Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20286

65 (2017) 52–59
February

Reconstituted and brackish waters desalination by neutralization dialysis process with ion-exchange membranes

Mona Chérif[a,b], Sonia Korchane[a], Lobna Chaabane[a], Lasaad Dammak[a,*], Abdelhamid Ben Salah[b], Khaled Walha[b], Anton Kozmai[c]

[a] *Institut de Chimie et des Matériaux Paris-Est (ICMPE), UMR 7182 CNRS – Université Paris-Est, 2 Rue Henri Dunant, 94320 Thiais, France, emails: dammak@u-pec.fr (L. Dammak); cherif_mona@hotmail.fr (M. Chérif); sonia_korchane@yahoo.fr (S. Korchane); Lobna.dammak@u-pec.fr (L. Chaabane)*

[b] *Laboratoire de Sciences des Matériaux et de l'Environnement (MESLAB), Université de Sfax, Route de la Soukra km 4 – BP no 802 – 3038 Sfax, Tunisie, abdelhamid.bensalah@fss.rnu.tn (A. Ben Salah); walha.khaled@yahoo.com (K. Walha)*

[c] *Membrane Institute, Kuban State University, Stavropolskaya str. 149, 350040 Krasnodar, Russia, kozmay@yandex.ru (A. Kozmai)*

Received 4 April 2016; Accepted 15 October 2016

ABSTRACT

Several international reports have pointed that 2.3 billion people are living in regions with absolute water scarcity, despite the availability of a surface water source that can be treated to become drinkable. We, thus, suggest to apply a new technique, called neutralization dialysis (ND). We described this technique meant to desalinate real brackish water in previous papers. The ND is a low energy intensive technique and is easy to implement even in isolated locations. Kinetics of reconstituted and brackish waters desalination by ND were studied in a three-compartment stack (acid, saline, and alkali compartments) with Neosepta® AMX and CMX ion-exchange membranes, and the process feasibility was evaluated. Brackish water samples were taken from the city of Gabes in the south of Tunisia and analysed in different terms. The pH and the ionic conductivity kinetics were measured in the saline solution during different ND operations for five different solutions: $CaCl_2$, Na_2SO_4, $MgSO_4$, the mixture of these three salts (which are used to have, by themselves, a reconstructed water very close to the reconstituted water), and Gabes brackish water. The correlation of ion transport through the cation- and the anion-exchange membranes was investigated. This work has shown that the desalination kinetics is similar in the cases of Na_2SO_4 and $MgSO_4$ solutions, while it is different in the case of $CaCl_2$. We found out that the time dependence of pH for the reconstituted and the real waters during desalination is quasi-similar. However, the conductivity evolution for both solutions is different. The values of ion charge (monovalent/divalent) and concentration in the feed solution have an impact on the ion-exchange rate. The total cost of Gabes brackish water desalination by the ND process (stopped at conductivity of 1 mS cm^{-1}) was estimated at 1.90 $/$m^3$.

Keywords: Ion-exchange membrane; Neutralization dialysis; Desalination; Reconstituted water; Gabes brackish water

1. Introduction

The lack of good quality water resources as well as the imbalance between the supply and the request of water constitutes two major constraints. In fact, 2.3 billion people (which correspond to 40% of the world population) live with lack of water [1]. This phenomenon is more common or widespread in North African countries and certain countries of the Mediterranean Basin. For example, Tunisia has a very limited water resource despite a continuous growth of water request (≈1.6%/year) [2]. Indeed, Tunisian water resources

---

* Corresponding author.

1944-3994/1944-3986 © 2017 Desalination Publications. All rights reserved.

represented only 460 m^3/year/inhab, in 2012, which is under the shortage limit of 500 m^3/year/inhab [3]. In Tunisia, the main water resources are divided into surface water (which represents 60% of the total water resources) and underground water (which represents 40% of the total water resources). 74% of surface water has a salinity of less than 1.5 g L^{-1}, however, only 20% of underground water has a salinity lower than 1.5 g L^{-1} [1]. These undrinkable water resources (surface and underground waters) require a desalination process to have a salinity of 0.5 g L^{-1}, a value fixed by the World Health Organization (WHO) [4]. Thus, the brackish water desalination can be the best alternative to produce drinkable water as it is a renewable and easy to access resource with a relatively low salinity.

It is well known that the surface waters with higher salt content (brackish waters) are generally treated by reverse osmosis (RO) [5–7] or electrodialysis (ED) processes [8]. The National Drinking Water Agency in Tunisia was created to satisfy the water request and to operate desalination plants for producing drinkable water. Most of the desalination plants apply the RO process (close to 80%) [9]. In Tunisia, there are only four RO plants that were installed from 1982 to 2007; in Kerkennah islands, Gabes, Djerba, and Zarzis with a total water desalination capacity of 72,300 m^3/d [10].

Thus, the use of RO and ED systems in the developing countries is very limited because of the high unit capital cost investment [11]. Despite the fact that the cost of brackish water desalination is relatively low (ranges from 0.10 to 1.00 \$/m^3 by RO techniques [12] and from 0.17 to 0.40 \$/m^3 by ED techniques [13] without taking into account the investment cost), it is difficult for the population of remote rural areas to purchase desalination systems.

Moreover, the ED and RO processes require the use of high electricity which is also in shortage in developing countries. Replacing the conventional electric energy by a photovoltaic system, a better adapted system for isolated locations, leads to an important increase in water treatment costs; i.e., for the coupled ED–photovoltaic desalination system, the costs are estimated between 4.6 and 6.8 \$/m^3 [14]. Furthermore, ED and RO techniques require qualified technicians and regular maintenance involving extra costs. In this paper, we will present our evaluation of real water desalination by ND process.

