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Investigation of seawater deionization using the minimization technique with electrodialysis processes (CED-BMED)

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ABSTRACT

Supplies of fresh water on earth are limited, and the rapid growth of the global population is making the search for new sources a priority. Seawater is one such source, and currently, the most widely used desalination methods include membrane processes and evaporation, although both have their disadvantages. In this study, electrodialysis (ED) processes, which have been found to be successful in terms of ion removal, are analyzed with synthetic seawater being deionized using conventional electrodialysis (ED) and bipolar membrane electrodialysis (BMED) processes where the issue of concentrate minimization – currently the most significant drawback of the membrane processes – was resolved. The concentrate was reduced to around 0.5% using the ED method, which can be considered relatively good value when compared with the findings of previous studies. Furthermore, the BMED process also produced anolyte and catholyte chamber solutions at 0.5% concentrations, but as these concentrates are acid and alkaline, it is fair to say that the process has resulted in the production of zero waste. In the following stages, Marmara seawater was deionized under optimum operational conditions, and the deionized seawater values were found to be within the drinkable water tolerances specified by the World Health Organization.

Keywords: Electrodialysis; Deionization; Concentrate; Acid–base recovery

1. Introduction

Although 71% of the earth is covered with water, only 2.6% of this is fresh water, and 69% of this is trapped in glaciers. This means that only 0.8% of the total is usable as fresh water [1]. The world population is increasing by 1.1% every year, and it is generally considered that this increase will continue for the foreseeable future, with current estimates predicting the global population will reach 10 billion by 2050 [2]. One of the leading problems stemming from this population growth relates to the sustainable supply of clean water, and this need increases with each passing day [3]. For this reason, the utilization of other sources of water around the globe, predominantly seawater, is likely to become inevitable [4]. There are already countries in the world where the lack of fresh water resources has compelled them to investigate how fresh water can be obtained from seawater [5,6]. Evaporation and membrane systems are the most commonly used methods [7], but given the cost and the other associated disadvantages, the need for new deionization solutions are becoming even clearer [8].

The deionization approach has gained popularity in recent years, with evaporation and membrane systems being the most common [6]. As the heating and cooling processes required for the evaporation method involve significant costs, it is the membrane processes that are witnessing broader use [9]. Of the available membrane processes, the reverse osmosis system, which ensures ion removal, has been adopted in many areas. This has achieved good results, although the main disadvantage of this method is that it generates a concentrate from 10% to 45%, and it uses pressure as its driving force [10,11]. In other words, the technique is more of a separation process than a treatment process, and it also leads to a significant discharge of concentrated pollutants [12]. Additionally, the treatment of the concentrated outputs of this process can be quite difficult, given the high level of pollutants involved [13]. For this reason, there are ongoing studies aimed at minimizing the concentrate that results from the reverse osmosis process [14]. In recent years, ED and capacitive deionization processes have seen broader use as an alternative to reverse osmosis [15–17]. Electrodialysis is a process that relies on ion transport, and many treatment processes adopt this method, although is known to result in a 20% concentrate [15,16].

Deionization is ensured with anion/cation membranes in the basic electrodialysis (ED) process. ED processes can be categorized into two groups: conventional electrodialysis (ED), and bipolar membrane electrodialysis (BMED) [16]. ED is based on the transfer of contaminants to an anolyte and catholyte chamber by means of ion transfer, and through the use of anion- and cation-exchange membranes [16]. In BMED, the process can be achieved by adding bipolar membranes to the ED processes. Thanks to the bipolar membranes, decomposed water molecules are converted to H^+ and OH^- ions by electrolysis. Thanks to this, the excess ions – anions and cations – are converted to acidic and alkaline solutions [18]. In other words, acid and alkaline solutions are produced simultaneously as a by-product of the deionization [18]. This approach ensures ion removal, while also reducing concentrate formation, thus resulting in a zero-waste process [19]. While there have been a number of efficiency studies analyzing the ED deionization of seawater, there have only been limited studies to date focusing on concentrate minimization and recovery [20].

The aim of this study was to deionize a synthetically prepared seawater (SSW) solution to produce fresh water, while aiming to minimize the formation of concentrated waste and also to convert the concentrate into useful products, namely acid and alkaline solutions. Afterwards, the World Health Organization (WHO) Drinking Water Standards were used to assess the results obtained from the seawater deionization process, which was carried out under optimum operating conditions defined by the synthetic studies.

