Production of Sodium Hypochlorite Water Disinfectant from Seawater Desalination Brine

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The research explores the onsite generation (OSG) of sodium hypochlorite (NaOCl) from desalination brine in Gaza, Palestine. The process produces NaOCl as a valuable water disinfectant and contributes to marine environment protection and public health by reducing brine discharged to the sea. Batch experiments were used to examined the characteristics of producing NaOCl studying five factors *viz.* electrolysis time, current density, electrode type, electrode spacing and stability of the produced NaOCl. The highest NaOCl concentration was 2.17%, achieved with graphite electrodes 1.3 cm diameter, with 1cm electrodes spacing, 120 min electrolysis time, 180 mA/cm² current density and 25 ± 2 °C solution temperature. The NaOCl degradation rate was 1.8% and 10% daily when stored in dark places or exposed to direct sunlight, respectively. Thus, it is recommended to store NaOCl in dark places to minimize its degradation. The present study suggests the OSG of NaOCl as a promising alternative for brine management in Gaza and worldwide.

Keywords: Brine, Seawater, Gaza strip, On-site generation, Electrolysis, Sodium hypochlorite.

INTRODUCTION

Water scarcity is widely recognized as a significant and pressing concern facing humanity in the present day. Gaza Strip-Palestine, as part of the global community, suffers from the severe shortage in the domestic water supply due to the limited conventional water resources and the rapidly increasing demand caused by the high population growth rate [1]. In response to this crisis, the Palestinian authorities built a number of seawater reverse osmosis (RO) desalination plants along the Mediterranean Sea coast to meet the demand of the Gaza population [2]. Reverse osmosis desalination is a membrane filtration method that is fed by a stream of saline water and produces two streams; the first is a freshwater called permeate and a second stream of a concentrated salt solution called brine [3,4]. The produced brine from the Gaza RO plants is recently disposed to the sea, posing a serious threat to the marine environment and the Palestinian community's recreational activities and public health. Consequently, appropriate brine management is required to mitigate these negative impacts and even to deal with the brine as a resource that can be utilized in useful applications.

One promising alternative for the brine management that could be employed in Gaza is to use it for onsite generation (OSG) of sodium hypochlorite (NaOCl), a common disinfectant employed in desalination facilities and conventional water treatment plants. The OSG technique for NaOCl is based on a well-established scientific principle [5]. It uses sodium chloride dissolved in brine and uses a low-voltage continuous electric current to generate NaOCl through a chain of electrochemical reactions. The most important application of OSG is the drinking water disinfection. The advantages of using OSG of NaOCl have encouraged many water utilities to change the conventional chlorine supply systems, such as chlorine gas and NaOCl solution by NaOCl onsite generation system [6,7].

The Gaza Strip is heavily dependent on the procurement of NaOCl as the primary water disinfectant utilized in all desalination facilities inside the region. Due to the restrictions imposed by Israel on importing different materials, including water disinfection materials and solutions with a concentration of over 11%, the Gaza Strip has suffered from a severe shortage of NaOCl on different occasions. Hence, the OSG of NaOCl can benefit Gaza in two different directions. Reducing the amount of brine produced is the first step toward reducing seaside effects of brine disposal. The second involves supplying, without limits, the NaOCl needed to sterilize the waters produced by the desalination facilities. The cost effectiveness of OSG

for NaOCl has been investigated and confirmed by early reports [8-10].

This study aims to determine the practical operating conditions for the electrochemical onsite production of NaOCl from seawater brine. The effect of the main process controlling variables: electrolysis time, current density, electrodes type, electrodes spacing and the stability of the produced NaOCl, were studied.

