

Denitrification of ground water by electro dialysis using a new anion exchange membrane

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ABSTRACT

Studies have been conducted to reduce nitrate in a Moroccan ground water by electro dialysis using a new nitrate permselective membrane. The initial total dissolved solids (TDS) was 814.3 ppm including 77 ppm of nitrate and 7.84 meq l⁻¹ of total hardness. The operation was carried out under different applied voltages. The results show that the desired product water quality can be obtained. Sulphate can be stopped in the diluate compartment, which minimized the possible precipitation of bivalent salts in the concentrate side. A control of the selectivity of the nitrate permselective membrane has been carried out. This study shows that electro dialysis is a simple process for reduction of nitrate in ground water.

Key words | denitrification, electro dialysis, ion exchange, membrane, nitrate

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INTRODUCTION

Contamination of ground and surface water by nitrate results from oxides of nitrogen in automobile exhausts, from industrial activities, from manure surpluses and from fertilizer activities in agriculture (Brezonik *et al.* 1978; Richard and Leprince 1982; Keevoy *et al.* 1987). Deleterious effects of nitrate, especially on infants are well known (World Health Organization 1987; Lakshmanan *et al.* 1986). Maximum permissible levels for nitrate in drinking water have been prescribed to minimize the effect. According to international standards, drinking water must contain no more than 50 ppm of nitrate. A guide level of 25 ppm is highly recommended.

Pollution of ground and surface water by nitrate is a serious problem in many countries. In Morocco, the concentration of nitrate in water in some regions exceeds 250 ppm (Elachheb and Bahi 1997; Berrada and Chefadi 1997). This is mainly caused by intensive agricultural activities.

To remove nitrate from water several techniques are available: dilution, ion exchange, biological denitrification, chemical reduction, reverse osmosis and electro dialysis (Dore *et al.* 1986; Rautenbach *et al.* 1986; Van Der Hoek *et al.* 1988). Among such processes, electro dialysis makes use of the electrical potential to transfer ions through a selective ion exchange membrane.

Electro dialysis has several advantages. It is a physical process, the ion balance of water is maintained, it involves low power consumption, is a fully automatic process, production is adjustable instantaneously to the user's needs, no chemical products are added to the feed or product water and the pretreatment is accomplished by a simple filtration.

The ONEP Co. (National Office of Drinking Water in Morocco) and Eurodia Co. (an affiliate of the Tokuyama Soda Co. Ltd, Japan) have an interest in the application of

the electro dialysis process to remove nitrate from Moroccan ground water using a new anion exchange membrane with good selectivity towards nitrate.

The aim of this work is to study the nitrate removal from ground water using an electro dialysis apparatus (supplied by Eurodia Co.) with a nitrate permselective membrane.

EXPERIMENTAL

The used apparatus was a TS-2-10 pilot which was a batch-type dialysis unit. The stack was fitted with one type of anion exchange membrane (ACS) and one type of cation exchange membrane (CMX) both made by Tokuyama Soda Co. The electro dialysis operation was conducted using 10 pairs of anion and cation exchange membranes providing an available membrane area of 200 cm² each. The two electrode compartments are separated from the others to prevent a modification of the composition of the solution, which could be caused by electrode reactions. A solution of 0.1 M Na₂SO₄ was used as an electrode rinse. For the concentrate compartment a 0.01 M NaCl solution was used. The scheme of installation and the principle of the denitrification process are shown in Figure 1.

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

The ion concentration was determined by discontinuous sampling of a small volume of water from the diluate circuit. Initial samples were collected just before electro dialysis. Ion concentrations were determined analytically. The concentration of nitrates and chlorides were determined by the specific ion method using an Orion 93-07 nitrate electrode, Orion 94-17 B chloride electrode, a single junction reference electrode and model 90-02 specific ion meter. Cations were estimated by atomic absorption spectroscopy (UNICAM 929 AA Spectrometer). The other parameters (pH, TDS, HCO₃⁻,

SO₄²⁻) were determined following Standard Methods (SMEW 1995).

RESULTS AND DISCUSSION

Permselectivity

Before the denitrification operation, an electro dialysis test was carried out on a synthetic water to control the permselectivity of the anion exchange membrane. The running conditions were as follows: temperature 25°C, voltage 15 V, flow rate 180 l h⁻¹ during 10 min. The operation was carried out on water containing a sodium salt mixture at various concentrations: NaCl + Na₂SO₄ + NaNO₃ + NaHCO₃.