2. Materials and methods

The general removal mechanisms of the conventional single-membrane electrodialyzer and the bipolar single-membrane electrodialyzer used in this study are shown in Figs. 1 and 2.

As shown in Fig. 1, under the effect of applied electrical current, thanks to anion-exchange membranes and cation-exchange membranes, anions and cations are transported to the anolyte and catholyte chambers that allow the deionization process to take place.

As can be seen in Fig. 2, while the transport of ions ensures deionization, the concentrate stream formed by the bipolar membrane is converted into acid and alkaline solutions [18].

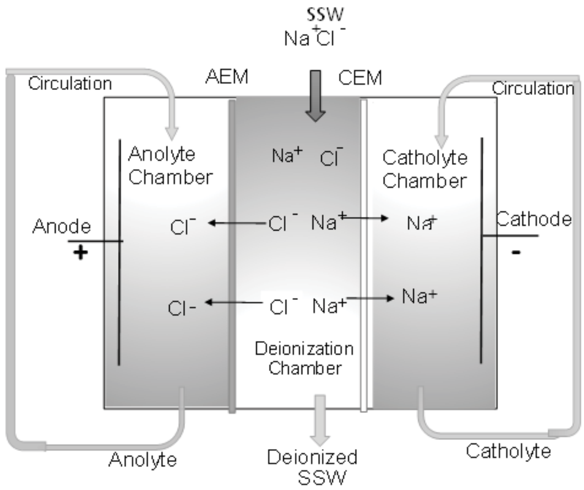

Fig. 1. Mechanism of the ED deionization process.

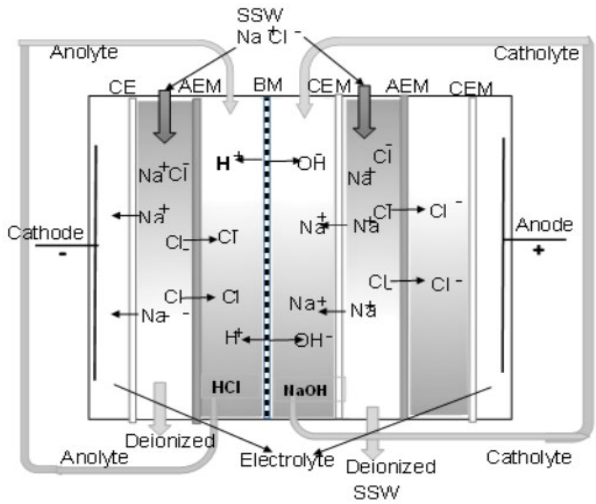

Fig. 2. Mechanism of the BMED deionization process.

All of the chemicals used in the study were supplied by Merck (Turkey), and all analyses were carried out according to standard methods (SM 4500 H^+, SM 2510 b [21]. A 1 L, 55 mS/cm NaCl (salty water representing seawater) solution of 99.5% purity from Sigma-Aldrich (Turkey) was used as the feed solution, and an 0.1 L NaCl solution of 2 mS/cm, prepared from the same chemical, was added to the concentrate section to provide the input conductivity required for the ED experiments. Similarly, trials were conducted involving the addition of a 1 L salt water (synthetic seawater) solution of 55 mS/cm to the BMED solution as feedwater for the reactor. Afterwards, 0.0001 M HCl and 0.0001 M NaOH were successively added to ensure high-quality acid and alkaline solutions were obtained from the BMED process. All of these electrolytes were added with a view to ensuring the initial conductivity required for the electrodialysis process [18]. An HQ40D model multimeter, made by HACH LANGE (Turkey), was used for the pH and conductivity analyses during the study, along with an ED-64-4 model electrodialyzer made by PC Cell. Depending on the membrane configuration, an electrodialyzer can be used for a conventional electrodialysis process or for a BMED process. Basic information on the pump units of these electrodialyzers is presented in Table 1.

The electrodialyzers contain an ion-exchange membrane, the characteristics of which are presented in Table 2.

In the final phase of the study, deionized water was obtained from Marmara seawater through the use of the optimum working conditions identified.