Theoretical background: The production of NaOCl from desalination brine is achieved by an electrolytic process that takes place in an electrolytic cell. The electrolytic cell is composed of two electrodes; a cathode and an anode, a container filled with the brine and a low-voltage DC energy source. The brine electrolysis begins by connecting the cathode and anode to the low-voltage DC energy source and running the electric current in the electrolytic cell. The NaCl dissolved in the brine dissociates into the chloride ion (Cl⁻) and the ions sodium ion (Na⁺). The Cl⁻ moves to anode, where it is oxidized to produce chlorine, while Na⁺ moves to the cathode to produce caustic soda. Then, chlorine and caustic soda react to produce NaOCl [7]. Oxidation reactions take place at the anode as the positive ion releases its valency electron. On the other hand, reduction reactions occur at the anode as the negative ion receives an electron [11,12].

Generally, the brine electrolysis process follows the chain of chemical reactions presented hereafter:

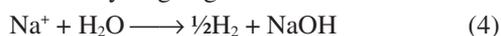First, chloride ions are oxidized at the anode:

$$2Cl^- \longrightarrow 2Cl_2 + 2e^- \tag{1}$$

A hydrolysis process then occurs to the produced chlorine:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl \tag{2}$$
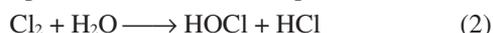
A reduction of sodium ions happens at the cathodic surface:

$$Na^+ + e^- \longrightarrow Na \tag{3}$$

The produced Na ions rapidly reacts with water producing sodium hydroxide and hydrogen gas:

$$Na^+ + H_2O \longrightarrow \tfrac{1}{2}H_2 + NaOH \tag{4}$$

The produced acids in reaction 2 (HCl and HOCl) react with the produced caustic soda (NaOH) at the cathode reaction:

$$HCl + NaOH \longrightarrow NaCl + H_2O \quad \text{and} \tag{5}$$

$$HOCl + NaOH \longrightarrow NaOCl + H_2O \tag{6}$$

The net reaction of electrolysis is:

$$NaCl + H_2O \longrightarrow e^- \longrightarrow NaOCl + H_2 \tag{7}$$
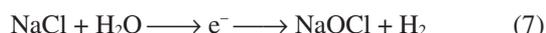
Rengarajan *et al.* [13] investigated the effect of current density, temperature and sodium chloride concentration in the brine on the efficiency of NaOCl production. Their findings indicated that the highest efficiency in producing NaOCl was achieved at a current density of 50-100 mA/cm², a temperature of 313 K and a sodium chloride concentration ranging from 40-50 g/L. Similarly, Hooper [14] discussed the technological advancements in OSG of 0.8% NaOCl. He stated that OSG of NaOCl is applicable, cost-effective and can be a safe alternative to commercially available 12.5% NaOCl and chlorine tablets. Abdul-Wahab & Al-Weshahi [11] examined the challenges related to brine generated from the desalination process and found that brine wastes can be used to generate NaOCl onsite.

The study revealed that the quantity of hypochlorite generated depended on the reaction time and the supplied DC voltage. Research conducted by Al-Areqi *et al.* [7] investigated the effect of utilizing the more affordable and accessible cathodic materials steel, aluminum and zinc on the efficiency of generation NaOCl onsite using a single batch electrolysis cell. The results showed that the efficient rate of onsite generated NaOCl was 0.054%, which was observed using a Zn electrode with 66.3 cm² electrode surface area, with 8 cm apart from the graphite anode during 120 min electrolysis time and applying DC voltage 9.5 V with a measured current density of 176.5 mA/cm [2].

EXPERIMENTAL

The experimental setup used in the experiments is shown in Fig. 1. The setup included Laboratory digital DC power supply (Type: GWINSTEK GPS 3303 with a voltage range of 0-30 V and a current range of 1.5-11 A), multi-meter (Type: GWINSTEK GDM-8135), 2 L cylindrical glass beaker (Type: Karter Scientific 213D20-BORO3.3 Glass), 2 bar electrodes (cathode and anode, 13 mm diameter each, 20 cm length, merged 15 cm in the brine electrolyte solution) made of 4 different materials that were interchangeably used (graphite, copper, aluminum and stainless steel). The reactor was filled in each experimental run with desalination brine with the characteristics is given in Table-1.
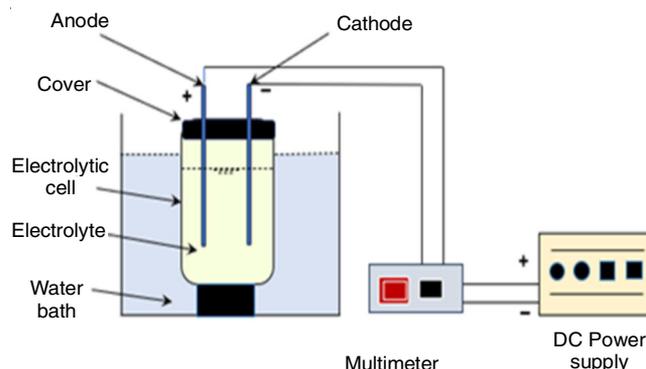