Figure 2 shows the variation of anion content and of TDS in the treated water as a function of electro dialysis time for different concentrations of each anion in the untreated water. The concentration of NO₃⁻ and Cl⁻ decreased rapidly with increasing time, the HCO₃⁻ content decreased gradually but the variations in SO₄²⁻ content were lowest. For the higher concentration in the untreated water the SO₄²⁻ content remained almost stable.

Table 1 gives the analytical results after 10 min of electro dialysis operation. For the higher concentration in the untreated water (500 ppm of each anion) after 10 min, 90.7% of NO₃⁻, 88.5% of Cl⁻, 48.3% of HCO₃⁻ and only 7.6% of SO₄²⁻ had been removed. The concentration of SO₄²⁻ remained almost stable. From these results, it appears that the membrane selectivity for nitrate is greater than for the other anions. The new ACS membrane transports anions in the following order: nitrate > chloride > bicarbonate > sulphate.

The lower selectivity of the anion exchange membrane for sulphate may be attributed to the nature of this monovalent anion exchange membrane. The ACS membrane has been specially elaborated to stop the transport of divalent anions.

Nitrate removal

The denitrification operations were carried out on ground water from the centre of Morocco containing

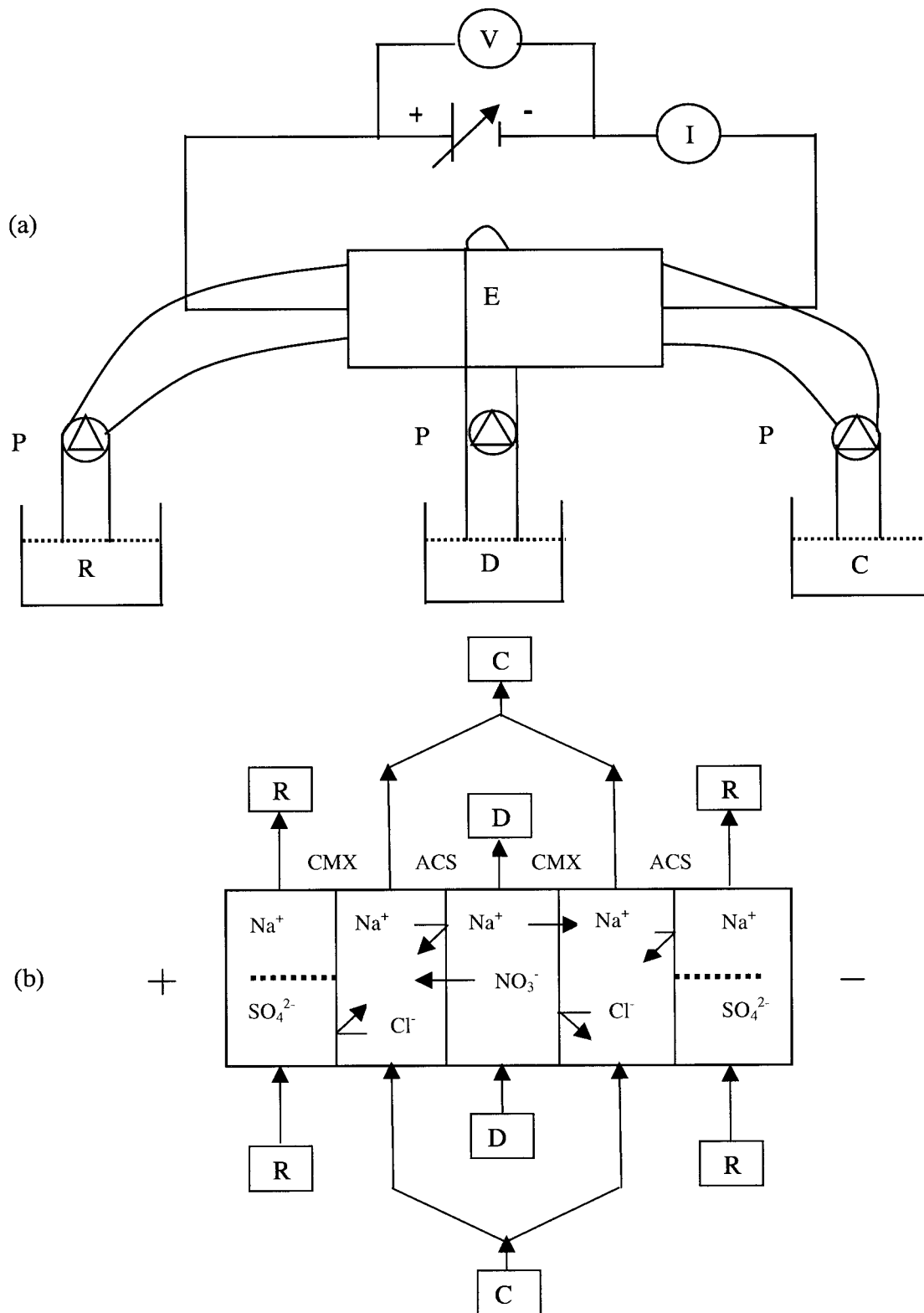


Figure 1 | (a) Scheme of installation; (b) principle of electrodiagnosis. R, rinse solution; D, diated solution; C, concentrated solution.

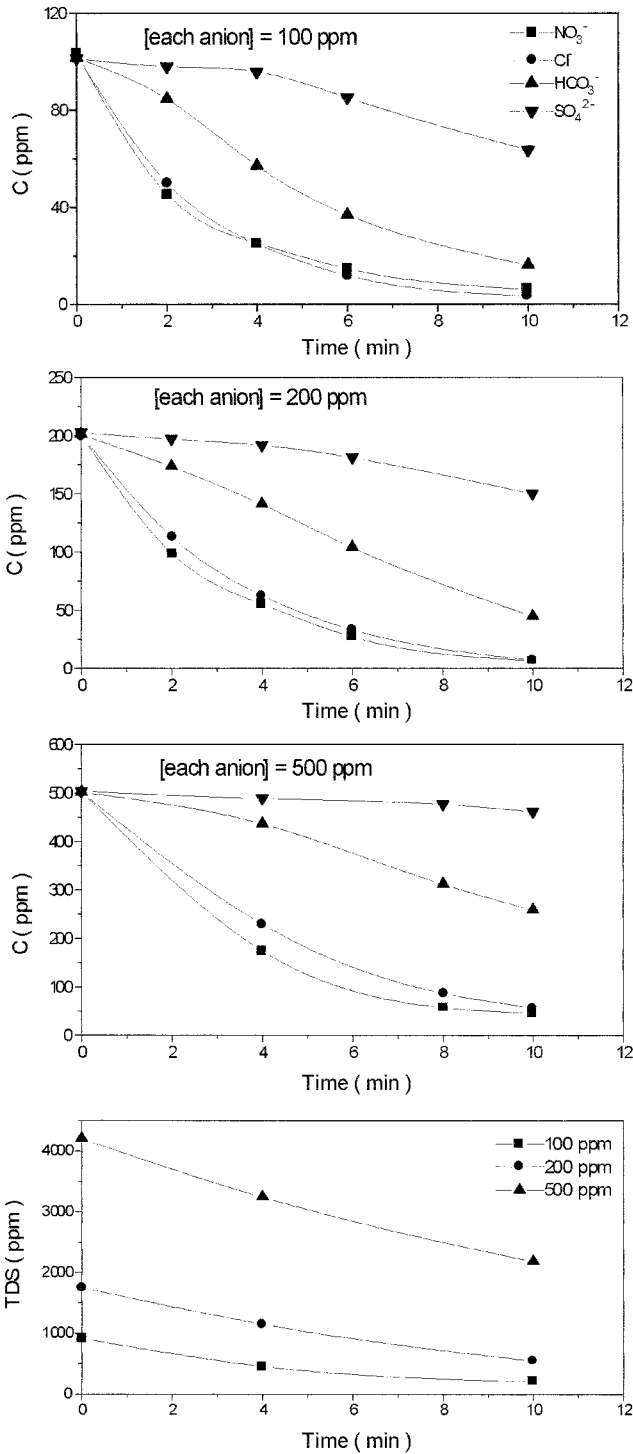


Figure 2 | Variations of the anion concentrations and TDS versus the electro dialysis time at different concentrations of each anion in the untreated water.

