



## Manganese dioxide coated on recycled graphite substrate as electrode material for sodium hypochlorite production

R. D. TEGUIA<sup>1</sup>, G. B. NOUMI<sup>1,\*</sup>, DOMGA<sup>2,3</sup>

<sup>1</sup>Department of chemistry, Faculty of Science (FS), University of Ngaoundere, P.O Box: 454, Ngaoundere, Cameroon

<sup>2</sup>Department of Applied Chemistry, National School of Agro-Industrial Sciences (ENSAI), University of Ngaoundere P.O Box: 455 Ngaoundere, Cameroon

<sup>3</sup>Processing Engineering Division, CSIR - Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, 630003, India

Received 22 Nov 2020,  
Revised 04 April 2020,  
Accepted 06 April 2020

### Keywords

- ✓ C/MnO<sub>2</sub> electrode,
- ✓ Dip coating,
- ✓ Graphite,
- ✓ Sodium hypochlorite,
- ✓ Sol-gel process.

[gnoumi@yahoo.fr](mailto:gnoumi@yahoo.fr) ;  
Phone: +237699549344

### Abstract

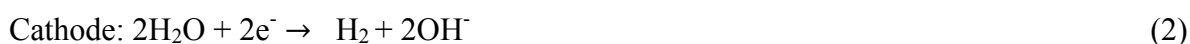
The purpose of this study was to produce a low-cost sodium hypochlorite's solution from manganese dioxide coated on graphite which comes from recycled batteries. Thus, a manganese dioxide electrode was prepared by the sol-gel process and has been used as anode in an electrochemical cell for production of sodium hypochlorite. Graphite were collected from recycled batteries. The colloidal suspension of MnO<sub>2</sub> were deposited onto the surface of a graphite by the dip coating technique. The results showed that MnO<sub>2</sub> films have been synthesized by the sol-gel process and deposited on graphite substrate. Thus, under the real conditions of operation, the lifetime of this electrode was improved. The main characteristics of sodium hypochlorite produced were: a pH of 11.53, a density of 1.02 g cm<sup>-3</sup> and an active chlorine concentration of 18.602 g L<sup>-1</sup> either an active chlorine percent of 1.823%. factors that affect the production of sodium hypochlorite solution were studied. The results also show that the optimum conditions for production of NaOCl solution were: a sodium chloride concentration ([NaCl]= 300g.L<sup>-1</sup>), an intensity (I=1A), an inter-electrode spacing (d= 0.5cm), a pH of the solution (pH=10), a temperature (T=20°C) and a time process (t= 60min). In recent research, sodium hypochlorite has attracted considerable attention, mainly due to its high oxidation potential.

## 1. Introduction

Sodium hypochlorite is widely considered as an important oxidizing agent and mediator in wastewater and/or water treatment and organic synthesis [1]. It is a best antiseptic on the worldwide market and it is now becoming the most chemical present in several houses. NaOCl is a substance widely and effectively used for water disinfection, surface purification, odor removal [2]. It is also known as an important oxidant in organic synthesis. The industrial solution of NaOCl is clear, of very pale yellow colour, with the characteristic odour of chlorine. In-situ produced hypochlorite was used for anodic oxidation of dye molecules and phenols in the wastewater [3–6]. It has numerous advantages namely: simple dosage, safe storage and transportation and leaves no residual effluent [7]. Besides ozone, hypochlorite has the greatest power to kill germs which can cause dangerous diseases like: cholera or typhoid fever [8]. NaOCl offers a better advantage because it is able to eliminate 99% microbe's forms in water. Industrially, the production of hypochlorite solution is evaluated at 600,000 tonnes per year. NaOCl is essentially produced by two methods: chemical and electrochemical. The most process

employed for its production in industry is the electrochemical process because it is easy to implement [9,10]. Moreover, the electrochemical pathway has a better effectiveness and makes it possible to obtain in great quantities [11].

Usually, in industry, the technique of production of chlorine gas is the electrochemical technique, which explains the significant number of studies concerning the electro-generation of hypochlorite on the spot of use [7]. The electrochemical production of sodium hypochlorite represents the best method to obtain a pure product. To have a good production, it is necessary to optimize the electrochemical process with the optimal of electrocatalytic electrodes (cathode and anode), the gap between electrodes, the temperature of electrochemical cell. It is very important for the product stability during a long period, avoid the presence of heavy metal ions and particularly impurity-like: carbon micro-powders in suspension etc. A rigorous control of the pH, of the final product is necessary for the optimal disinfection power of the hypochlorite solution. In the electrolysis of brine, chlorine is mainly generated at the anode while hydrogen and caustic soda are produced at the cathode [12,13].



It's possible to recover chlorine gas by separating the two electrodes by an exchanging membrane ion, this process is commonly called electro-dialysis. In the absence of a membrane,  $\text{OH}^-$  diffuse towards the anode and there, the reaction of formation of the sodium hypochlorite takes place following the Eq. (3).



Electrosynthesis of NaClO is preferred due to the environmental hazard associated with the storage and transportation of liquid chlorine. It is now becoming popular for users to produce their own hypochlorite solutions by means of undivided electrolytic cells by direct electrolysis of weak brine or seawater [11]. However, this product is seldom produced in the countries where the residents suffer from waterborne diseases and where it is difficult to import and to distribute<sup>1</sup>.

During the process, anode material plays an important role because it is the seat of chlorine evolution reaction (CER). Thus, the development of electrocatalysts for this anodic process is an interesting topic. To obtain high current efficiency, electrolytic preparation of hypochlorite is necessary to reduce energy-loss reactions. The choice of an anode material of satisfactory longevity in the economic plan constitutes a difficult point. Metallic oxide coatings have been studied and developed since 1969 [16]. Also called Dimensionally Stable Electrode (DSE), it consists of titanium; substrate covered with an oxide coating layer that is mainly made up of platinum group metals. These electrode materials for the production of sodium hypochlorite are used as an anode to generate chlorine in an electrolysis process that uses seawater and diluted brine in an electrolysis bath. Among these materials, the most used are Pt/RuO<sub>2</sub>, Ti/SnO<sub>2</sub>, Ti-Ta<sub>2</sub>O<sub>5</sub>, Ti/RuO<sub>2</sub>, Ti/IrO<sub>2</sub>, Ti/PtOx, Ti/ZrO<sub>2</sub>, Ti/RuO<sub>2</sub>-IrO<sub>2</sub> [1,14–16]. RuO<sub>2</sub>-TiO<sub>2</sub>/Ti anode presents the best electrocatalytic activity among all kinds of DSE [17,18] for NaOCl production. Both IrO<sub>2</sub> and RuO<sub>2</sub> having rutile structure, have been widely used in industries. On the other hand, this technology is relatively expensive based on the raw materials (metal oxides, substrates Ti or Pt), they are extremely infrequent in some countries. Moreover, these metallic oxides are harmful to the environment. Graphite is considered as active anodes and is one of the most used material having much higher electrocatalytic power for oxidizing chloride ions than for generating reactive oxygen species. The choice of carbon in this study can be justified by its abundance in nature in various forms, its chemical inertia and its moderate cost. Carbon-based materials are widely used in electrochemical like