The ND process is a potential promising desalination technique that could be implemented in developing countries as shown in our previous publication [15]. On the one hand, ND is an easy to use technique for isolated locations and does not require high technicality and staff qualification. Indeed, ND is a membrane process based on the simultaneous use of two Donnan dialysis operations [16,17]: the saline solution is placed between an acidic and an alkaline solution separated by cation-exchange membrane (CEM) and anion-exchange membrane (AEM), respectively (Fig. 1).

The mineral charge (cations and anions) will be removed from the saline solution and replaced by H^+ and OH^- ions through both ion-exchange membranes (IEMs). In fact, the CEM (AEM) allows the ion-exchange between salt cations (anions) and H^+ (OH^-) under the influence of the concentration gradients. H^+ and OH^- neutralize each other to form water. Thus, the mineral charge decreases in the saline solution leading to drinkable water.

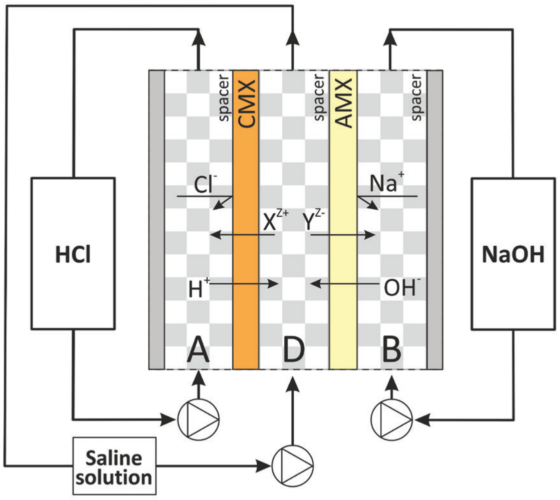

Fig. 1. Schematic representation of ND with a three-compartment membrane stack.

On the other hand, the ND process requires a low investment, low operational, and maintenance costs. In fact, this process allows low energy consumption (only the pumps) and is relatively easy to implement. The main costs concern the purchase of chemical agents (alkali and acidic solutions). However, there is the possibility to use local products (for example, limewater and phosphorus acids, respectively) to reduce these costs.

In previous studies, we have identified and examined the effect of the main parameters on the ND desalination process using NaCl solution [15,18–29]. We have also employed a fractional factorial design to optimize the ND desalination process [30]. These studies were important to understand the transport phenomenon of ions through membranes by the ND process but insufficient to perform a real water desalination operation. In fact, real water contains multivalent ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}, Fe^{3+}, etc.) that can contaminate the membranes by inhibiting some functional sites (the case of Fe^{3+} ions) and reduce the exchange kinetics (low mobility in the membranes).

The aim of this study is to apply the optimum desalination conditions achieved in the fractional factorial design study, first on a reconstituted water and then on real water (Gabes brackish water from the south of Tunisia). Specifically, we have investigated the influence of the polyvalent ions in saline water by studying the pH and ionic conductivity evolutions throughout the time. We have also evaluated the ND process costs for Gabes brackish water desalination and the possibilities of optimization. The objective is contributed to the development of an efficient process to produce an affordable drinking water in developing countries especially in isolated locations.

2. Experimental study

2.1. Membranes

The performances of ND cells essentially depend on the properties of IEMs used. In this work, two homogeneous membranes (Neosepta® CMX and AMX, Astom, Japan) were used. Those membranes have a uniform distribution of functional sites and are known for their excellent permselectivity, chemical durability, and electrochemical properties, what makes them suitable for a variety of applications [31].

Prior to any membrane process, membranes were conditioned by following the French standard NF X 45-200 [32] in order to stabilize their physicochemical properties, remove any impurities that may come from their manufacturing process and achieve reproducible initial conditions for all membranes. We have also used this standard to characterize both membranes: ion exchange capacity, water uptake, thickness, and altering current conductivity. Table 1 shows the main physicochemical characteristics of the cationic and anionic membranes.

2.2. ND process and conditions

Fig. 2 shows a schematic representation of the ND process. The cell used here corresponds to a PCCell electrodialysis stack (ED 64-004). It is composed of three compartments (corresponding to Nylon® spacer thickness, Fig. 2): acidic (A), alkaline (B), and desalination (D) compartments. The width of each compartment is equal to 450 µm. A, B, and D were fed, respectively, with HCl solution, NaOH solution, and saline solution. Both IEMs are placed between compartments; CMX separates A and D compartments whereas AMX separates B and D. The fluid circulation through the three compartments is ensured by Masterflex® pumps. This cell allows the use of a significant number of IEM pairs that can reach 20 pairs. In our case, a single pair of IEMs was used with an active surface of 64 cm² per membrane (8 × 8 cm).