Table 1 | Permselectivity: analytical results after 10 min of electro dialysis operation

	$C_X=100$ ppm		$C_X=200$ ppm		$C_X=500$ ppm	
	c (ppm)	%	c (ppm)	%	c (ppm)	%
NO_3^-	6.1	94.1	7.0	96.5	46.7	90.7
Cl^-	3.5	96.6	7.5	96.3	57.5	88.5
HCO_3^-	16.2	84.1	45.1	77.6	259.1	48.3
SO_4^{2-}	63.6	36.3	150.2	26.0	462.1	7.6
TDS	207.8	77.5	544.1	69.1	2184.6	48.1

Table 2 | Untreated water composition

Elements	c (mg l ⁻¹)
NO_3^-	77
Cl^-	240
HCO_3^-	200
SO_4^{2-}	59
Na^+	105.4
K^+	6.9
Ca^{2+}	78
Mg^{2+}	48
TDS	814

approximately 80 ppm of nitrate. The analysis of the water is shown in Table 2. The flow rate of the diluate compartment was 180 l h⁻¹ and the temperature of the streams was maintained at 20°C.

Figures 3–5 show the change with time of ion concentrations and of the other parameters (pH, conductivity, TDS, current and hardness). All cations were easily removed at various applied voltages (Figure 3). This may be attributed to the nature of the standard cation exchange membrane which facilitates the transport of practically all

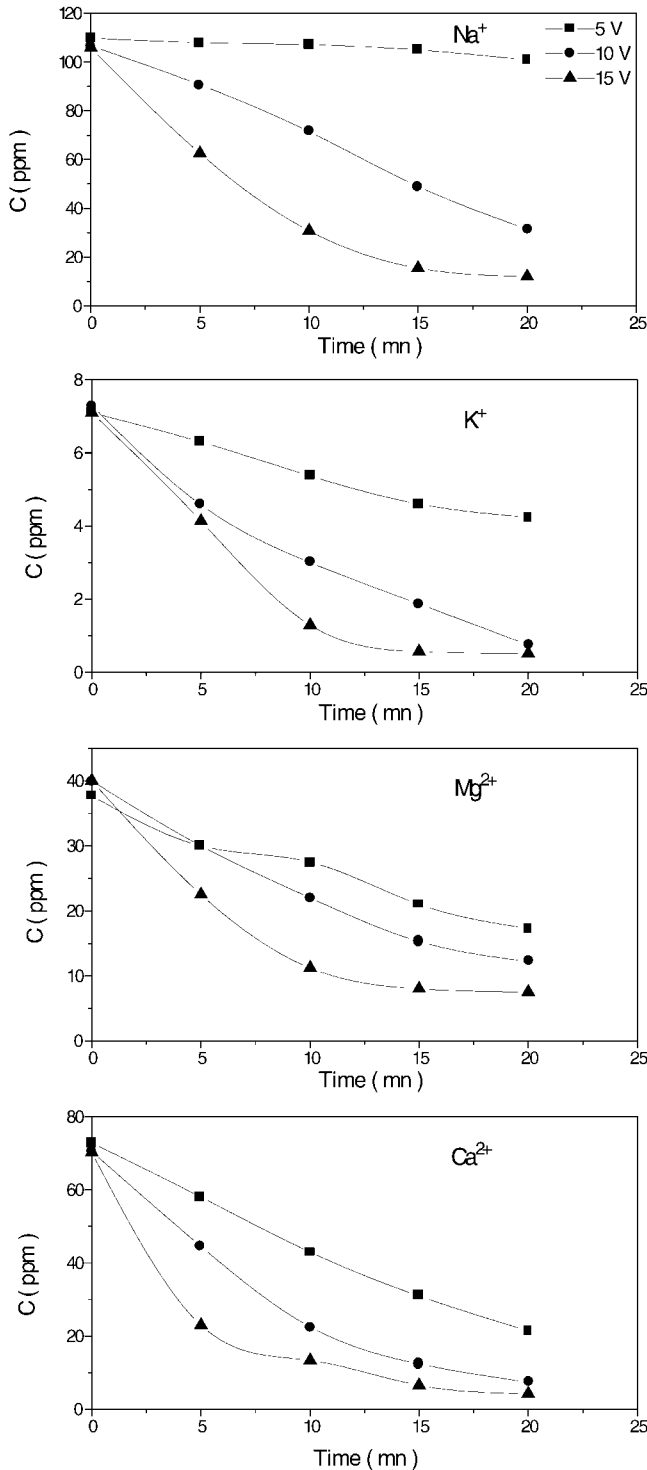


Figure 3 | Evolution of the cation contents in the treated water during electro dialysis.

cations. The difference in results between Na^+ , K^+ , Ca^{2+} and Mg^{2+} can be explained essentially by the difference in concentration of these cations in the untreated water. The total hardness follows the same kinetic as the cation kinetics.