3. Results and discussions

3.1. Concentrate stream minimization

In the most basic terms, electrodialysis can be described as a process in which pollutant ions are transported and removed through the use of an anode and a cathode, and also by way of the circulation that occurs during the passage of ions. This is why anion- and cation-exchange membranes are used. The removal of ions is ensured through transport [22]. As in the basic mechanism shown in Fig. 1, an output of deionized water can be obtained by transporting ions to different chambers. In other words, rather than ensuring deionization, the process creates a higher concentration of pollutants. To achieve this, the present study began with the minimization of the concentrate volume, and in a trial carried out following the conventional electrodialysis process (as shown in Fig. 1), liquid was first added to 1 L of salty water to form a 1 L volume of concentrate. The results obtained, up to the target value of 5 mS/cm, are given in Fig. 3.

As shown in Fig. 3, the level of concentrate volume was reduced such that 1 L of concentrate/1 L of SSW became 0.1 L of concentrate/2 L of SSW. It was observed that volume minimization reduced the concentrate volume value down to around 5%.

A review of published literature reveals that such treatments are usually carried out using the evaporation or reverse osmosis methods, although both methods have disadvantages related to the cost and management of the concentrate part [23–25].

Evaporation is a method with high energy requirements and is very difficult to use in the absence of solar energy [8–24]. Therefore, it is more convenient to use it in areas where there is plenty of solar energy and water resources [9–26]. In the reverse osmosis process, the most important disadvantage is the cost resulting from high pressure as well as the concentrated high pollution content flow [14–23]. The fact that the reverse osmosis technique results in a concentrate formation of up to 40% defines this as a separation process rather than a treatment process [25]. It is known that the concentrate ratio in the electrodialysis process is in the region of 20% [15], although in the present study the repeated use of the concentrate allowed this value to be decreased to around 0.5%. Concentrate stream minimization was the aim of this study, by aiming to reduce the amount of concentrate to 10%, then that concentrate fraction was kept constant throughout the reaction while desalination was performed.

In short, the optimization was performed for a number of cycles on the concentrate. The optimum point is the number of cycles (optimum amount of influent solution) at which efficiency decreases and time starts to increase.

3.2. Deionization of SSW using the ED process

Conventional electrodialysis can be considered as one of the most important deionization processes in which the most effective operational parameters are current and time. The results obtained in the present study are shown in Fig. 4.

The most important point to consider at this stage is that the concentrate volume can be reduced to levels below 0.1 L/20 L (0.5%) through continued treatment. Fig. 5 shows the conductivity values of the concentrate volume generated during the deionization of SSW using the conventional electrodialysis process.

An analysis of these values shows that the treatment slows down slightly in its final stages as a result of the formation of osmotic pressure. It was observed that optimum operating conditions, which are determined based on the time (the electrolyte was recirculated 20 times, electrolyte volume was 0.2 L/20 L of SSW, with an operation

Table 2
Characteristics of ion exchange membranes

Membrane type	Units	AEM	CEM
Thickness	μm	180–200	160–200
Functional groups	–	NH_4Cl	SO_3, Na
Surface potential	Ωcm^2	1.5	0.75–3.0
Water content	wt%	14	9
Ion exchange capacity	meq/L	ca. 1.5	ca. 1

Table 1
Specification of the ED and bench BMED pump unit

Specification	Units	ED-64/4	BMED 1/3 pumping unit
Membrane size	mm × mm	110 × 110	–
Cell thickness	mm	0.5	–
Nominal flow rate	L/h	4–8	1,500
Max. voltage	V	30	24
Max. amperage	A	5	5
Dimension	cm × cm × cm	16.5 × 15 × 19	82.5 × 38 × 41
Weight	kg	3	28

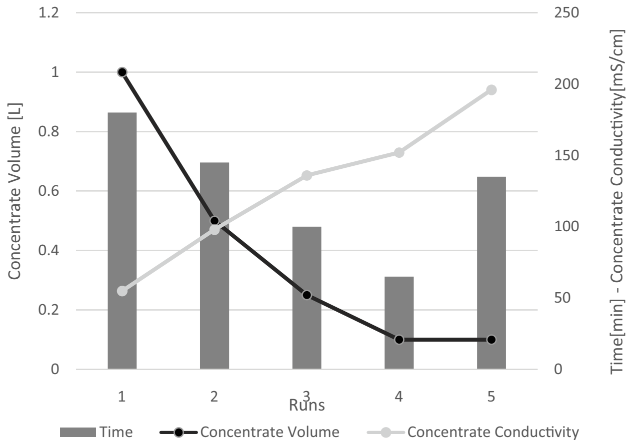

Fig. 3. Minimization of concentrate volume in ED.

time of 215 min/recirculation) and the level of concentrate formation (1%).