energy [18,19], electrosynthesis [1], wastewater treatment [21], and so on. However, it is important to note that in most study it is used as a substrate [22]. Manganese dioxide offers some good electrochemical properties, because it has some excellent anti-corrosion properties in several media, good compatibility with the environment and it is low cost [23]. Furthermore, MnO<sub>2</sub> material have received a substantial amount of recent attention due to their distinct structure–property relationships in multiple fields, eg, energy [24], electrocatalysis [25], and Biomedical [27] etc. Furthermore, Mn is the twelfth most common element on the planet and the third most abundant transition element after iron and titanium. Consequently, MnO<sub>2</sub> has attracted attention for use as an insoluble anode both for chlorine evolution and oxygen evolution and is regarded as a DSE material with a bright future [16]. However, the chlorine solutions were produced from graphite anode. During the process, these electrodes are degraded into CO<sub>2</sub> and/or CO [5,10,26]. Thus, considering the cost of various materials used for the production of this substance, we orientated our idea for the utilization of low-cost materials (graphite from recycled batteries and manganese dioxide) in order to develop an anode material. In literature, several novel and effective routes have been devoted to prepare manganese oxide nanomaterials with various shapes and excellent properties, such as chemical vapor deposition [27], spray-pyrolysis [28,29], pulverization [30], electrodeposition [20], sol-gel [31–33]. In sol-gel process, the materials are obtained from solution via gelation. But the high homogeneity of constituent elements and the mild processing conditions of the sol-gel synthesis, such as moderate preparation temperatures, also makes it possible to obtain unique materials, not accessible with other techniques [34,35]. The sol-gel process does not require any grinding procedures to achieve homogeneous single-phase ceramics, thereby avoiding a potential source of contamination [36]. This, along with the purity of the precursors, makes the sol-gel process an excellent method for making high purity material. Jiang et al., [22] reported that when manganese oxide nanoparticles are deposited onto carbon based-material (graphite), its electrochemical active surface area and number of active sites increase and lead to improve the performance of MnO<sub>2</sub> catalysts. For this purpose, oxide nanoparticles prepared from alkoxide precursors are of great interest, and is one of the most important of the technological applications of the sol-gel processing. The aim of this paper is to produce sodium hypochlorite at low cost from manganese oxide deposited on graphite substrate (C/MnO<sub>2</sub>). C/MnO<sub>2</sub> was used as anode for the generation of NaOCl brine solution. Different operating conditions and factors affecting the production process of NaOCl were studied and optimized.

## 2. Material and Methods

### 2.1. Material and methods

In this study, the main material used was graphite. The samples of graphite tube were obtained from the recycling of used batteries. Indeed, alkaline batteries contain manganese dioxide, graphite, steel and zinc. Thus, the used batteries Tiger Head brand (type R20 UM-1) were collected and shredded to recover the samples of graphite. These samples having apparent density of 1.63 g cm<sup>-3</sup> and an effective area 12.058 cm<sup>2</sup>. Sodium chloride, sodium sulfate, sodium hydroxide, sulfuric acid, sodium thiosulfate, potassium permanganate and potassium iodide were of analytical grade and were purchased from Merck. MnCl<sub>2</sub>·4H<sub>2</sub>O and isopropanol were purchased from Prolabo. All the chemicals were used as received.

### 2.2. Electrode preparation

The substrates must be deprived of grease and stripe to ensure a uniform thickness of the layer deposited. Firstly, graphite samples were washed using acetone. Secondly graphite was sandblasting in alumina during five minutes and thirdly, the supports were treated by the chemical treatment in oxalic solution 10% during 45minutes and dried at 105°C for 5 min [37]. After that, the substrate is ready to receive

doped MnO<sub>2</sub>. The precursor solution of manganese dioxide was prepared dissolving an amount of manganese chloride (MnCl<sub>2</sub>·4H<sub>2</sub>O) in 50 mL of isopropanol, the mixture is heated at 80°C in a refluxing process during 45min. Then, a permanganate solution (0.189mol/L) was added fast in the mixture. Afterwards, 5mL of acetic acid was added in the medium after 2 hours. Thus, after 4 hours of refluxing, heating; the dark-brown solution was obtained. This preparation-based method was reported by Lin et al. [38] and Sheng et al. [39] with modification.

After pretreatment of substrate, the solution of MnO<sub>2</sub> has been deposited on the graphite substrate. The material is dried at 105°C for 15min and burned at 400°C for 5 min in furnace for the deposition of one layer. The previous steps were repeated sometime. After deposition of the later layer, the material was burned at 400°C for 2h. This temperature is selected in the aim to obtain the manganese dioxide most stable.

### 2.3. Implementation of the electrochemical cell used in sodium hypochlorite production

In this study, the experiments were carried out in a 150 mL Pyrex cylindrical glass cell with the brine solution. A constant agitation was assured by the magnetic stirrer XANXIN. A titanium plate with an effective area of 3.5cm<sup>2</sup> was used as the cathode. The elaborated electrode was the anode (C/MnO<sub>2</sub>). The electrodes were connected to a D.C power supply DIDALAB including a voltmeter and an amperemeter. A more detailed description of the electrolysis and a design of this electrochemical cell are illustrated in Figure 1 below. The operating electrolysis was carried out under the following condition: current intensity, 0.2-1.0 A; pH 2-12, temperature, 10-40°C, and the concentration of NaCl solution, 50-300 g.L<sup>-1</sup>, the time of electrolysis ranged from 15 to 75 min and the distance between the two electrodes (anode and cathode) varies from 0.5 to 1.5 cm. The main physicochemical characteristics of the sodium hypochlorite solution are: pH, density, and active chlorine concentration.