Table 1
Main physicochemical characteristics of CMX and AMX membranes

Membranes	CMX	AMX
Ion-exchange capacity of dry membrane (meq g^{-1})	1.6	1.3
Water uptake (wt%)	25	26
Thickness (µm)	170	140
Conductivity in NaCl 0.1 M (mS cm^{-1})	2.1	1.2

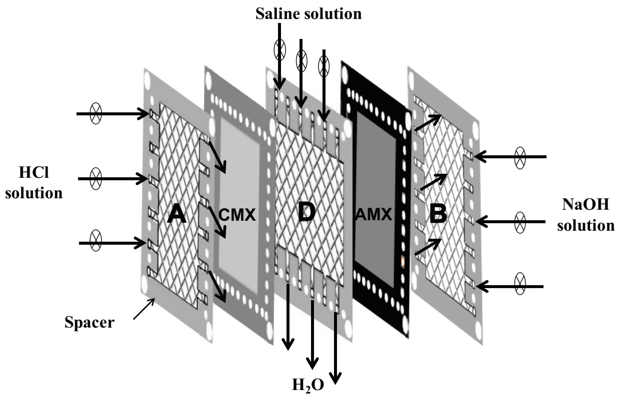

Fig. 2. Neutralization dialysis process of saline solution.
Note: CMX – cation-exchange membrane; AMX – anion-exchange membrane; A – acidic compartment; D – desalination compartment; and B – alkaline compartment.

In this work, we used the optimum conditions obtained in our pervious study [30] to perform the desalination of different saline solutions. Thus, the initial acidic and alkaline solutions concentrations are five times higher than that of the saline solution's one.

The flow rates in A, D, and B compartments have been chosen which is equal to 100, 75, and 50 mL min^{-1}, respectively, referring to our previous optimizations [30]. The corresponding linear flow rates are 4.17, 3.13, and 2.10 cm s^{-1}, respectively. The volumes were fixed, respectively, to 1.5, 1.5, and 0.5 L for A, B, and D solutions maintained at 25°C.

During the desalination process, the pH and ion conductivity values were measured in the D solution using a combined pH–conductivity–meter (Jenway 3540 setup at 10 kHz AC frequency). According to the WHO, drinkable water should correspond to a conductivity value under 1 mS cm^{-1} and a neutral pH (5.5–8.5) [4].

2.3. Reconstituted water

In this work, the study of ion-exchange kinetics influence was first carried out on reconstituted surface water (which contains different salts) by ND process. The optimum conditions obtained in previous study [30] were used for this investigation.

Reconstituted water was performed using the composition of Gabes brackish water located in the south of Tunisia [10] (Table 2).

Table 3 shows the ionic strength of each ion (cations and anions) of Gabes water. From those data, we performed reconstituted water composed of three different salts: $CaCl_2$,

Table 2
Physicochemical analysis of Gabes brackish water and the standards for drinking water

	Gabes water	Standards water according to WHO standards
pH	7.6	6.5–8.5
Turbidity (NTU)	1.6	5.0
Conductivity (mS cm^{-1})	4.18	–
TDS (mg L^{-1})	2,633	500
Hardness (°F)	117	50
Alkalinity (°F)	10	–
Ca^{2+} (mg L^{-1})	365	–
Mg^{2+} (mg L^{-1})	64	–
Na^{+} (mg L^{-1})	409	250
K^{+} (mg L^{-1})	42	–
Fe^{3+} (mg L^{-1})	0.20	0.30
HCO_3^{-} (mg L^{-1})	120	–
SO_4^{2-} (mg L^{-1})	1,040	400
Cl^{-} (mg L^{-1})	674	250
NO_3^{-} (mg L^{-1})	2	44
F^{-} (mg L^{-1})	1.28	1.50

Table 3
Cations and anions ionic strength in Gabes brackish water

Gabes brackish water	m (mg)	C_i (mmol L^{-1})	Z_i	Z_iC_i	ΣZ_iC_i
Cations					
Ca^{2+}	365	9.1	2.0	18.3	
Mg^{2+}	64	2.6	2.0	5.3	
Na^+	409	17.8	1.0	17.8	
K^+	42	1.1	1.0	1.1	
Fe^{3+}	0.2	0.004	3.0	0.012	
					42.4
Anions					
HCO_3^-	120	2.0	1.0	2.0	
SO_4^{2-}	1,040	10.8	2.0	21.7	
Cl^-	674	19.0	1.0	19.0	
					42.6

Na_2SO_4, and $MgSO_4$. The choice of these salts was made according to their solubility, and the ions amount contained in the Gabes brackish water. The sodium and potassium ions were combined due to the low contents of potassium. In addition, the iron ion was not taken into account due to its very low concentration in Gabes water (0.004 mmol L^{-1}). However, for the prospect of industrialization, the accumulation of Fe^{3+} ions inside CEM can be an inconvenient.

In order to prove the influence of Fe^{3+} ions on the CMX physicochemical characteristics, a static study is carried out using $FeCl_3$ solution. In fact, the CMX membrane sample (S = 10 cm^2) was immersed in 0.5 L of $FeCl_3$ solution with a concentration equal to 0.4 mmol L^{-1} (which is 100 times higher than the iron ion concentration in Gabes water) during 24 h. Then, the exchange capacity and the electrical conductivity were measured by following the French standard NF X 45-200 [32].

After immersing the membrane sample in $FeCl_3$ solution, CMX becomes darker. Thus, we can conclude that Fe^{3+} ions are trapped inside the membrane.

The exchange capacity of CMX decreases from 1.6 to 1.3 meq g^{-1} due to the presence of iron ions inside the membrane. However, the electrical conductivity in NaCl solution increases from 2.1 to 2.4 mS cm^{-1}. In fact, the functional sites of the membrane are inhibited by the iron ions. Thus, the Donnan exclusion will be less important, and the salt absorption (co- and counter-ions) will be easier [33].

Consequently, Gabes brackish water must be pretreated through a ventilated sand filter to reduce its contents in iron before starting the desalination operation [10].

The kinetics of $CaCl_2$, Na_2SO_4, and $MgSO_4$ solutions desalination as well as the reconstituted water desalination were made in a three-compartment stack.