After analyzing the results of the study, it was found that it was possible to obtain water with characteristics close to that of drinking water, and the conductivity parameter was particularly significant in this regard. Given that seawater solutes are almost entirely made up of sodium and chloride, this parameter can be considered representative [26]. As a result of synthetic studies, operating conditions for maximum removal efficiency were as follows: the concentrate volume is 0.1 L and the influent solution is 20 L. The remainder of the study was conducted according to these parameters. Maximum amperage/voltage was selected as part of the operating conditions.

3.3. Deionization of SSW using the BMED process

In this part of the study, a bipolar membrane-based removal mechanism was used to process deionization and to obtain acid and alkaline solutions, and the concentrations of these solutions increased as a result of minimizing the concentrate. As a result, the parameters of current and time – being the most important parameters – were investigated first. The results obtained in the 20 L trial using the BMED process are given in Figs. 6 and 7.

As can be seen in Fig. 6, depending on the time, the current value increases initially, and then decreases. Simultaneously, the time value first decreases and then increases, which can be attributed to the close association of the current and time values associated with ion transport – the leading mechanism in the deionization process. Accordingly, an increase in the current value is associated with a decrease in the time value, while a decrease in the current value is similarly associated with an increase in the time value. Because this increase in current value in the system accelerates the electrolytic activity, the increase in this activity will increase the reaction rate and decrease the reaction time. This situation can clearly be seen in Fig. 7, which shows the conductivity changes in the treated SSW and the fixed anolyte and catholyte chambers.

It can be seen in Fig. 7 that deionization slows towards the end, which is thought to be a result of both the high osmotic flux and contamination on the membrane surface. Anolyte and catholyte values were slowed down considerably and the duration increased; the reaction was terminated and this point was accepted as the optimum concentrate cycle value.

From an economic standpoint, and considering global energy prices in Europe, the cost of energy generally stands

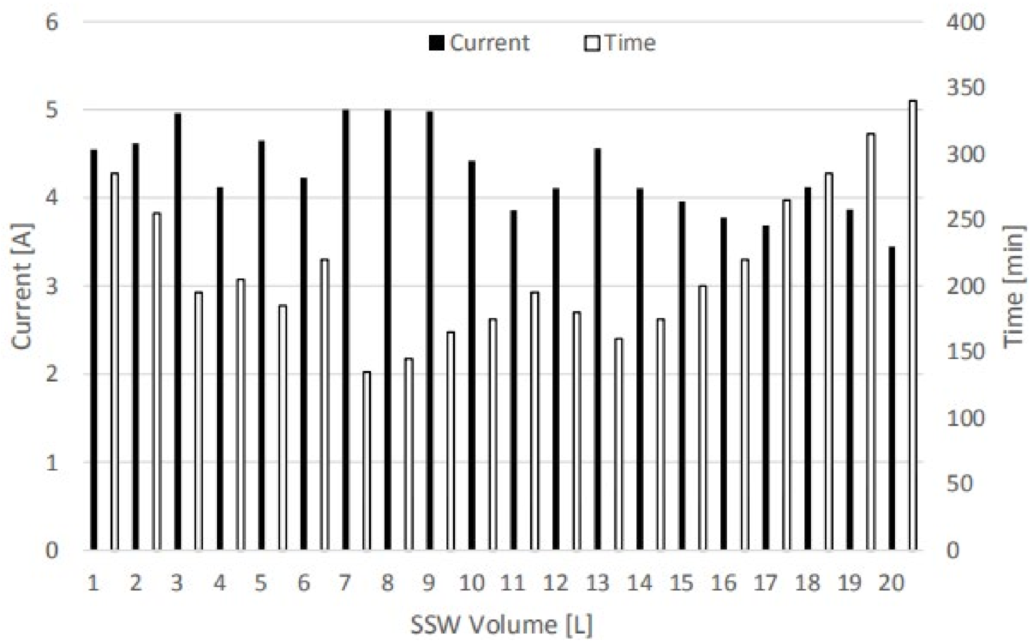

Fig. 4. Change in current and time during deionization of SSW by ED process.