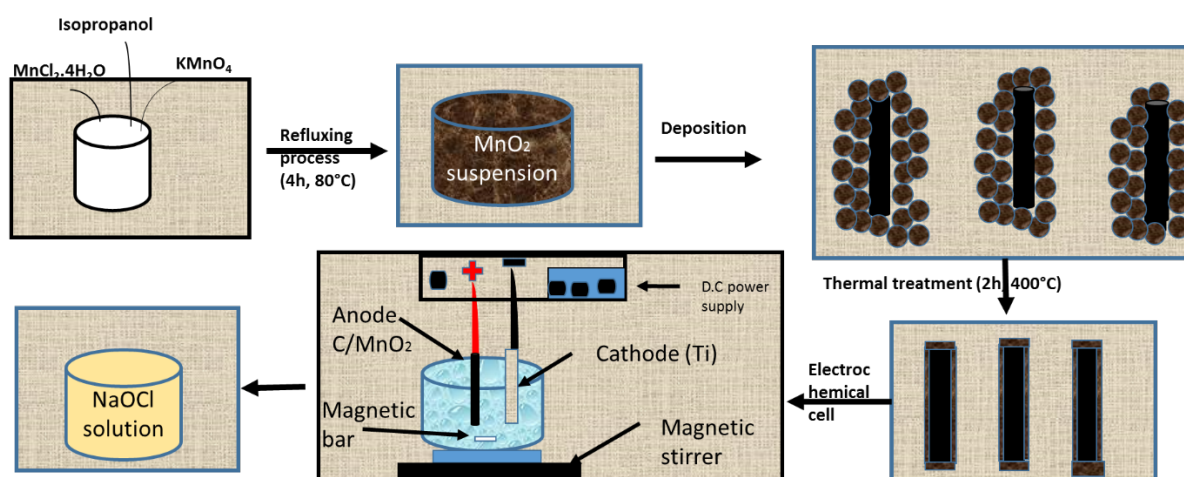


Figure 1: Different steps of the process

### 2.4. Kinetic study of the production of active chlorine

The different tests are carried out by using well-known volumes of distilled water containing a fixed concentration of brine. The initial active chlorine concentration in the prepared solution was measured at the beginning of each test. The mixture in the cell is carried out using a magnetic stirrer. The intensities of D.C. current (0.2, 0.4, 0.6, 0.8, 1A), were fixed by a D.C power supply. In order to follow the kinetic of active chlorine production, the samples of 10 ml were collected from the cell every 15 min for active chlorine determination following standard procedures [40].

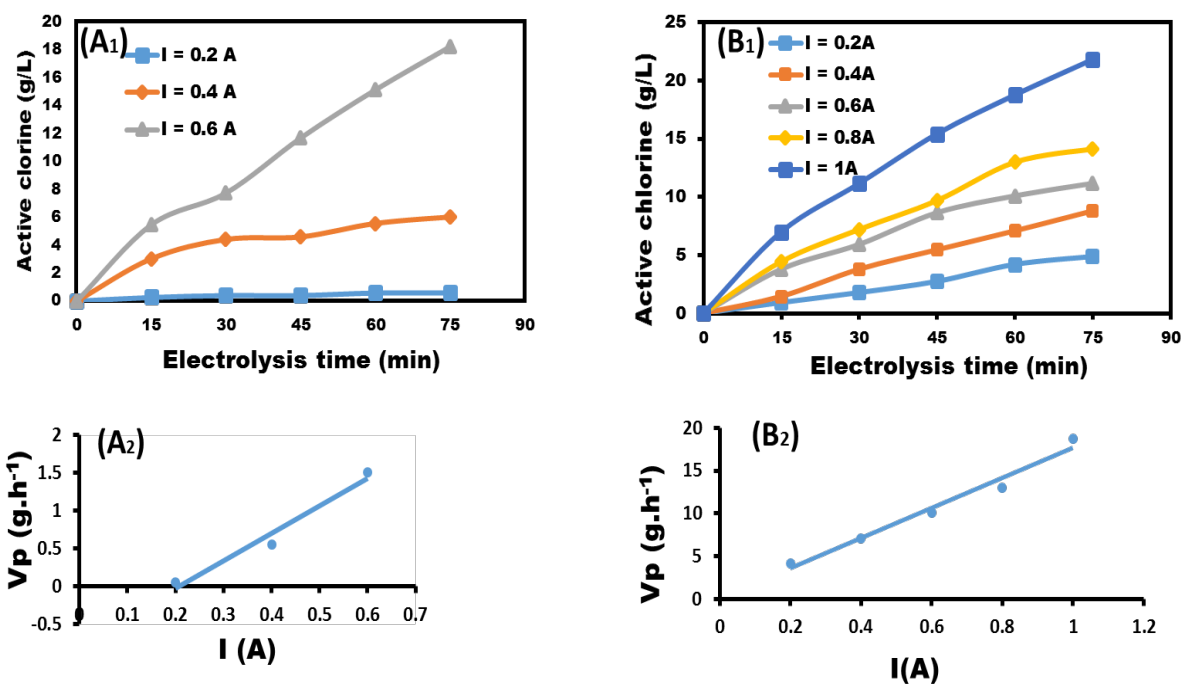
### 2.5. Active chlorine determination

Active chlorine is the sum of the concentrations of the species  $\text{NaClO}$ ,  $\text{Cl}_2$  and  $\text{ClO}^-$  in a sodium hypochlorite solution. It is determined by reacting liquid bleaches with iodides and treating iodine produced with a measured excess of thiosulfate solution previously standardized calorimetrically [41].

## 3. Results and Discussion

### 3.1. Kinetic active chlorine production

The kinetics active chlorine production was carried out on two anodes: graphite (Figure 2.A<sub>1</sub>) and the elaborated anode (Figure 2.B<sub>1</sub>). Thus, the results are represented on the following figures.



**Figure 2:** Kinetic active chlorine production (A<sub>1</sub>) on C anode and (B<sub>1</sub>) C/MnO<sub>2</sub> anode, Active chlorine rate dependence on current intensity at pH 10 (initial chloride concentration 300g/L, electrolyte volume 150 cm<sup>3</sup>) (A<sub>2</sub>) on C anode and (B<sub>2</sub>) on C/MnO<sub>2</sub> anode.

In the pH range of 6-9, active chlorine is mainly formed from  $\text{HClO}$  and  $\text{ClO}^-$  [42]. Under our operating conditions, active chlorine is the term used to denote the sum of hypochlorous acid ( $\text{HClO}$ ) and the hypochlorite anion ( $\text{ClO}^-$ ).

Results show that the evolution of the active chlorine concentration according to time for imposed intensities, an intensity of 0.2A, it is very weak although increasing. On the other hand, for an intensity of 0.4A, the active chlorine concentration increases, time also increases for the sixtieth minutes of electrolysis then tends towards a stage. Whereas for an intensity of 0.6A, the concentration grows with the increase in time. Figure 2.B<sub>1</sub> shows that the concentration of active chlorine grows with time. This is for all the imposed intensities. Nevertheless, it is significant to notice that for an intensity of 0.2A, the production of active chlorine is higher for C/MnO<sub>2</sub> anode. The increase of active chlorine production could be due to an increase of material conductivity because the manganese dioxide deposited on graphite increases the conductivity of the material. We also note that after sixty minutes of electrolysis, the active chlorine concentration does not more have the same speed of active chlorine concentration this for all the intensities.