Fig. 1. Schematic of the experimental sodium hypochlorite production electrochemical setup

TABLE-1
CHARACTERISTICS OF THE BRINE IN THE
Al-BASSA SEAWATER DESALINATION
PLANT (CMWU LABORATORY, 2022)

Parameter	Value	Parameter	Value
pH	7.53	Alkalinity (mg/L)	216
EC (µS)	95000	Nitrate (mg/L)	5.4
TDS (mg/L)	68800	Sulfates (mg/L)	5850
Chloride (mg/L)	37562	Sodium (mg/L)	18929
Hardness (mg/L)	19800	Potassium (mg/L)	625
Calcium (mg/L)	700	Boron (mg/L)	7.1
Magnesium (mg/L)	2926	Quantity (m³/h)	15

Brine characteristics: The Al-Bassa seawater desalination plant in Gaza, Palestine was selected as the source of brine samples used and is operated by the Palestinian Coastal Municipalities Water Utility (CMWU). The characteristics of the brine in the Al-Bassa seawater desalination plant were tested

in the CMWU laboratory. The results of the analysis are shown in Table-1.

Experimental procedures: In this work, four experiments were conducted to study the effect of the main variables affecting the electrolysis process used for NaOCl production from seawater brine. The four experiments were designed to investigate the effect of electrolysis time (T_e), current density ($C_{density}$), electrode type and electrode spacing (S), respectively. Table-2 presents the applied experimental program during the investigations.

It illustrates the number of runs performed in each experiment and the values of the operating parameters in each run. In each experimental run, the electrolytic cell was filled with 1500 mL of brine solution having the characteristics mentioned in Table-1. Then, the appropriate electrodes were immersed in the cylindrical beaker, spaced according to the experimental program and connected to the DC power supply. After that the DC power supply was put on and the electric current (i) was adjusted to give the required current density ($C_{density}$) as per the experimental program according to the equation:

$$C_{density} = \frac{i}{A_s} \qquad (8)$$

where $C_{density}$ is the current density; i is the electric current in mA and (A_s) is the surface area of submerged part of electrode in brine, which was 62.56 cm^2 in all the conducted experiments. The electrolytic cell was operated for 210 min in each run. The temperature of the electrolytic cell was controlled in the range of 25 ± 2 ºC by immersing the electrolytic cell in a water bath. A brine sample was taken every 30 min and tested for the produced NaOCl concentration (C_{NaOCl}) using the analytical method as mentioned in Table-3.

In addition to the above-mentioned four experiments, a 5th experiment was conducted to study the stability of produced NaOCl in case of exposure to sunlight. In this experiment, six samples of the produced NaOCl solution (2.1% NaOCl) with a volume of 500 mL each were filled in six glass bottles. Three of the bottles were kept in sunlight inside a water bath to control their temperature at 25 ± 2 ºC. The other three bottles were placed in an incubator in a dark environment at a controlled temperature of 25 ± 2 ºC. The remaining NaOCl concentration in the six bottles was measured daily for 14 consecutive days using the analytical method as mentioned in Table-3. The NaOCl degradation rate was estimated and recorded for the two cases (*i.e.* exposure to light and incubation in darkness).