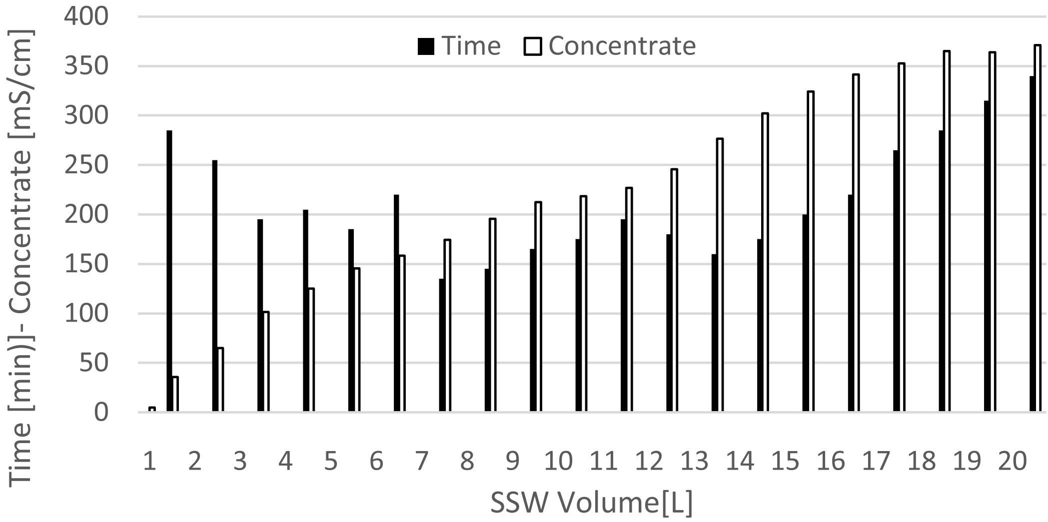

Fig. 5. Change in time and concentrate conductivity during the deionization of SSW using the ED process.

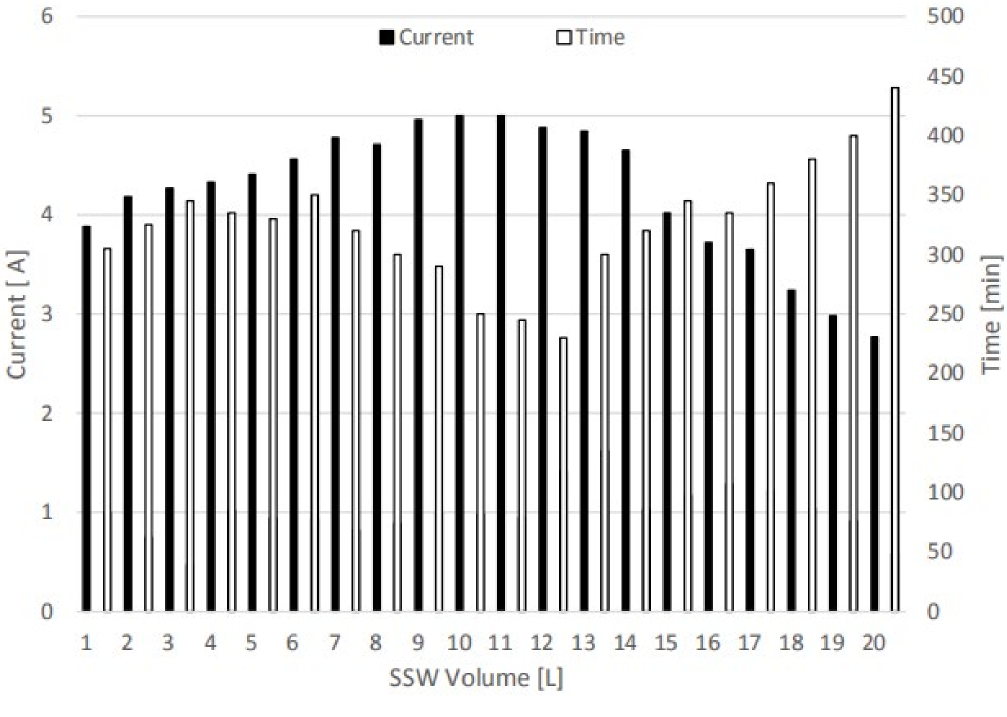

Fig. 6. Change in current and time during SSW deionization conducted through BMED process.

at €0.10/kWh without taxes and levies [27]. In this study, the economic evaluations were based only on the energy consumption calculation during the processes [28].