This state which seems to be stationary can be attributed to a deficiency in chloride ions. This with a time, or by a certain existing balance between the rate of production ( $V_p$ ) and the rate of decomposition ( $V_d$ ) of active chlorine. During electrolysis, we saw the continuous consumption of chloride ions. Given that the conductivity of the brine is a function of the ionic species present in the solution, and active chlorine concentration according to the conductivity. The impoverishment of the medium in chloride ions will have as consequence the reduction of active chlorine concentration. This is because the conductivity of the solution was reduced Marc-Andre [11]. The second assumption must also be taken into account, because during electrolysis, the temperature of water increases, which is favorable to the decomposition of active chlorine [9]. The decomposition reaction of the active chlorine carries away the formation of chlorates ions and hydrochloric acid in solution. This reaction is also called parasitic reaction because the consumption of active chlorine gives two, not desired species (eq.7).



When the two anodes are used into the same operating conditions, the optimal time of active chlorine production is sixty minutes. For the C anode, an intensity of 0.6A and C/MnO<sub>2</sub> anode an intensity of 1A. From these results, the kinetics of active chlorine production ( $V_p$ ) was given according to the different current intensities between 0.2 and 0.6A for the C anode and 0.2 and 1A for the C/MnO<sub>2</sub> anode for a chloride ions concentration of 300g L<sup>-1</sup> and a time of 60 min.

From the two graphs above (Figure 2.A<sub>2</sub> and Figure 2.B<sub>2</sub>), the production rate of active chlorine increases almost linearly with the current intensity. The slope of each graph Fig 2.A<sub>2</sub> and Fig 2.B<sub>2</sub> respectively indicate a production rate of 3638.8 mg.h<sup>-1</sup>.A<sup>-1</sup> (C) and 17504 mg.h<sup>-1</sup>.A<sup>-1</sup> (C/MnO<sub>2</sub>).

Kraft and co-workers [10], studied the kinetics of active chlorine production starting from an electrolytic cell using iridium oxide electrode and current intensities (2, 5, 10 and 20A). The electrolyte was a demineralized water containing 150mg L<sup>-1</sup> in chloride ions concentration. They obtained a production speed of 60 mg h<sup>-1</sup>.A<sup>-1</sup>. Likewise, Marc-Andre used the same electrode, same current intensities, but the brine concentration was 1800 mg L<sup>-1</sup> and he obtained a production speed of 1565 mg h<sup>-1</sup>.A<sup>-1</sup>. These different values are far from that obtained in the present study. This difference could be mainly due to the initial concentration of chloride ions but also the current intensities used in the three studies. In the present study, a concentration of 300 g L<sup>-1</sup> was used compared to Kraft and co-workers, [10] which was of 150mg L<sup>-1</sup> and to Marc-Andre [11] which was of 1820 mg L<sup>-1</sup>. Indeed, the increase of chloride ions concentration in the brine carry away a larger dispersion of the ions and thereafter the conductivity of the solution. Thus, when the conductivity of the saturated solution of NaCl increases, the chlorine active production increases [26]. If we consider the electrolysis definition which is “a process whereby electrical energy is transformed into chemical energy in order to carry out chemical reactions”, the intensity of the current plays a significant role in a process of electrolysis. Indeed, the current intensity increases, the hypochlorite production increases which has an important consequence on the increased rate of active chlorine production kraft et al. [10].

### 3.2. Comparative study of the generation of active chlorine from both materials

The comparison between the two anodes was carried out on their kinetics of active chlorine production. During the study of the kinetics of active chlorine production, C anode could not work with intensities higher than 0.6A, because the formation of a dark yellow solution characteristic of chlorates ions in solution is observed. The characteristic test of the presence of the hypochlorite ions realized in this solution obtained from the aniline solution did not reveal any blue coloration, which proves the absence

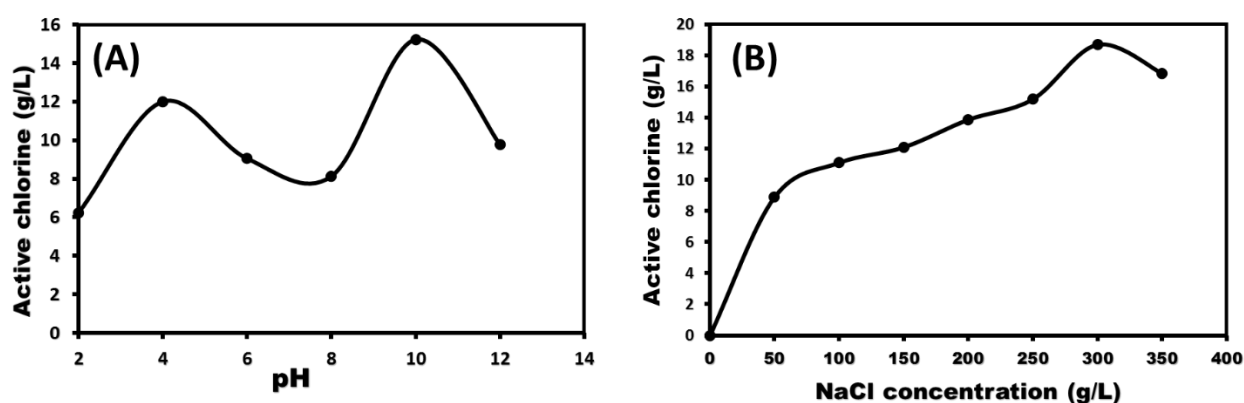
of sodium hypochlorite in solution. On the other hand, C/MnO<sub>2</sub> anode can work beyond 0.6A but for an intensity of 1.2A the same problems are present. Thus, the rate of production of active chlorine with C/MnO<sub>2</sub> anode was 17504 mg h<sup>-1</sup>A<sup>-1</sup> which is higher than the production rate of active chlorine with C anode (3638.8 mg h<sup>-1</sup>A<sup>-1</sup>).

These results show that the C/MnO<sub>2</sub> anode work at high intensities than the C anode, these high intensities have as role to carry away an active chlorine production efficiency and a rise in temperature during electrolysis. The increase of active chlorine temperature also carries away the decomposition of formed chlorine. These results corroborate those of certain authors following the example [1,43,44].

All these remarks, we can say that the electrode material elaborated has a corrosion resistance and has the good electrochemical properties for sodium hypochlorite production. Thus, in the following study, we will use only C/MnO<sub>2</sub> anode for an optimization of parameters during the electrolysis.