RESULTS AND DISCUSSION

The production of Sodium hypochlorite (NaOCl) by electrolysis from seawater desalination brine was investigated by studying the main parameters affecting this electrochemical process. These parameters included the electrolysis time (T_e), current density ($C_{density}$), electrodes type and electrodes (S). Moreover, the stability of the produced NaOCl solution was investigated as well.

Effect of electrolysis time: The effect of electrolysis time (T_e) on the production of NaOCl expressed as C_{NaOCl} was examined for each electrode type separately (*i.e.*, graphite, aluminum, copper or stainless steel) by setting the current density ($C_{density}$) at a fixed value of 100 mA/cm^2 and the electrodes spacing (S) at a fixed value of 4 cm while running the electrolysis batch reactor for a total T_e of 210 min in each experimental run (3 experimental runs for each electrode type). The concentration of NaOCl (C_{NaOCl}) in the brine solution was

TABLE-2
EXPERIMENTAL PROGRAM AND SUMMARY OF OPERATING PARAMETERS FOR EACH EXPERIMENTAL RUN

Experiment No.	Experiment title	Number of runs	Electrode's type	Current density; ($C_{density}$) (mA/cm^2)	Electrodes spacing; (S) (cm)
1	Effect of electrolysis time (T_e)	3	Graphite	100	4
		3	Aluminum	100	4
		3	Copper	100	4
		3	Stainless steel	100	4
2	Effect of current density ($C_{density}$)	15 (3/per each $C_{density}$)	Graphite	25, 70, 100, 120, 180	4
		15 (3/per each $C_{density}$)	Aluminum	25, 70, 100, 120, 180	4
		15 (3/per each $C_{density}$)	Copper	25, 70, 100, 120, 180	4
		15 (3/per each $C_{density}$)	Stainless steel	25, 70, 100, 120, 180	4
3	Effect of electrode type	15 (3/per each type)	Graphite	25, 70, 100, 120, 180	4
		15 (3/per each type)	Aluminum	25, 70, 100, 120, 180	4
		15 (3/per each type)	Copper	25, 70, 100, 120, 180	4
		15 (3/per each type)	Stainless steel	25, 70, 100, 120, 180	4
4	Effect of electrode spacing (S)	3	Graphite	180	1
		3	Aluminum	180	2
		3	Copper	180	4
		3	Stainless steel	180	6

TABLE-3
ANALYTICA METHODS

Parameter	Method	Ref.
Sampling procedures	IS 3025 (Part 26) method of sampling and test	[15]
Sodium hypochlorite (NaOCl)	APHA method 4500-CL	[16]
Total dissolved solids in seawater, desalinated water and brine (TDS)	APHA method SM 2450C gravimetric method	[16]

measured at 30 min intervals. As observed from Fig. 2, the concentration of NaOCl (C_{NaOCl}) increases with the increase of the electrolysis time (T_e) until it reaches a steady state value [(C_{NaOCl})$_{steady}$]. For example, when using graphite electrodes, the concentration of NaOCl gradually increased with time until a steady state concentration (C_{NaOCl}) steady of 1.6 % was reached at T_e of 120 min. Similarly, (C_{NaOCl})$_{steady}$ of 0.13%, 0.18% and 0.25% were reached at 60, 60 and 90 min when using copper, aluminum and stainless-steel electrodes, respectively. The direct proportionality between C_{NaOCl} and T_e is attributed to the fact that more NaCl existing in the brine is electrolyzed with time, leading to the production of more NaOCl. However, a steady state (C_{NaOCl}) steady value is reached when most of the NaCl in brine electrolytic cell is electrolyzed to NaOCl and no further significant electrolysis is observed.
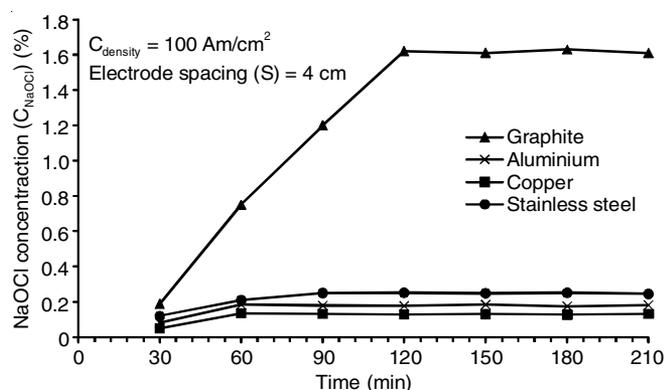

