	SR%	1 h	SR%	1 h	SR%	1 h	SR%	1 h	OR%
AFN	57.1	14.4	6.84	1.02	3.0	72.2	27.0	80.5	78.2	75.5	22.0	68.1	370	69.0
ACS	60.4	16.1	5.30	2.88	3.6	65.4	31.2	77.1	104.3	68.0	30.0	56.4	385	68.5
AMX	58.0	13.8	5.72	2.45	3.3	69.4	32.5	75.0	85.5	73.4	21.1	69.3	376.5	69.9
ADP	59.4	12.1	5.04	3.33	3.4	67.3	30.7	76.0	98.0	69.7	14.0	78.6	364	69.7
ADS	65.2	22.6	6.27	2.00	3.0	72.2	28.0	78.9	81.7	75.0	14.5	78.9	306	75.4

(the best) sulfate rejection was obtained with ACS membrane (56%), and the higher with ADP and ADS membrane. Variations of the hardness were practically the same for all the tested couples. The ADP membrane presents the higher energetic consumption and the lower energetic cost was obtained with the ADP membrane.

Figs. 2 and 3 show the variations of the nitrate rejection and of the sulfate rejection with the overall rejection for all the tested membranes. These results show that the best behaviour in nitrate removal by electro dialysis was obtained with the ACS membrane. The NEOSEPTA ACS monoanion permselective membrane has an excellent nitrate selectivity. The overall rejection and the sulfate rejection were the lower and the nitrate rejection is higher. Fig. 4 showing the

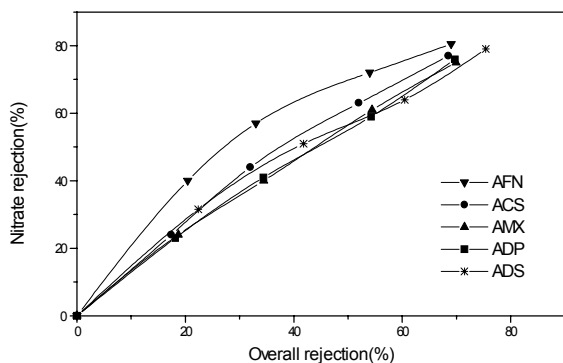


Fig. 2. Nitrate rejection vs. overall rejection.

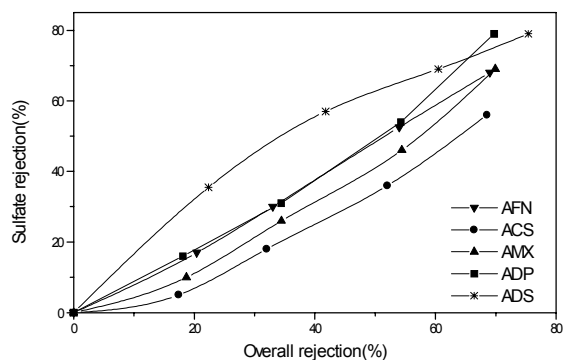


Fig. 3. Sulfate rejection vs. overall rejection.

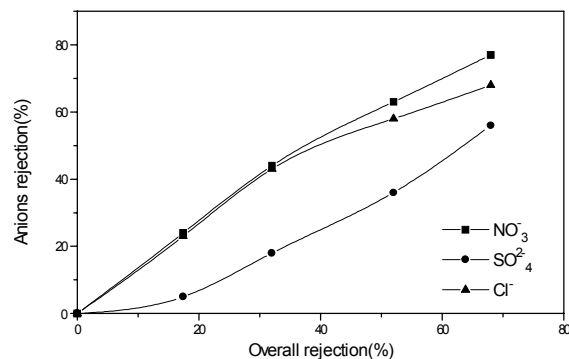


Fig. 4. Anion rejections vs. overall rejection for the ACS membrane.

variations of the anion rejections vs. the overall rejection confirms the excellent selectivity of the ACS membrane toward nitrate.

3.2. Permselectivity

To control the permselectivity of the used ACS membrane, an electro dialysis operation was carried out on a synthetic water containing a sodium salt mixture at concentration of 500 ppm of each anion: $\text{NaCl} + \text{Na}_2\text{SO}_4 + \text{NaNO}_3 + \text{NaHCO}_3$. The electro dialysis was carried out on the electro dialysis pilot equipped with CMX membrane (standard cationic ion exchange membrane) and ACS membrane (mono-anion permselective membrane). The running conditions were as follows: temperature 20°C, voltage 15V, flow rate 180 l/h.

Fig. 5 shows the variations with time of the anion rejection and the overall rejection. After 10 min of electro dialysis time 90.7% of NO_3^- , 88.5% of Cl^- , 48.3% of HCO_3^- and only 7.5% of SO_4^{2-} have been removed. The concentration of SO_4^{2-} in the treated water remained almost stable. These results confirm the good selectivity of the used anionic exchange membrane toward nitrates. The ACS membrane transports anions in the following order: Nitrate > chloride > bicarbonate > sulfate.