### 3.3. Study of some electrolysis parameters

The study is undertaken in order to follow the evolution of active chlorine production according to the NaCl concentration, the results are presented on the following Figure:



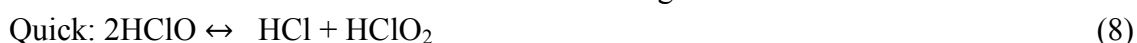
**Figure 3:** A) Effect of pH on active chlorine production and B) Effect of NaCl concentration on active chlorine production

The analysis of Figure 3.A reveals that the sodium hypochlorite under our operating conditions requires a basic pH to be obtained in great quantities. With a pH ranging from 2 to 8, the quantity of sodium hypochlorite produced is fairly weak. This report could be explained by at acid pH, the chlorine gas is released in great quantities and it will escape from the medium and consequently the hydroxide ions present in the medium will react with the quantity of chlorine available. For basic pH in particularly 10 and 12, the maximum active chlorine production is obtained with a pH of 10. If we always consider our assumption, this result could be justified by the quantity of released chlorine that reacts with the hydroxide available in great quantities from where, increase in the bleach production. At pH 12, the active chlorine concentration falls again. This report is justified by the hydroxide ions being in majority in the medium. The quantity of chlorine gas available during the process is weak to react with all the quantity of hydroxide ions. Thus, the value retained for the continuation of our study is a pH of 10. Therefore, the optimum maximum values of the hypochlorite generation were obtained at pH 10.

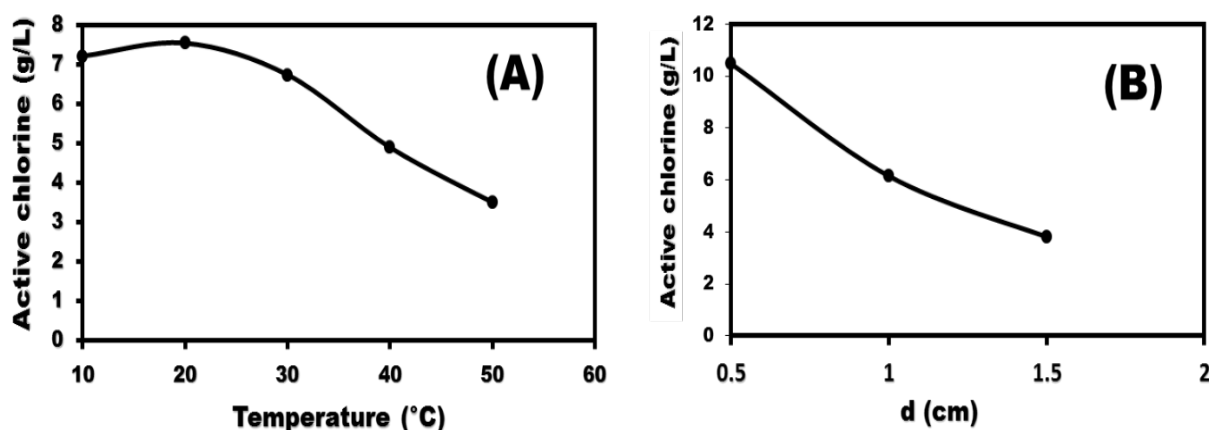
Figure 3.B shows the effect of NaCl concentration on active chlorine production. The results obtained show that active chlorine concentration increases with an increase in [NaCl] up to a maximum (18.7085g L<sup>-1</sup> is [NaCl]=300g L<sup>-1</sup>). Above this NaCl concentration, the active chlorine concentration decreases. Thus, we can notice that the recommended concentration for our study is 300g L<sup>-1</sup> but above this, the active chlorine falls. This decrease of hypochlorite production for high NaCl concentrations could be

due to the fact that all the  $\text{Cl}^-$  ions present in solution were not transformed into hypochlorite. It could be also explained by above  $300\text{g L}^{-1}$ , the cell potential decreases from where the electric power provided by the D.C supply power is insufficient to be able to further oxidize the chloride ions in the medium. Likewise, this remark could be also justified by the solution being too saturated that carry away a deposit of salt on electrode surface reducing their active area [26].

During this study, we showed the effect of temperature and of the inter-electrode spacing on active chlorine production. Temperature plays an important role in the electrogeneration of chlorinated species using  $\text{C}/\text{MnO}_2$  electrode. Figure 4.A shows the results of the effect of temperature on active chlorine generation. The figure presents two stages. The first stage is included between 10 and  $20^\circ\text{C}$ , the active chlorine concentration is strictly increasing. During the second stage which is between 20 and  $50^\circ\text{C}$ , the active chlorine concentration decreases considerably with the increase in temperature. Indeed, we can mention that the increase in temperature during this process carry away the decomposition of active chlorine into chloride and chlorate anions following the reactions:



However, few authors [45] have studied the effect of temperature on the decomposition of hypochlorite ions into chlorate. They showed that as temperature increases, the rate of chlorate ions formation increases. This is for a temperature from  $40^\circ\text{C}$ . Thus, to have a good active chlorine yield, during electrolysis, the use of a thermometer or a bath including/understanding a thermostat is necessary for the temperature control of the electrolytic bath. The temperature of the medium must thus be of  $20^\circ\text{C}$ . These results are in agreements with those of Czarnetzki, [45] and kraft et al, [10] which have suggested to use a temperature lower than  $40^\circ\text{C}$  for the  $\text{NaOCl}$  production.



**Figure 4:** A) Effect of temperature and B) the inter-spacing electrode on active chlorine production

The inter-electrode spacing plays a capital role in an electrochemical process because it has an influence on the effectiveness and production cost. Figure 4.B illustrates the effect of the distance between the anode and cathode on active chlorine production. It is clearly seen that there is of decrease in active chlorine when the inter-electrode spacing increases up to 0.5 cm using  $\text{C}/\text{MnO}_2$  anode.

This observation could be justified by the idea that a small distance between the anode and cathode should support the conversion of chloride ions into hypochlorite since it reduces the ohmic potential drop and increases the current density of the cell. In the same study, Nasser et al. [1] had obtained an inter-electrode spacing of 10 mm. They observed that the active chlorine concentration was high for



short distances and for distances above 20 mm, this concentration falls down. Resistance (R) is given by the formula  $R = \frac{L}{\gamma S}$  with  $\gamma$  conductivity, L the distance between the electrodes and S the area of the electrodes. If the electrode spacing is large, resistance will increase but also the ohmic potential drop (U) in the electrochemical reactor will be high which is given by the formula  $U = R.I$ . Thus, energy (W) is related to current intensity and time (t) by the following formula  $W = U.I.t$ , if the ohmic drop increases, the power consumption also increases.

This consumption of energy has for principal disadvantage the increasing of operational cost of sodium hypochlorite production. Therefore, the optimum maximum values of the active chlorine production were obtained at an inter-spacing of 0.5 cm.

During the study of parameters influencing active chlorine concentration produced by our electrolytic device, the optimum maximum values of parameters selected are presented in the following table.