The concentration of NO_3^- and Cl^- in the treated water decreased rapidly with increasing time of the operation at various applied voltages. Those of bicarbonate and sulphate decreased rapidly at the higher voltage (15 V) and slowly at the lower one (5 V). However, at 5 V, HCO_3^- and SO_4^{2-} concentrations remained almost constant in the diluate compartment with increasing electro dialysis duration up to 10 min and then decreased slowly (after 10 min, only 5% of HCO_3^- and 6% of SO_4^{2-} had been removed). The transport of HCO_3^- and SO_4^{2-} at the lower voltage became significant when the concentration of NO_3^- and Cl^- decreased considerably (Figure 4). These results can be attributed in part to the nature of the monovalent anion exchange membrane and to the difference in the anionic contents of the untreated water.

The TDS decreased gradually with time at 5 V and rapidly at the higher voltage as shown in Figure 5.

The pH of the water is imposed by the bicarbonate concentration until the solution becomes depleted in HCO_3^- ions, then the pH becomes controlled by neutral water. However little variation in water pH was observed.

Current and conductivity changed gradually with time at the lower applied voltage (5 V) and rapidly at the higher ones (Figure 5). The initial value of the current is directly proportional to the applied voltage (the initial conductivity of the water remains the same for the various voltages).

Figure 6 shows the variations with time of the percentage reduction ratio of TDS and NO_3^- for all voltages. The percentage of NO_3^- reduction was always higher than that of TDS reduction. The percentage reduction ratio increased with time and with the applied voltage.

As shown in Figures 3–5, the electro dialysis operation not only removes nitrate but also the other anions. After some time, one thus obtains a demineralized water which is not really suitable for drinking purposes. It is therefore necessary to stop the operation after a predetermined time. On the other hand to minimize the eventual precipitation of salt, especially the divalent salt of