Fig. 2. Effect of electrolysis time on the production of NaOCl

Effect of current density: The effect of the current density ($C_{density}$) on the production of NaOCl was examined for each electrode type separately by setting the spacing between the electrodes (S) at a fixed value of 4 cm while changing the current density ($C_{density}$) to values of 25,70,100, 120 and 180 mA/cm^2. Each experimental run was performed until the steady-state concentration of NaOCl (C_{NaOCl})$_{steady}$ was reached (3 experimental runs for each electrode type and each $C_{density}$ value). Fig. 3 illustrates the effect of the current density ($C_{density}$) on the production of NaOCl expressed as (C_{NaOCl})$_{steady}$. When the current density ($C_{density}$) increased, the steady-state concentration of NaOCl (C_{NaOCl})$_{steady}$ increased as well for all electrode types.
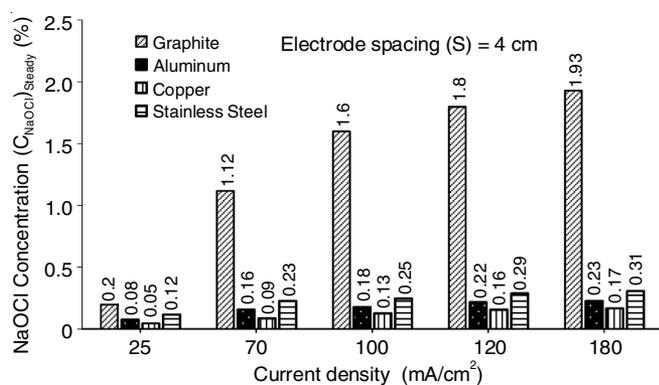
For example, when using graphite electrodes, the steady state concentrations of NaOCl (C_{NaOCl})$_{steady}$ were 0.2%, 1.2%, 1.6%, 1.8% and 1.93% at $C_{density}$ values of 25, 70,10,120 and 180 mA/cm^2, respectively. A similar trend was interpreted from Fig. 3 for the other three electrode types (*i.e.* aluminum, copper and stainless steel). The direct proportionality between $C_{density}$ and (C_{NaOCl})$_{steady}$ is attributed to the fact that the increase in the $C_{density}$ is achieved by increasing the electric current (i), which in turn increases the electrolysis process leading to the production of more NaOCl. Therefore, the optimal operational parameters for the synthesis of NaOCl utilizing graphite electrodes involve setting the current density to 180 mA/cm^2.

Effect of electrode type: The effect of electrode type on the production of NaOCl was examined by installing one electrode type in each experiment (*i.e.* graphite, aluminum, copper, or stainless steel) and setting the spacing between electrodes (S) at a fixed value of 4 cm while changing the current density ($C_{density}$) to values of 25, 70, 100, 120 and 180 mA/cm^2. Fig. 4 illustrates the effect of the electrode type on the production of NaOCl expressed as (C_{NaOCl})$_{steady}$. As depicted in Fig, 4, the graphite electrodes performance was significantly better than that of the other three electrode types. The average steady-state concentrations (C_{NaOCl})$_{steady}$ of the produced NaOCl using the graphite electrodes were 0.20%, 1.12%, 1.6%, 1.8% and 1.93% at $C_{density}$ values of 25, 70, 100, 120 and 180 mA/cm^2, respectively. On the other hand, the performance of copper , aluminum and stainless-steel electrodes was almost similar to each other, with NaOCl steady-state concentrations (C_{NaOCl})$_{steady}$ that are much less than that produced by graphite electrodes and were in the range of 0.05% to 0.31%. The excellent performance of graphite is attributed to its unique structure, which is composed of layers of carbon atoms arranged in a hexagonal arrangement allowing large numbers of electrons to move freely between layers [17]. This large number of free valance electrons gives graphite its excellent conductive properties over other types of electrodes [18]. Moreover, the graphite electrodes are inert electrodes and do not take part in electrolysis reactions [19]. Thus, graphite is more stable compared to other electrode types (*i.e.* aluminum, copper and stainless steel) that take part in the electrolytic reactions and gradually degrade during the electrolysis process.