**Table 2.** Values of parameters selected

Time (min)	Intensity (A)	d (cm)	Temperature (°C)	pH	[NaCl] (g.L <sup>-1</sup> )
60	1	0,5	20	10	300

### 3.4. Production and characterization of sodium hypochlorite

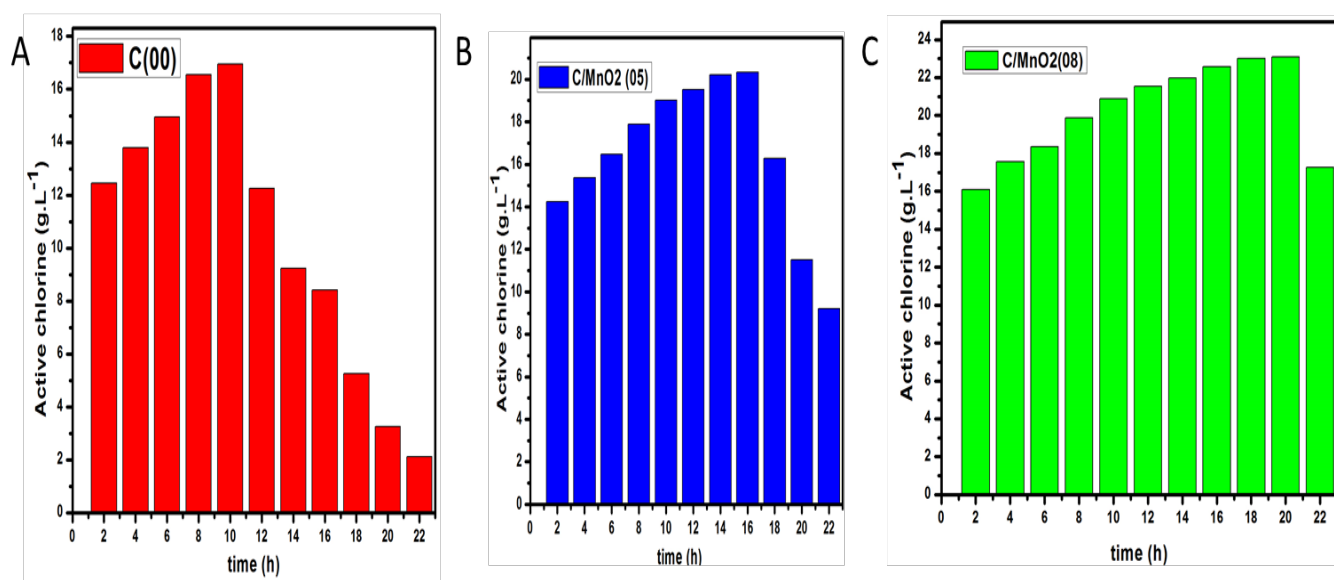
The sodium hypochlorite production during this research tasks was carried out according to the electrochemical process. However, before producing the sodium hypochlorite, it is judicious to know and study the effect of parameters that have a capital role for its production. Indeed, these parameters were studied in the preceding part. The assembly thus carried out enabled us to produce a significant quantity of NaOCl solution which will be characterized thereafter. This unit is simple and very economic. The sodium hypochlorite produced from the electrolysis device conceived previously has been characterized by determining the following parameters: pH, density, colour and its active chlorine concentration. The results are represented in table 3 below.

**Table 3:** Physico-chemical characteristics of sodium hypochlorite solution

pH	density	Color	Active chlorine (g/L)
(11.53± 0.01)	(1.04± 0.02)	Yellow	(18.602±0.002)

### 3.5. Electrochemical characterization: comparative study of electrocatalytic performance of elaborated materials on active chlorine generation

Addition, in electrochemical process, one of the characteristics of electrode material is their lifetime. It is always hazardous to predict the success of an electrode material and in particular the lifetime without having to studying it under real conditions. Different electrodes were developed and were used under real conditions to produce the sodium hypochlorite. Here, three materials denominated C (00) C/MnO<sub>2</sub> (05) (five layers) and C/MnO<sub>2</sub> (08) (eight layers) have been studied in order to evaluate the time that each material works in the same conditions to generate active chlorine (I=0.6A, d=0.5cm, pH 10, temperature 20°C, [NaCl]=300g L<sup>-1</sup>). Thus, the time that each material does to produce active chlorine was identified when the high active chlorine concentration was recorded. Graphite works correctly until ten hours after his activity decreases. According Fig 5.B. C/MnO<sub>2</sub> (05) works correctly until 16 hours after their activity decreases.



**Figure 6:** Electrochemical activity of A) C (00), B) C/MnO<sub>2</sub> (05) and C) C/MnO<sub>2</sub> (08)

Fig 5.C shows C/MnO<sub>2</sub> (08) works correctly until 20 hours after their activity decreased. These figures show that the number of oxide coating deposited on the surface of graphite is proportional to the lifetime of the elaborated anode. Indeed, in this study, the elaborate anode C/MnO<sub>2</sub> (having 08 manganese dioxide layers) has the highest lifetime (20 hours). However, the lifetime of our electrodes materials is improved. This can be due to the fact that the manganese oxide was good deposited and adheres well on the surface of graphite. Given that the release of chlorine is carried out in an acid medium, this result proves that the elaborated anode has a property to better fight against the attacks in acid medium.

## Conclusion

The aim of this work was to produce a sodium hypochlorite solution from recycled graphite as material of anode. Thus, C/MnO<sub>2</sub> electrode has been prepared by the sol-gel process from manganese oxide on graphite substrate from used batteries, then characterized and applied for the sodium hypochlorite production. The results showed that MnO<sub>2</sub> films have been synthesized by the sol-gel process and deposited on graphite substrate. A study of some electrolysis parameters was achieved. Results indicated that C/MnO<sub>2</sub> electrode is cheaper than dimensional stable anode and is higher anti-corrosion than C electrode. Also, C/MnO<sub>2</sub> electrode is more efficient in generating sodium hypochlorite than the C electrode in sodium chloride solution and the rate of active chlorine production using C/MnO<sub>2</sub> was 17504 mg.h<sup>-1</sup> A<sup>-1</sup> compared to 3638.8 mg.h<sup>-1</sup> A<sup>-1</sup> using C electrode so, the C/MnO<sub>2</sub> anode is more efficient than C anode. The results have also revealed that for a sodium hypochlorite production (active chlorine 1.82%), the use of an intensity of 1A, a concentration of 300 g L<sup>-1</sup>, a pH 10, an inter-electrode spacing of 0.5cm, a time of electrolysis 60 min and a temperature from approximately 20°C are necessary. The coating of recycled graphite from batteries could be a good alternative to enhance the activity of graphite substrate during electrochemical processes.

## Acknowledgments

The authors wish to thank the Department of Chemistry, Faculty of Science, University of Ngaoundere, for all the help provided to complete this project.