Table 4 shows the ionic strength (I) of the three salts separately ($CaCl_2$, Na_2SO_4, and $MgSO_4$) as well as that of the reconstituted water. These I values correspond to 18.30, 5.30, 18.90, and 42.50 mmol L^{-1} for $CaCl_2$, Na_2SO_4, $MgSO_4$, and to the mixture of three salts (reconstituted water), respectively. Thus, the acidic and alkaline solution concentrations are fixed at 5 × I in A and B compartments.

Table 4
Ionic strength of salts and reconstituted water

Salt	$CaCl_2$	$MgSO_4$	Na_2SO_4	Reconstituted water
C (mmol L^{-1})	9.15	2.65	9.45	–
I (mmol L^{-1})	18.30	5.30	18.90	42.50

2.4. Gabes brackish water

Brackish water samples were collected from the Gabes desalination plant of the Tunisian National Water Distribution Utility (SONEDE) located in the south of Tunisia. The water samples were pretreated to remove the suspended matter.

Table 2 presents the physicochemical analysis of Gabes brackish water (real surface water) as well as the standards for drinking water fixed by the WHO [4,10]. This water contains different mineral charges with a total dissolved salt (TDS) of 2,633 mg L^{-1} which corresponds to almost 0.04 mol L^{-1} of NaCl. The Gabes water hardness corresponds to 117°F with ionic conductivity equal to 4.18 mS cm^{-1}. This water is not potable and needs a desalination operation to be consumable. Thus, brackish water desalination was carried out in the same optimum conditions used for the reconstituted water desalination by ND process.

3. Results and discussion

3.1. $CaCl_2$, Na_2SO_4, and $MgSO_4$ desalination by ND process

In this study, we investigated the desalination kinetics of three different salts ($CaCl_2$, Na_2SO_4, and $MgSO_4$) used to reconstitute the Gabes brackish water by ND process. To illustrate our results, Table 5 represents the different experimental conditions of ND operations that were carried out. For example, experiment 1 corresponds to $CaCl_2$ solution desalination with I_D = 0.018 mol L^{-1} and $I_A = I_B$ = 0.100 mol L^{-1} (ionic strength of salt, acidic, and alkaline solutions, respectively) and a Q_A = 100 mL min^{-1}, Q_D = 75 mL min^{-1}, and Q_B = 50 mL min^{-1} (circulation flow rates of respective solutions).

Each experiment was carried out three times in order to check their repeatability, and the results presented in figures are the average of the three tests. In each case, the relative differences did not exceed 5%.

Figs. 3(a) and (b) present the kinetics of pH and the ion conductivity (σ), respectively, measured in the saline compartment during the desalination process for three salts ($CaCl_2$, Na_2SO_4, and $MgSO_4$). In all the experiments, the desalination operation is stopped at an ionic conductivity value close to zero.

The pH vs. time plots (Fig. 3(a)) show almost the same pH evolution for both $MgSO_4$ and Na_2SO_4 salts during the desalination operation. First, pH decreases quasi-immediately to acidic value and it takes about 100 min (pH < 3). Then, both a slow and low pH transition is observed from 2.9 to 5.2 for $MgSO_4$ and from 2.7 to 4.9 for Na_2SO_4. Thus, the desalinated solutions remain acidic.

The saline solution pH decrease is due to higher ion-exchange rate across CMX (between Na^+ and H^+ ions for Na_2SO_4 desalination as well as between Mg^{2+} and H^+ for $MgSO_4$

Table 5
Experimental conditions of ND operations for three salts

		Compartment A (HCl)	Compartment D (saline solution)	Compartment B (NaOH)
Flow rate (Q, mL min^{-1})		100	75	50
Experiments	Salts	I_A (mol L^{-1})	I_D (mol L^{-1})	I_B (mol L^{-1})
1	$CaCl_2$	0.100	0.018	0.100
2	$MgSO_4$	0.020	0.005	0.020
3	Na_2SO_4	0.100	0.018	0.100

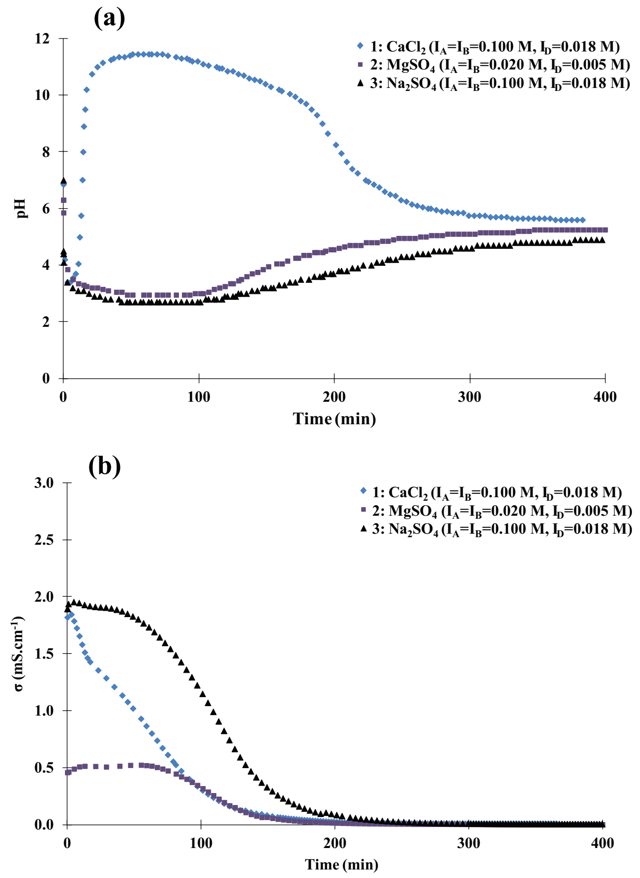

Fig. 3. (a) pH and (b) conductivity of $CaCl_2$, Na_2SO_4, and $MgSO_4$: Q = 100, 75, and 50 mL min^{-1} in A, D, and B compartments, respectively.