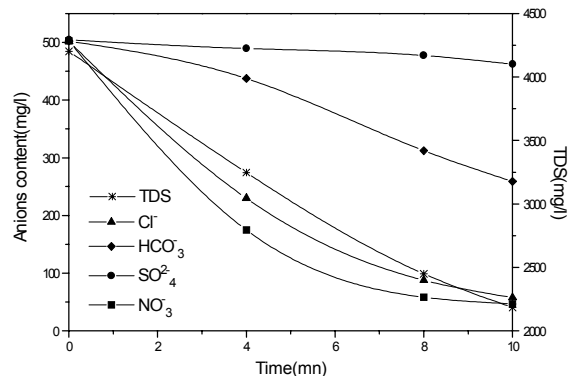


Fig. 5. Time dependence of the anion concentrations and of the TDS.

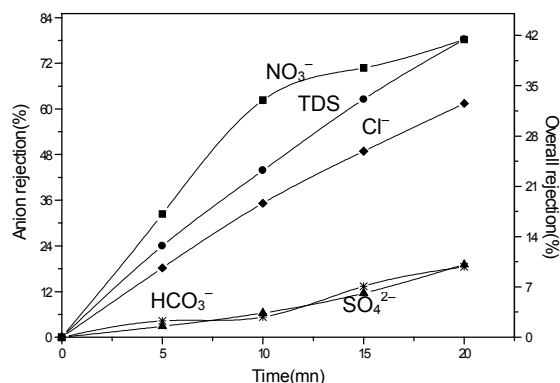


Fig. 6. Time dependence of the anion rejection and of the overall rejection. Applied voltages – 5V.

3.3. Nitrate removal

The denitrification operations were carried out on a ground water of the centre of Morocco (Nzalaat Laadem in the region of Marrakech) containing 80ppm of nitrate, 820ppm of TDS and 7 meq/l of hardness.

Table 5 gives the mean composition of the untreated water and the analytical results of the treated water after 10mn for an applied voltages of 5V and after 5mn for an applied voltages of 10V. Figs. 6 and 7 show the variation with time of the overall rejection and of the anion rejections for the above applied voltages. The nitrate rejection is always higher than the other anions rejections and than the overall rejection. The current efficiency is not depicted, it was always >85%. The quality of the obtained water after 10mn (for 5V) or after 5mn (for 10V) of electro-dialysis was satisfactory: the nitrate content reaches the recommended guide level, the sulfate is practically stopped, the TDS and the total hardness were satisfactory.

The desalination power consumption was 0.044Kw.h/m³ for 5V and 0.107Kw.h/m³ for 10V of applied voltages. The power for pumping was not included.

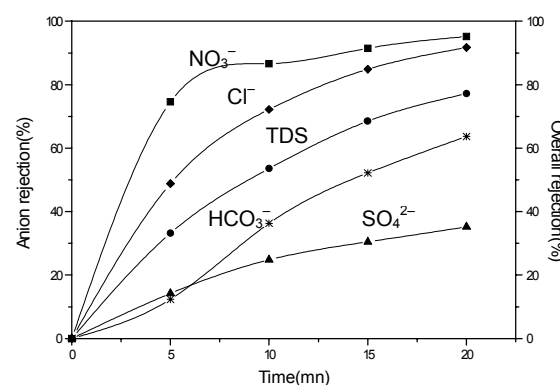


Fig. 7. Time dependence of the anion rejection and overall rejection. Applied voltages – 10V.

4. Conclusion

Using nitrate permselective membrane, a desired drinking product water containing a satisfactory TDS and nitrate content can be easily obtained by electro-dialysis. The divalent anions can be stopped in the diluate compartment which minimises the eventual precipitation of divalent salts in the concentrate side.

Technically, the electro-dialysis process is more simple to conduct in comparison with the conventional denitrification processes. Economically, the operating cost is not high. The

Table 5

Analytical results of the treated water after 5 and 10 mn of electro dialysis operation

Analysed parameters	Untreated water, ppm	Treated water, 5 V		Treated water, 10 V	
		C, ppm	SR%	C, ppm	SR%
NO ₃ ⁻	78.86	30.15	61.77	19.98	74.66
Cl ⁻	236.38	153.10	35.23	121.01	48.81
HCO ₃ ⁻	231.26	219.60	5.04	201.30	12.95
SO ₄ ²⁻	57.70	54.00	6.41	49.50	14.21
Na ⁺	107.47	105.10	2.21	90.70	15.60
K ⁺	7.17	5.37	25.11	4.58	36.12
Mg ²⁺	39.23	27.50	29.90	30.00	23.53
Ca ²⁺	71.16	43.00	39.57	44.50	37.46
TDS	829.23	637.82	23.08	561.57	32.28
Hardness, meq/l	6.78	4.41	34.95	4.68	30.97
pH	7.95	7.80	—	7.84	—

membrane replacement and electricity constitute the greater part of the operating cost. Chemical and spare parts costs are not significant. The investment cost depends on the capacity of the industrial plant. This investment decreases when capacity increases. In many industrial plants installed by our partner Eurodia Co. in Europe, it was demonstrated that the replacement cost does not exceed US\$0.05/m³ and electricity US\$0.04/m³ when nitrate removal rate is superior than 80%. In most of cases where 85% nitrate removal is required, the operating cost not exceeds US\$0.1/m³.

The concentrated nitrate in the concentrate compartment can be eliminated following four possibilities: by a discharge into a sewage treatment plant, by direct biodegradation, by evaporation or by irrigation when the concentrate quality is satisfactory for irrigation.

In conclusion, the availability of permselective membranes and electro dialysis technology improvements open great possibilities to electro dialysis, in both water desalination market and nitrate removal in the world.

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