Based on the values in this study, energy consumption in conventional electrodialysis processes is approximately 106 kWh/m^3 SWW, while previous studies in literature estimated this to be valued at €10.6/m^3 SSW [27]. When the literature is examined, it is seen that the cost for deionization of sea water by ED process is approximately € 5.3/m^3 SW. However, in the same study, a concentrated flow of 16% is formed and the disposal of this concentrated stream is also a significant cost [29]. This value shows that it is more economical than evaporation which is a similar process in terms of concentrate formation. From an economic point of view, the evaporation cost is 25.9 €/m^3 SW. In addition, 13% rejection occurs by evaporation [30].

3.4. Acid and base recovery using the BMED process

The most important feature distinguishing BMED from other membrane processes is that the concentrate stream, which is generally viewed as a problem in membrane processes, can instead be converted into acid and alkaline solutions. Accordingly, deionization trials were conducted in the present study with synthetically prepared solutions with initial NaOH and HCl concentrations of 10^{-4} M, and the results obtained are presented in Fig. 8.

As can be seen in Fig. 8, while the resulting concentrate volume is very low, it can still be converted into recoverable by-products. In this laboratory study, the pH value reached 0.0001, and the MH^+ concentration reached 0.99 M. Due to this substantial difference in values, the relevant value is shown in terms of pH. Similarly, the concentration of OH ions was determined to be 0.925 M.

It can be seen that the results obtained in this study concur with those described in previous published literature

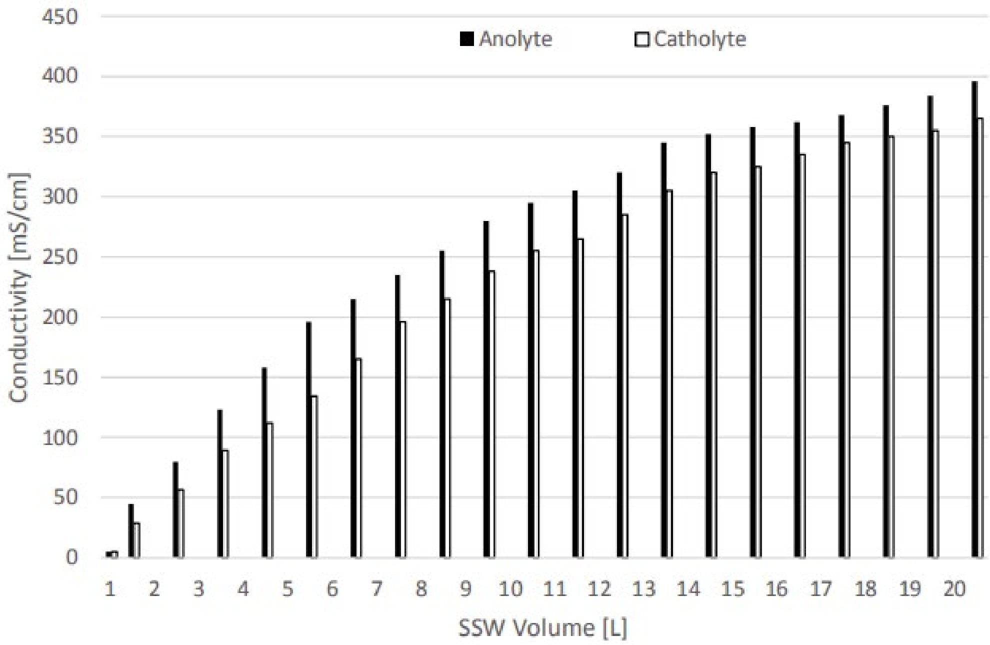

Fig. 7. Conductivity change in the anolyte and catholyte chambers during SSW deionization with the BMED process.