desalination) than that across the AMX (between SO_4^{2-} and OH^- ions for both solutions). Thus, the amount of the H^+ ions entering into the D compartment through CMX is higher than that of the OH^- ions entering into the same compartment through AMX. Similarly, a higher amount of Na^+ (Mg^{2+}) ions leaves the D compartment than SO_4^{2-}. Consequently, a decrease in Na_2SO_4 ($MgSO_4$) concentration engenders an increase of H_2SO_4 concentration in the D compartment, and the desalinated solution remains acidic.

However, the $CaCl_2$ salt desalination kinetic is different from $MgSO_4$ and Na_2SO_4 salts desalination kinetics. First, the pH declines quasi-immediately and becomes acidic about 5 min. Then, a rapid pH transition is observed when the pH value increases from 3.4 to 11.0 and remains constant for about 100 min. In fact, the number of chloride ions (n_{Cl^-} = 18.30 mmol) is two times higher than the number of calcium ions ($n_{Ca^{2+}}$ = 9.15 mmol). In addition, the amount of OH^- ions entering into the D compartment in exchange with Cl^- ions across AMX is higher than the amount of H^+ ions exchanged with Ca^{2+} ions because the divalent ions, which are strongly hydrated, are less removed. Thus, the ion-exchange rate across both membranes changes and becomes higher across AMX. Finally, a slow pH decrease is noticed to achieve a constant value of 5.9. Thus, the solution becomes neutral.

For desalination solution, the ionic conductivity increases slightly and remains constant at the beginning of the experiments for Na_2SO_4 and $MgSO_4$ salts (Fig. 3(b)). This behavior is due to a rapid exchange rate between Na^+ (Mg^{2+}) and H^+ for Na_2SO_4 ($MgSO_4$) solution, respectively. Then, it decreases progressively to achieve a conductivity value close to zero. The desalination of $MgSO_4$ solution is faster than that of Na_2SO_4 solution because the amount of salt used is smaller than that of Na_2SO_4.

Concerning $CaCl_2$ solution desalination, the ionic conductivity decreases immediately and the desalination duration is shorter (less of 60 min) compared with Na_2SO_4 desalination for a conductivity value equal to 1 mS cm^{-1}. This can be explained by a higher mobility of the Cl^- ion in AEM in comparison with the SO_4^{2-} ion. As a consequence, the differences between the fluxes across CEM (J^C) and across AEM (J^A) become smaller during desalination. In fact, a previous study [15] demonstrated that for saline solution concentration of 0.02 M, the ion-exchange kinetics is mixed diffusion-controlled where the membrane and the diffusion boundary layers contribute or act similarly. Given the fact that CMX thickness of 170 µm is higher than that of AMX (140 µm), we can expect that an increase in salt anion mobility would result in a strong increase in the kinetics of anion exchange.

3.2. Reconstituted water desalination by ND process

The reconstituted water desalination was carried out using the optimum conditions obtained in the factorial design previously published [30].

The initial saline solution concentration was fixed at 0.04 mol L^{-1} which corresponds to a Gabes brackish water TDS of 2,633 mg L^{-1} (Table 2). Thus, the initial acidic and alkaline concentration solutions are fixed at 0.2 mol L^{-1}, flow rates of A, D, and B compartments are fixed at 100, 75, and 50 mL min^{-1}, respectively.

The pH and ion conductivity vs. time plots are presented in Fig. 4. These values represent the average of three reconstituted water desalination experiments. The relative standard deviation does not exceed 10%.

During saline solution desalination, the conductivity decreases progressively to achieve a value close to zero. The desalination duration takes about 174 min in order to obtain potable water with a conductivity lower than 1 mS cm^{-1} (for reminder the membrane area is of 64 cm^2), and the pH remains acidic during the desalination process. This behavior

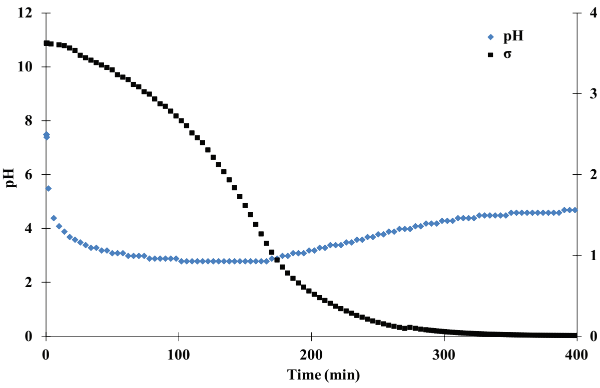

Fig. 4. (♦) pH and (■) conductivity kinetics of reconstituted water: $I_A = I_B = 0.20$ mol L^{-1}, $I_D = 0.04$ mol L^{-1}, and Q = 100, 75, and 50 mL min^{-1} in A, D, and B compartments, respectively.