Effect of electrodes spacing: The effect of the electrodes spacing (S) on the production of NaOCl was investigated using

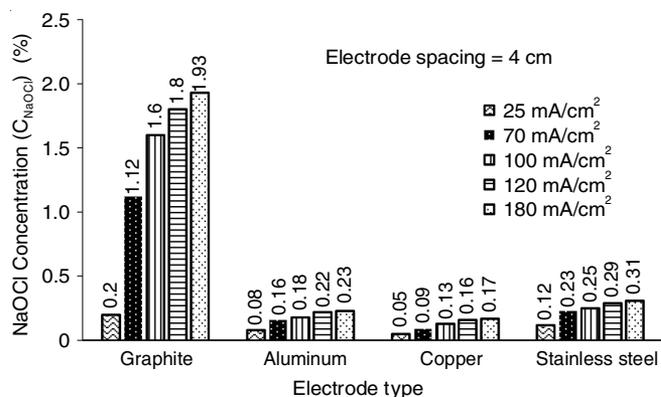Fig. 3. Effect of current density on the production of NaOCl

Fig. 4. Effect of electrode type on the production of NaOCl

graphite electrodes. During the experiments, $C_{density}$ was kept constant at 180 mA/cm^2 while changing the electrodes spacing (S) to 1, 2, 4 and 6 cm (3 experimental runs for each electrode spacing, a total of 12 runs). Fig. 5 illustrates the effect of electrodes spacing (S) on the production of NaOCl expressed as (CNaOCl)$_{steady}$. It was observed that when the electrodes spacing (S) increased, the average steady-state concentration (CNaOCl)$_{steady}$ of the produced NaOCl decreased. For example, at electrodes spacing (S) of 1 cm, the average (CNaOCl)$_{steady}$ was 2.17%, while when S was increased to 6 cm, the average (CNaOCl)$_{steady}$ significantly decreased to 1.19%. The inverse proportionality between (C$_{NaOCl}$)$_{steady}$ and S is attributed to the fact that the resistance to the electric current (i) in the brine solution increases when the distance between the electrodes (S) increases and the electric current decreases [20]. Consequently, the electrolysis of NaCl existing in the brine solution to NaOCl decreases. Thus, the best performance conditions for NaOCl production using graphite electrodes were achieved when the electrodes spacing is 1 to 2 cm and when the current density is set at 180 mA/cm^2.
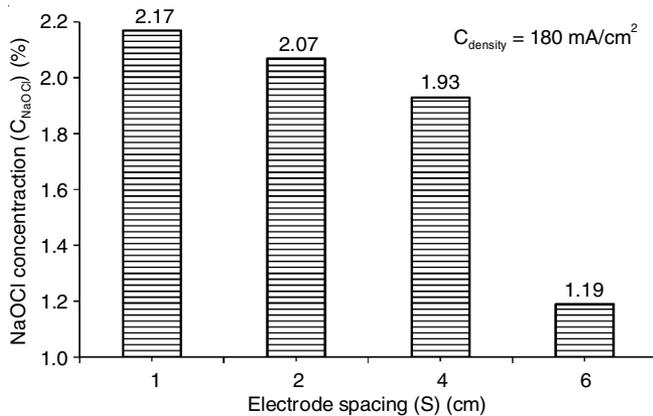
Fig. 5. Effect of electrode spacing on the production of NaOCl