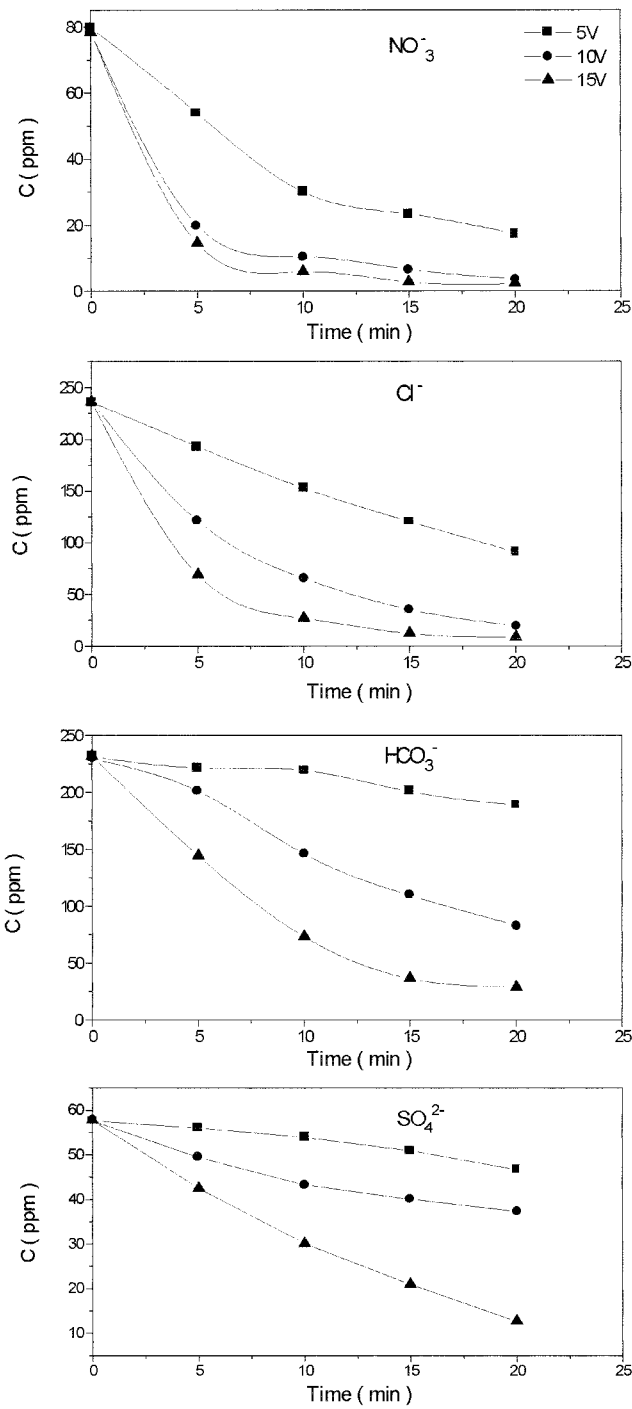


Figure 4 | Evolution of the anion contents in the treated water during electrodiagnosis.

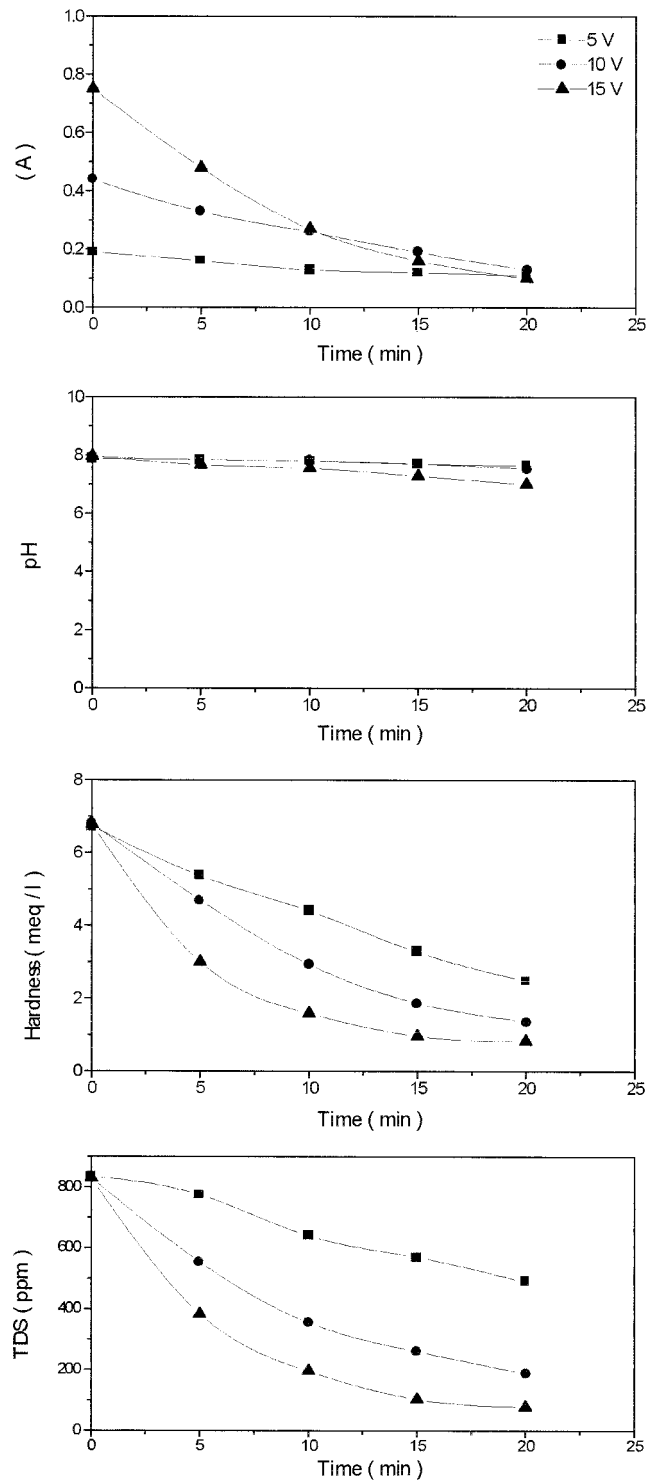


Figure 5 | Evolution of pH, hardness, current, conductivity and TDS during electrodiagnosis.