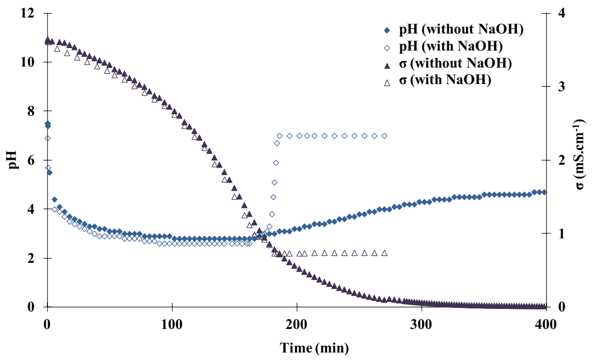

Fig. 5. pH and conductivity kinetics of reconstituted water with and without addition of NaOH solution.

can be explained by the fact that the ion-exchange rate across CMX is more important than that across the AMX. Hence, $J^C > J^A$ the amount of Na^+, Ca^{2+}, and Mg^{2+} ions that leaves the D compartment across CMX is higher than Cl^- and SO_4^{2-} ions across AMX as well as the amount of H^+ ions entering into the D compartment is higher than OH^- ions. Thus, a decrease in saline solution concentration goes along with an increase of both acidic solutions concentration (HCl and H_2SO_4).

As for the desalination solution conductivity, it remains constant at 3.63 mS cm^{-1} for a few minutes (about 10 min) and then decreases down to zero during the desalination process.

In order to obtain potable water ($\sigma \leq 1$ mS cm^{-1} and pH = 6.5–8.5), the experiment is repeated and stopped at 1 mS cm^{-1} value. Then, 8.5 mL of 0.1 M NaOH solution were added to increase the pH up to 7. Thus, the conductivity value decreases from 1.0 to 0.7 mS cm^{-1} and the pH solution become neutral (pH = 7) as shown in Fig. 5.

3.3. Gabes brackish water desalination by ND process

For the Gabes brackish water desalination, acidic and alkaline solutions concentration, flow rates as well as volumes of A, D, and B compartments are fixed according to the conditions used for the reconstituted water desalination. Before ND operation, the water sample was pretreated though a filter paper to remove the suspended matter. Figs. 6(a) and (b) present the pH and ionic conductivity plots vs. times, respectively, for Gabes brackish water and reconstituted water in order to compare them and to highlight the difference between both operations.

The pH evolutions during the desalination operation, for real and reconstituted waters, are similar. In fact, at the beginning of the desalination, the pH of Gabes water and reconstituted water decrease immediately and become acidic. The pH plots are stacked up to 10 min of desalination. Then, Gabes reconstituted waters remain acidic and achieve pH values of 2.3 and 2.9, respectively. A slight pH increase is observed for both solutions. At the end of the desalination process, pH values are 4.7 and 4.3 for reconstituted and real waters, respectively.

Note that the pH of real water becomes inferior to pH of reconstituted water after 10 min of desalination. In fact, the preparation of reconstituted water uses only three salts ($CaCl_2$, Na_2SO_4, and $MgSO_4$). The presence of Fe^{3+} ions is neglected; the K^+ ions are combined with Na^+ as well as HCO_3^- with SO_4^{2-}. Thus, the reconstituted water composition is simplified, which can explain why the pH values are slightly different.

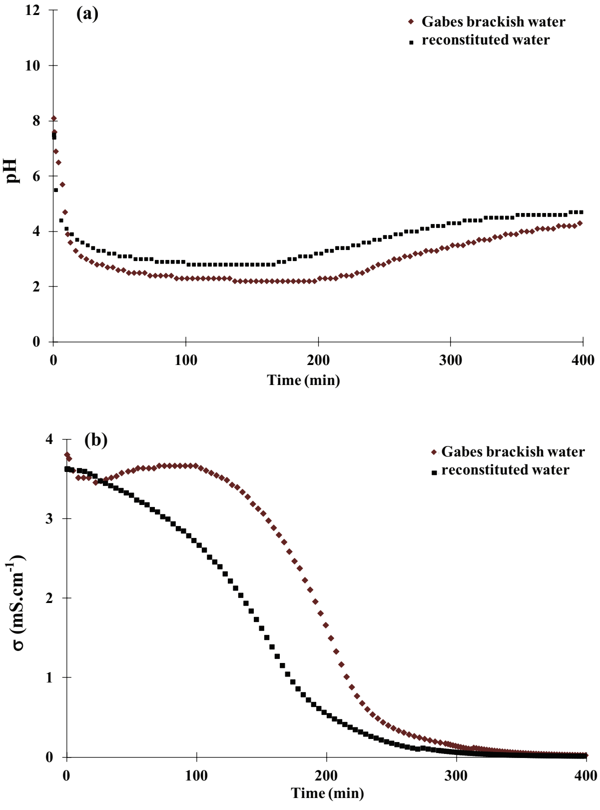

Fig. 6. (a) pH and (b) conductivity kinetics for (■) reconstituted and (♦) Gabes brackish waters: Q = 100, 75, and 50 mL min^{-1} in A, D, and B compartments, respectively.

As for Fig. 6(b), the ionic conductivity evolution for real and reconstituted waters was different during the

Table 6
ND Gabes brackish water desalination costs

Capacity (m^3/year)	8,760.00
Total membrane area (m^2)	42.80
Membrane price ($/$m^2$)	120.00
Maintenance costs, 15% of total investment ($/year)	1,071.71
Total investment costs ($/year)	1,303.91
Chemical agent costs ($/$m^3$)	1.76
Overall desalination costs ($/$m^3$)	1.90

desalination operation. First, for real water desalination, conductivity decreases from 3.81 to 3.46 mS cm^{-1} during 22 min, then, increases gradually up to a value of 3.67 mS cm^{-1} (it takes about 100 min) to finally decrease progressively up to ≈0 mS cm^{-1}. The conductivity increase is followed by a pH decrease. This indicates a higher ion-exchange rate across CMX than that across AMX, involving higher amounts of H^+ ions than OH^- ions entering into the D compartment. Also, the amount of cations leaving the D compartment across CMX is higher than anions across AMX. Thus, the rapid ion-exchange between H^+ and the cations existing in Gabes brackish water across CMX leads to the formation of three acidic solutions (HCl, H_2SO_4, and H_2CO_3) in the D compartment.