## References

1. N.A. Ghalwa, H. Tamos, M. Elaskalni, A. Rhman, E. Agha, Generation of sodium hypochlorite (NaOCl) from sodium chloride solution using C/PbO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes, *International Journal of Minerals, Metallurgy and Materials*, 19 (2012) 561–566. <https://doi.org/10.1007/s12613-012-0596-0>
2. L.N. Fesenko, I. V. Pchel'nikov, R. V. Fedotov, Analysis of Economic Efficiency of Production of Low-Concentrated Sodium Hypochlorite by Direct Electrolysis of Natural Waters, *IOP Conf. Ser. Mater. Sci. Eng.* 262 (2017) 236-243. <https://doi.org/10.1088/1757-899X/262/1/012185>
3. J. Hastie, D. Bejan, M. Teutli-León, N.J. Bunce, Electrochemical methods for degradation of Orange II (sodium 4-(2-hydroxy-1-naphthylazo)benzenesulfonate), *Ind. Eng. Chem. Res.* 45 (2006) 4898–4904. <https://doi.org/10.1021/ie060310b>
4. M. Saleem, Biofouling management in the cooling circuit of a power industry using electrochemical process, *J. Chem. Soc. Pakistan.* 33 (2011) 295–304.
5. R. D. Tegua, G. B. Noumi, J. L. Akoulah, Domga, Indirect electrochemical degradation of methyl orange dye on graphite bifunctional electrode. *International Journal of Applied Research*, 6 (1) (2020) 01-13. DOI: <https://doi.org/10.6084/m9.figshare.12161202>
6. B. Yang, Y.X. Li, J. Song, Indirect anodic oxidation applied for treatment of simulated wastewater containing cationic red X-grl and disperse red 3B, *J. Water Reuse Desalin.* 7 (2017) 197–204. <https://doi.org/10.2166/wrd.2016.213>
7. K. Asokan, K. Subramanian, Design of a Tank Electrolyser for In-situ Generation of NaClO, Proceedings of the World Congress on Engineering and Computer Science Vol I WCECS 2009, San Francisco, USA I (2009) 20–23.
8. M. Mokoena, L. Mudau, M. Mokgobu, M. Mukhola, The Use of Sodium Hypochlorite at Point-of-Use to Remove Microcystins from Water Containers, *Toxins.* 13 (2021) 1-8.
9. S. Luciana. M. Tomazinho, Flares Baratto-Fihlo. Jao B. Pereira L. Gabardo M. 2021. Biocompatibility of the 8.25 % sodium hypochlorite solution in endodontics: an in vivo study. *Journals.* 12, 3. 56-63. <https://doi.org/10.1002/jmet.23706>
10. A. Kraft, M. Stadelmann, M. Blaschke, D. Kreysig, B. Sandt, F. Schro, J. Rennau, Electrochemical water disinfection Part I: Hypochlorite production from very dilute chloride solutions, *Journal of Applied Electrochemistry.* 29 (1999) 861–868.
11. Marc-André Bureau. Stabilisation et traitement électrochimique des boues d'épuration municipales et industrielles, Thèse: Université du Québec. (2004) 47-60
12. H. Ha, K. Jin, S. Park, K. Lee, K.H. Cho, H. Seo, H. Ahn, Y.H. Lee, K.T. Nam, Highly Selective Active Chlorine Generation Electrocatalyzed by, *J. Phys. Chem. Lett.* 10 (2019) 1226–1233. <https://doi.org/10.1021/acs.jpcelett.9b00547>
13. M. Portarapillo, M. Muscetta, A. Benedetto, R. Andreozzi, Risk analysis of sodium hypochlorite production process, *Chemical Engineering Transactions.* 82 (2020) 49-54. <https://doi.org/10.3303/CET2082009>
14. C. Hummelgård, R.K.B. Karlsson, J. Bäckström, S.M.H. Rahman, A. Cornell, S. Eriksson, H. Olin, Physical and electrochemical properties of cobalt doped (Ti,Ru)O<sub>2</sub> electrode coatings, *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* 178 (2013) 1515–1522. <https://doi.org/10.1016/j.mseb.2013.08.018>
15. F.J.R. Zambrano, Développement d'un Procédé d'Élimination de l'Arsenic en Milieu Aqueux, associant Électrocatalyse et Filtration, ph.D. Thesis, University of grenoble. (2012) 127-132.

16. G. Sotgiu, D. Montanaro, M. Orsini, E. Petrucci, Manganese-Containing Mixed Oxide Electrodes as Anode Materials for Degradation of Model Organic Pollutants, *Chemical Engineering Transactions*. 57 (2017) 1639-1644. <https://doi.org/10.3303/CET1757274>
17. S. Ferro, A. De Battisti, Electrocatalysis and Chlorine Evolution Reaction at Ruthenium Dioxide Deposited on Conductive Diamond, *J. Phys. Chem. B*. 106 (2002) 2249-2254. <https://doi.org/10.1021/jp012195i>
18. G. Sotgiu, M. Foderà, F. Marra, E. Petrucci, Production and characterization of manganese oxide-based electrodes for anodic oxidation of organic compounds, *Chem. Eng. Trans.* 41 (2014) 115–120. <https://doi.org/10.3303/CET1441020>
19. J.D. Houck, V.S. Amar, R. V. Shende, Mesoporous nanocomposites of Mn and Ti oxides for supercapacitors, *TechConnect Briefs 2018 - Adv. Mater.* 2 (2018) 75–78.
20. J. Yan, Z. Fan, T. Wei, Z. Qie, S. Wang, M. Zhang, Preparation and electrochemical characteristics of manganese dioxide/graphite nanoplatelet composites, *Journal of Materials Science*. 151 (2008) 174–178. <https://doi.org/10.1016/j.mseb.2008.05.018>
21. A.T. George, R. Ganesan, T. Thangeeswari, Redox Deposition of Manganese Oxide Nanoparticles on Graphite Electrode by Immersion Technique for Electrochemical Super Capacitors, *Indian Journal of Science and Technology*, 9 (2016) 1–7. <https://doi.org/10.17485/ijst/2016/v9i1/>
22. N.H. Jawad, S.T. Najim, Removal of Methylene Blue by Direct Electrochemical Oxidation Method Using a Graphite Anode, *IOP Conf. Ser. Mater. Sci. Eng.* 454 (2018) 0–9. <https://doi.org/10.1088/1757-899X/454/1/012023>
23. B. Jiang, J.E. Soc, B. Jiang, T. Muddemann, U. Kunz, G. Silva, H. Bormann, M. Niedermeiser, D. Haupt, O. Schl, Graphite/MnO<sub>2</sub> and MoS<sub>2</sub> Composites Used as Catalysts in the Oxygen Reduction Cathode of Microbial Fuel Cells, *J. Electrochem. Soc.* 164 (2017) 1-9. <https://doi.org/10.1149/2.0801714jes>
24. P. Hou, L. Dong, L. Cai, Z. Chen, Manganese dioxide nanosheets : from preparation to biomedical applications, *Biomedical journal*. 8 (2019) 1-8.
25. M. Xu, S. Bao, Nanostructured MnO<sub>2</sub> for Electrochemical Capacitor, Energy Storage in the Emerging Era of Smart Grids, Prof. Rosario Carbone (Ed.), ISBN: 978-953-307-269-2, InTech, Available from: [http://www.intechopen.com/books/energy-storage-in-the-emerging-era-of-smart-grids/nanostructured-MnO<sub>2</sub>-for-electrochemical-capacitor](http://www.intechopen.com/books/energy-storage-in-the-emerging-era-of-smart-grids/nanostructured-MnO2-for-electrochemical-capacitor), (2010) 252-278.
26. R. De Marco, G.A. Crespo, A. Cornell, Selective Hydrogen Evolution on Manganese Oxide Coated Electrodes: New Cathodes for Sodium Chlorate Production, *ACS Sustainable Chem. Eng.* 7 (2019) 12170–12178. <https://doi.org/10.1021/acssuschemeng.9b01279>
27. Domga, G.B.Noumi. Domga Richard, J.B. Tchatchueng, Study of Some Electrolysis Parameters for Chlorine and Hydrogen Production Using a New Membrane Electrolyzer, *Int. J. Chem. Eng. Anal. Sci.* Vol. 2 (2017) 1–8.
28. A.N. Subba Rao, V.T. Venkatarangaiah, Metal oxide-coated anodes in wastewater treatment, *Environ. Sci. Pollut. Res.* 21 (2014) 3197–3217. <https://doi.org/10.1007/s11356-013-2313-6>
29. A. Chen, X. Zhu, J. Xi, H. Qin, Z. Ji, Ultra-high oxidation potential of Ti/Cu-SnO<sub>2</sub> anodes fabricated by spray pyrolysis for wastewater treatment, *J. Alloys Compd.* 683 (2016) 501–505. <https://doi.org/10.1016/j.jallcom.2016.05.075>
30. N.A.A. Ghany, S. Meguro, N. Kumagai, K. Asami, K. Hashimoto, Anodically deposited Mn-Mo-Fe oxide anodes for oxygen evolution in hot seawater electrolysis, *Nippon Kinzoku Gakkaishi/Journal Japan Inst. Met.* 68 (2004) 447–455. <https://doi.org/10.2320/matertrans.44.2114>
31. X. Liu, C. Chen, Y. Zhao, B. Jia, A Review on the Synthesis of Manganese Oxide Nanomaterials