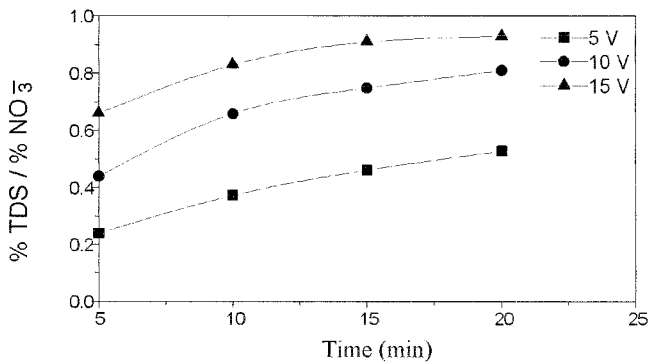


Figure 6 | Percentage reduction of TDS and NO₃⁻ versus time.

sulphate, in the concentrate compartment it is preferable to operate in conditions which allow the blocking of sulphate (or the divalent cations) in the treated water. It is therefore necessary to find a compromise between time and the value of the applied voltage. For the present

treated water, it is preferable to operate at the lower voltages in order to control the transport of sulphate through the membranes.

Table 3 gives the analytical results of the treated water after 10 min of electro dialysis operation at various applied voltages. The percentage NO₃⁻ reduction was always greater than the percentage reduction of the other anions and of the TDS. The percentage TDS reduction and of the total hardness were almost the same.

For the higher applied voltages (15 V, 1.5 V/cell) the total hardness and the TDS reached the limit level while the percentage reduction of SO₄²⁻ reached 47%.

The best results were obtained with the lower voltage and especially with 0.5 V/cell (5 V). The nitrate content reached the recommended guide level, the sulphate remained practically constant in the diluate compartment (after 10 min, only 6% of SO₄²⁻ had been removed), the TDS and the total hardness were satisfactory.

Table 3 | Analytical results of the treated water after 10 min of electro dialysis operation at various voltages

	Untreated water	Treated water at 5 V		Treated water at 10 V		Treated water at 15 V	
	C (ppm)	C (ppm)	%	C (ppm)	%	C (ppm)	%
NO ₃ ⁻	78.3	30.1	61.5	10.5	86.5	5.9	92.5
Cl ⁻	236.4	153.1	35.2	65.7	72.2	26.9	88.6
HCO ₃ ⁻	232.0	219.6	5.3	146.4	36.9	73.2	68.4
SO ₄ ²⁻	57.7	54.0	6.4	43.4	24.8	30.1	47.8
Na ⁺	109.8	107.1	2.5	71.5	34.9	30.8	71.9
K ⁺	7.3	5.4	26.0	3.0	58.9	1.3	82.3
Ca ²⁺	73.0	43.0	41.1	22.5	69.2	13.3	81.8
Mg ²⁺	40.0	27.5	31.2	22.0	45.0	11.2	72.0
TDS	834.8	639.8	23.4	385.0	53.9	192.7	76.9
Hardness (meq l ⁻¹)	6.9	4.4	36.2	2.9	58	1.6	76.8
pH	7.9	7.8		7.8		7.6	

CONCLUSIONS

- (1) An electro dialysis operation was carried out to reduce nitrate in Moroccan water using a new anion exchange membrane with good selectivity towards nitrate. The membrane transports anions in the following order: nitrate, chloride, bicarbonate and sulphate.
- A product drinking water containing a satisfactory TDS concentration and nitrate content lower than the permissible level can be obtained easily by electro dialysis.
 - The divalent anions can be held in the diluate compartment, which minimizes the eventual precipitation of divalent salts in the concentrate side.
 - Technically, the electro dialysis process is simpler to conduct in comparison with conventional denitrification processes.

ACKNOWLEDGEMENTS

This work was supported in part by ONEP Co. (Morocco) and Eurodia Co. (France); the authors express their thanks for this support. Thanks are also due to Dr C. Gavach (CNRS—Montpellier, France) for his co-operation and discussion during the preparation of this work.

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