The desalination duration of Gabes brackish water takes about 215 min to achieve 1 mS cm^{-1}. It is 40 min longer than the reconstituted water desalination one.

3.4. ND costs evaluation

Table 6 summarizes the main costs for Gabes brackish water desalination. The total cost is estimated at about 1.90 $/$m^3$ when 92.6% of this cost is due to chemicals consumption (HCl and NaOH solutions). The chemicals cost is about 1.76 $/$m^3$. This cost evaluation is carried out to desalinate 1 m^3 of Gabes brackish water in order to obtain desalted water corresponding to a TDS of 0.5 g L^{-1}. It is noticed that ND process is relatively costly compared with ED and RO processes, yet remains quite competitive compared with others using photovoltaic energy. If we can replace HCl and NaOH reagents by others of local origin (e.g., lime water instead of caustic soda), the cost could further decrease.

4. Conclusion

The kinetics of neutralization dialysis process for desalination of $CaCl_2$, Na_2SO_4, and $MgSO_4$ solutions, which constitute the main salts contained in Gabes brackish water, were studied. We have found out that the time variation of pH of the feed solutions in the case of Na_2SO_4 and $MgSO_4$ solutions during desalination was quasi-similar and characterized by a decrease in pH. However, $CaCl_2$ solution desalination led to an increase of pH a few minutes after starting desalination. This change in the kinetics mechanism was explained by the higher mobility of Cl^- compared with SO_4^{2-} in the AMX membrane.

During desalination of the reconstituted water (composed of $CaCl_2$, Na_2SO_4, and $MgSO_4$ salts) and Gabes brackish water, the pH vs. time curves are quasi-similar. This behavior was explained by a higher rate of ion-exchange across the CMX than across the AMX, resulting in a higher amount of H^+ ions than OH^- ions entering into the D compartment. Similarly, the amount of salt cations leaving the D compartment across the CMX is higher than that of anions across AMX. Thus, this behavior leads to the formation of acidic solutions (HCl, H_2SO_4, and/or H_2CO_3), in the D compartment, for reconstituted and real waters. However, the conductivity kinetics for both solutions (reconstituted and real waters) was different. We observed an increase of conductivity values at the beginning of Gabes brackish water desalination that does not exist in the reconstituted water desalination followed by a more important desalination duration (40 min of difference). In fact, the presence of multivalent ions, such as Fe^{3+}, in the real water can reduce the process efficiency.

Even if the ND process cost is relatively high compared with ED and RO (1.90 $/$m^3$ compared with 0.1–0.4 or 0.17–1 $/$m^3$, respectively), it remains a promising technique due to its relatively easy implementation and to the possibility to replace the chemical reagents by cheaper products.

We are working on the modeling of these results to take into account the interactions between ions and membranes: ion fluxes, membranes permselectivities, and rejection rates of different ions.

Acknowledgments

This investigation was realized within the French-Russian International Associated Laboratory 'Ion-exchange membranes and related processes'. The authors are grateful to CNRS, France, and to RFBR, Russia (grants Nb16-48-230911) for financial support.

Symbols

A — Acidic compartment
AEM — Anion-exchange membrane
B — Alkaline compartment
D — Desalination compartment
C — Solution concentration
CEM — Cation-exchange membrane
C_i — Ion concentration, mmol L^{-1}
DBLs — Diffusion boundary layers
I_A — Acidic solution ionic strength, mmol L^{-1}
I_B — Alkaline solution ionic strength, mmol L^{-1}
I_D — Ionic strength in the desalination compartment, mmol L^{-1}
IEMs — Ion-exchange membranes
J^A — Ion flux in the CEM
J^C — Ion flux in the AEM
ND — Neutralization dialysis
Q_A — Acidic flow rate, mL min^{-1}
Q_B — Alkaline flow rate, mL min^{-1}
Q_D — Saline solution flow rate, mL min^{-1}
S — Membrane active area, m^2
V_A — Solution volume in the A compartment, L
V_B — Solution volume in the B compartment, L
V_D — Solution volume in the D compartment, L
σ — Solution conductivity, mS cm^{-1}
Z_i — Charge number

References

[1] R.F. Service, Desalination freshens up, Science, 313 (2006) 1088–1090.

[2] A. Yezza, A.L. Gars, J.L. Sasseville, M. Zaara, Tunisia and the public model of distribution and exploitation of drinking water: the role of public-private partnerships, Desalination, 171 (2005) 77–84.

[3] H. Belhadj, State of Play and Prospects for Desalination Development in Tunisia, International Congress AEDyR, Madrid, 2012.

[4] Organization World Health, Water Quality Assessments: A Guide to Use of Biota, Sediments and Water in Environmental Monitoring, UNESCO/WHO/UNEP, 2nd ed., F & FN Spon, London, 1996.

[5] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res., 43 (2009) 2317–2348.

[6] K.L. Tu, L.D. Nghiem, A.R. Chivas, Boron removal by reverse osmosis membranes in seawater desalination applications, Sep. Purif. Technol., 75 (2010) 87–101.