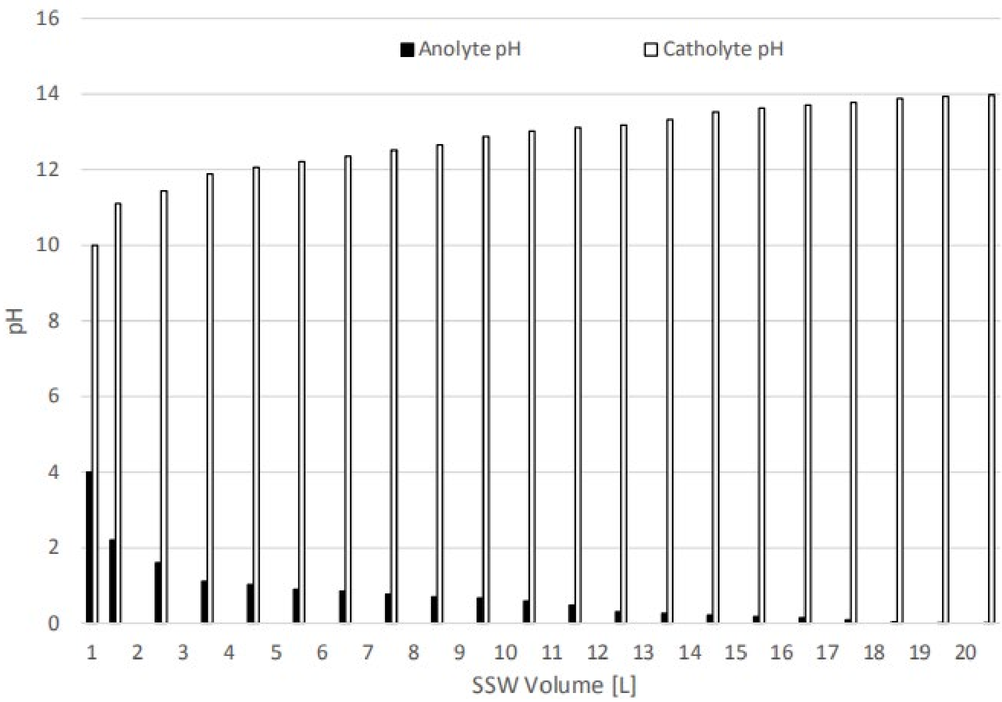

Fig. 8. Change in pH values during SSW deionization using the BMED process.

Table 3
Comparison of deionized water obtained from seawater through ED process with the drinking standards defined by WHO

Parameters	Units	WHO (2017)	ED
Turbidity	NTU	4	0.8
Nitrate $(NO_3)^{-2}$	mg/L	50	36.2
Chloride (Cl^{-1})	mg/L	250	170
Sulfate $(SO_4)^{-2}$	mg/L	500	5.3
Color	Pt-Co	15	4
TDS	mg/L	1,000	310
Total hardness	mg $CaCO_3$/L	500	65

[31,32]. It should also be considered that the additional treatment costs associated with the concentrate stream are a significant disadvantage of the classical membrane processes [33]. From this perspective, the method used here forms a low level of concentrate and stands out in terms of its formation of acid and alkaline solutions that are reusable and offer added value.

The average energy consumption in the BMED process is ≈170 kWh/m^3 SSW, compared with the €17/m^3 SSW reported in published literature [27]. Furthermore, considering that 1 M HCl and 1 M NaOH solutions form 50 L of HCl/m^3 SSW and 50 L of NaOH/m^3 SSW, respectively, it can be seen that the concentrate treatment, rather than bringing additional costs, will actually convert into reusable by-products as a mixed acid–base.

3.5. Seawater desalination for drinking water through an ED process

The results obtained from the seawater deionization process, which was carried out under optimum operating conditions defined by the synthetic studies, were similar to those obtained in the synthetic study. A comparison of the clean water obtained via real seawater deionization following the ED process with the standard values specified by the WHO is presented in Table 3 [34].

Table 3 reveals that the water obtained from the Marmara Sea following the ED process was drinkable according to the WHO standards.

4. Conclusions

This study puts forward a process that can serve as an important solution to the growing need for potable water around the world. The method may bring into use the vast quantities of water that cover 71% of the globe as an alternative to fresh water sources, which constitute only 0.8% of the total water on the planet. The number of studies describing ways of converting seawater into fresh water have seen a marked increase in recent years, and this study can be considered as holding an important place among them, in that it not only proposes a method for obtaining fresh water from seawater but also a means of minimizing the amount of concentrate resulting from such processes, and obtaining acid and alkali solutes that can be reused. Despite having similar operating costs, it should be noted that processes that result in the formation of up to 40% concentrate will incur significant additional costs associated with the treatment of that concentrate. The process covered in this study results in a significant reduction in concentrate formation, while acid and alkali solutions – which are reusable by-products – are produced by means of BMED. Taking the above data and observations into consideration, it can be suggested that converting seawater into fresh water through the electrodialysis method can be considered an important and viable alternative when compared with other deionization processes.

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