Stability of the produced NaOCl: As evident from the literature, NaOCl solution degrades from exposure to sunlight and elevated temperatures [21,22]. The stability of NaOCl was investigated by producing a 2.1% NaOCl solution in a graphite electrolytic cell with 2 cm between electrodes. During the investigation, six samples having 500 mL each were taken from 2.1% NaOCl solution. Three of the bottles were kept in sunlight inside a water bath to control their temperature at 25 ± 2 °C. The rest of the three bottles were placed in an incubator in a dark environment at a constant temperature of 25 ± 2 °C. The remaining NaOCl concentration in the six bottles was measured daily for 14 consecutive days. Fig. 6 illustrates the results of the degradation of NaOCl under a constant solution at 25 ± 2 °C for two cases (i) the case of exposure of the samples to sunlight and (ii) the case of the samples incubation in a dark environment.

According to the two regression equations in Fig. 6, the degradation rate of NaOCl from the samples exposed to sunlight was -0.0915% per day account for a 4.35% daily reduction from the original NaOCl concentration (reduced from 2.1% to 0.83% in 14 days). On the other hand, the degradation rate
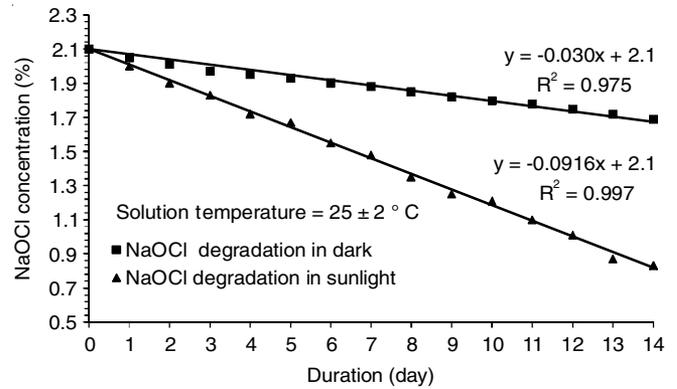
Fig. 6. Sodium hypochlorite degradation as a function of exposure to sunlight

of the samples kept in darkness was -0.038% per day account for a 1.8% daily reduction from the original NaOCl concentration (reduced from 2.1% to 1.55% in 14 days). This indicates that the degradation of NaOCl due to exposure to sunlight is around 2.5 times faster than the degradation in the samples kept in the dark environment inside the incubator. The results of this study indicate that the produced NaOCl solution should be stored in a dark location. Moreover, it is recommended to use the produced solution within 5 days from its production to keep the degraded amount of NaOCl to less than 10% (*i.e.* 5 days × 1.8% per day = 9%) of the initial concentration of the produced NaOCl solution. This degradation rate is practically acceptable since the produced NaOCl will be mostly used onsite to disinfect the desalinated water in the same desalination plant.

Conclusion

In this study, the practical operating conditions for the electrochemical production of NaOCl from seawater brine were investigated. The effect of the electrolysis process controlling variables, namely, electrolysis time, current density, electrodes type, electrodes spacing and stability of the produced NaOCl, were studied. Under the same operation conditions, graphite electrodes always performed the best compared to aluminum, copper and stainless-steel electrodes in the production of NaOCl using brine electrolytic cell. The best conditions for the production of NaOCl in a brine electrolytic cell were found by using 1.3 cm diameter graphite electrodes spaced 1cm apart at a current density of 180 mA/cm^2 and a controlled solution temperature of 25 ± 2 °C. Under these conditions, the electrolysis time was 120 min to reach the best steadystate concentration of NaOCl was 2.17%. Thus, it is practically feasible to use seawater brine for onsite generation (OSG) of NaOCl with a concentration of 0.8% or more is suitable for drinking water disinfection since it was generated at a concentration of 2.1%. The produced NaOCl has acceptable stability if kept away from sunlight. In this work, the daily degradation of the NaOCl, if stored in a dark place, is only around 1.80% of the initial concentration.This degradation rate is practically acceptable since the produced NaOCl will be mostly used onsite to disinfect the desalinated water in the same desalination plant. If the storage time is kept in the range of up to 5 days, then the total reduction of NaOCl will be limited to less than 10% of the initial concentration of the produced NaOCl solution.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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