[7] B. Peñate, L. García-Rodríguez, Seawater reverse osmosis desalination driven by a solar Organic Rankine Cycle: design and technology assessment for medium capacity range, Desalination, 284 (2012) 86–91.

[8] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications, Desalination, 264 (2010) 268–288.

[9] K. Walha, R.B. Amar, F. Quemeneur, P. Jaouen, Demineralization of brackish waters in southern Tunisia by electrodialysis or reverse osmosis, J. Soc. Chim. Tunis., 9 (2007) 133–142.

[10] K. Walha, R.B. Amar, L. Firdaous, F. Quéméneur, P. Jaouen, Brackish groundwater treatment by nanofiltration, reverse osmosis and electrodialysis in Tunisia: performance and cost comparison, Desalination, 207 (2007) 95–106.

[11] J. Ayoub R. Alward, Water requirements and remote arid areas: the need for small-scale desalination, Desalination, 107 (1996) 131–147.

[12] J.E. Miller, Review of Water Resources and Desalination Technologies, Sandia National Labs Unlimited Release Report SAND 2003-0800, 2003.

[13] V.V. Nikonenko, A.V. Kovalenko, M.K. Urtenov, N.D. Pismenskaya, J. Han, P. Sistat, G. Pourcelly, Desalination at overlimiting currents: state-of-the-art and perspectives, Desalination, 342 (2014) 85–106.

[14] Y. Zhang, L. Pinoy, B. Meesschaert, B.V. Bruggen, A natural driven membrane process for brackish and waste water treatment: photovoltaic powered ED and FO hybrid system, Environ. Sci. Technol., 47 (2013) 10548–10555.

[15] M. Chérif, I. Mkacher, L. Dammak, A. Ben Salah, K. Walha, D. Grande, V. Nikonenko, Water desalination by neutralisation dialysis with ion-exchange membranes: flow rate and acid/alkali concentration effects, Desalination, 361 (2015) 13–24.

[16] M. Igawa, K. Echizenya, T. Hayashita, M. Seno, Donnan dialysis desalination, Chem. Lett., 15 (1986) 237–238.

[17] M. Igawa, K. Echizenya, T. Hayashita, M. Seno, Neutralization dialysis for deionization, Bull. Chem. Soc. Jpn., 60 (1987) 381–383.

[18] M. Bleha, G.A. Tishchenko, Neutralization dialysis for desalination, J. Membr. Sci., 73 (1992) 305–311.

[19] H. Tanabe, H. Okochi, M. Igawa, Separation of weak acids and bases by neutralization dialysis, Ind. Eng. Chem. Res., 34 (1995) 2450–2454.

[20] A. Dieye, C. Larchet, B. Auclair, C. Mar-Diop, Elimination des fluorures par la dialyse ionique croisée, Eur. Polym. J., 34 (1998) 67–75.

[21] H. Garmes, F. Persin, J. Sandeaux, G. Pourcelly, M. Mountadar, Defluoridation of groundwater by a hybrid process combining adsorption and Donnan dialysis, Desalination, 145 (2002) 287–291.

[22] Y. Çengeloğlu, A. Tor, E. Kir, M. Ersöz, Transport of hexavalent chromium through anion-exchange membranes, Desalination, 154 (2003) 239–246.

[23] C.T. Matos, S. Velizarov, J.G. Crespo, M. Reis, Simultaneous removal of perchlorate and nitrate from drinking water using the ion exchange membrane bioreactor concept, Water Res., 40 (2006) 231–240.

[24] Y. Zhang, S. Paepen, L. Pinoy, B. Meesschaert, B.V. Bruggen, Selectrodialysis: fractionation of divalent ions from monovalent ions in a novel electrodialysis stack, Sep. Purif. Technol., 88 (2012) 191–201.

[25] M. German, A.K. SenGupta, J. Greenleaf, Hydrogen ion (H+) in waste acid as a driver for environmentally sustainable processes: opportunities and challenge, Environ. Sci. Technol., 47 (2013) 2145–2150.

[26] A.H. Galama, G. Daubaras, O.S. Burheim, H.H.M. Rijnaarts, J.W. Post, Fractioning electrodialysis: a current induced ion exchange process, Electrochim. Acta, 136 (2014) 275–265.

[27] M. Chérif, I. Mkacher, R. Ghalloussi, L. Chaabane, A.B. Salah, K. Walha, L. Dammak, D. Grande, Experimental investigation of neutralization dialysis in three-compartment membrane stack, Desal. Wat. Treat., 56 (2015) 2567–2575.

[28] S. Velizarov, Transport of arsenate through anion-exchange membranes in Donnan dialysis, J. Membr. Sci., 425 (2013) 243–250.

[29] G. Wang, H. Tanabe, M. Igawa, Transport of glycine by neutralization dialysis, J. Membr. Sci., 106 (1995) 207–211.

[30] M. Chérif, I. Mkacher, L. Dammak, A.B. Salah, K. Walha, V. Nikonenko, S. Korchane, D. Grande, Fractional factorial design of water desalination by neutralization Dialysis process: concentration, flow rate and volume effects, Desal. Wat. Treat., 57 (2015) 14403–14413.

[31] J.A. Wiśniewski, M. Kabsch-Korbutowicz, S. Łakomska, Donnan dialysis and electrodialysis as viable options for removing bromates from natural water, Desalination, 281 (2011) 257–262.

[32] AFNOR, Polymer Ion-exchange Membranes, French Standard, NF X 45–200, 1995.

[33] F.G. Donnan, The theory of membrane equilibrium in presence of a non-dialyzable electrolyte, Z. Electrochem., 17 (1911) 572–581.