- and Their Applications on Lithium-Ion Batteries, *Journal of Nanomaterials*. 11 (2013) 1-7. <http://dx.doi.org/10.1155/2013/736375>
32. S.S. Falahatgar, F.E. Ghodsi, Annealing Temperature Effects on the Optical Properties of MnO<sub>2</sub> : Cu Nanostructured Thin Films, *Int. J. Nanosci. Nanotechnol.* Vol 12 (2016) 7–18.
  33. R.N. Reddy, R.G. Reddy, Sol-gel MnO<sub>2</sub> as an electrode material for electrochemical capacitors, *J. Power Sources*, 124 (2003) 330–337. [https://doi.org/10.1016/S0378-7753\(03\)00600-1](https://doi.org/10.1016/S0378-7753(03)00600-1)
  34. S. Ching, S.M. Hughes, T.P. Gray, E.J. Welch, Manganese oxide thin films prepared by nonaqueous sol-gel processing: Preferential formation of birnessite, *Microporous Mesoporous Mater.* 76 (2004) 41–49. <https://doi.org/10.1016/j.micromeso.2004.07.031>
  35. Z. Durmus, B.Z. Kurt, A. Durmus, Synthesis and Characterization of Graphene Oxide/Zinc Oxide (GO/ZnO) Nanocomposite and Its Utilization for Photocatalytic Degradation of Basic Fuchsin Dye, *ChemistrySelect*. 4 (2019) 271–278. <https://doi.org/10.1002/slct.201803635>
  36. N.R.T. Shahrabi, Optimization the selectivity property of graphene oxide modified dimensionally stable anode (DSA) produced by the sol–gel method, *J. Sol-Gel Sci. Technol.* 10 (2019) 1-8. <https://doi.org/10.1007/s10971-019-04966-9>
  37. X. Li, C. Shao, J. Yu, K. Zhu, Preparation and Investigation of Nickel – Antimony co-doped Tin Oxide Anodes for Electro-catalytic Oxidation of Organic, *Pollutions*, 14 (2019) 205–218. <https://doi.org/10.20964/2019.01.23>
  38. C.K. Lin, K.H. Chuang, C.Y. Lin, C.Y. Tsay, C.Y. Chen, Manganese oxide films prepared by sol-gel process for supercapacitor application, *Surf. Coatings Technol.* 202 (2007) 1272–1276. <https://doi.org/10.1016/j.surfcoat.2007.07.049>
  39. S. Chen, J. Zhu, Q. Han, Z. Zheng, Y. Yang, X. Wang, Shape-Controlled Synthesis of One-Dimensional MnO<sub>2</sub> via a Facile Quick-Precipitation Procedure and its Electrochemical Properties, 4 (2009) 77-83. <https://doi.org/10.1021/cg900223f>
  40. Rodier Jean, Bernard Legube, Nicole Merlet. L'analyse de l'eau : eaux naturelles, eaux résiduaires, eaux de mer, chimie, physicochimie, microbiologie, biologie, interprétation des résultats, Paris (France), Dunod, 2009; ISBN 978-2-10-054179-9, 1384-1395.
  41. V.T. Lieu and G.E. Kalbus, Analysis of hypochlorite in commercial liquid bleaches by coulometric titration, *J. Chem. Educ.*, 52 (1975) 335-345.
  42. J. Yi, Y. Ahn, M. Hong, G. Kim, N. Shabnam, B. Jeon, B. Sang, H. Kim, applied sciences comparison between OCl<sup>-</sup> -injection and in situ electrochlorination in the formation of chlorate and perchlorate in seawater, *Appl. Sci.* 9 (2019) 1-12. <https://doi.org/10.3390/app9020229>
  43. M. Saleem, B. Chakrabarti, B. Hasan, On site electrochemical production of sodium hypochlorite disinfectant for a power plant utilizing seawater, *Int. J. Electrochem. Sci.*, 7 (2012) 3929 - 3938.
  44. A. Kraft, M. Blaschke, D. Kreysig, B. Sandt, F. Schroè Der And J. Rennau J. Part II : Hypochlorite production from potable water, chlorine consumption and the problem of calcareous deposits, *Journal of Applied Electrochemistry* 29 (1999) 895–902.
  45. L.R. Czarnetzki, F.M. Everhaerts, Aspects of electrochemical production of hypochlorite and chlorate, *Technische Universiteit Eindhoven*. 26 (1989) 154-188. <https://doi.org/10.6100/IR316966>

(2021) ; <http://www.jmaterenvirosci.com>