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Generation of a Chlorinated Disinfectant from Sodium Chloride Electrolysis

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The production of sodium hypochlorite in situ is useful for the disinfection of water in aqueducts located in areas of difficult access; published studies on the optimum parameters of electrolysis for the production of sodium hypochlorite are carried out at laboratory scale. The paper includes the results of the evaluation of a prototype for the production of 22 liters of hypochlorite solution, the optimum operating parameters were identified through a design of experiments; the electrodes of the equipment are made of graphite with an anodic surface of 1868 cm2, the retention times, current intensities and the initial concentration of chlorides were varied. The iodometry technique was used to quantify the hypochlorite ion, obtaining 4.46 $g.l^{-1}$ in conditions of 120 min, 80 A and 150 g $Cl^{-}.l^{-1}$, with an energy efficiency of 42.58 $mgCl2.(kJ)^{-1}$. According to the results in the statistical analysis of variance correlate the influence of each variable in the hypochlorite production and energy efficiency of the process.

1. Introduction

Access to safe drinking water has been limited in rural areas, consumption of untreated water leads to severe microbiological diseases in sensitive populations (Rehman, 2018), these diseases are usually caused by pathogens (Lin et al., 2022) that will have caused the death of more than 2 million people by 2016 (UN-Water, 2016). To mitigate this problem, disinfection methods including electrolysis have been developed, especially in developing countries (Al-weshahi, 2009). This technology requires an electrolyte, inside which electrodes are placed forming electric poles, favoring the reactivity of the system (Ronco et al., 2007). The most commonly used substances for water purification are oxidizing substances containing chlorine, which are found in different phases, gaseous in the form of Cl2, ClO, and liquid as NaClO and HClO (Zaviska et al., 2012). Another disinfection alternative includes solid compounds such as calcium chloride, which acts as an oxidizing substance forming calcium hypochlorite (World Health Organization, 2020). The synthesis of oxidizing substances via electrolysis has proven to be an efficient disinfection method for the inactivation of different microorganisms (Eryilmaz and Palabiyik, 2013), one of the most influential variables is current intensity, a variable associated with the flow of electrons through a conductor for a given time, according to Nurul et al, the current intensity is proportional to the concentration of sodium hypochlorite, in their research they were able to obtain 10.45 mg.l-1 of hypochlorite by evaluating the intensity in an interval from 0 to 5 A (Nurul Aniyyah et al., 2022). The concentration of the electrolyte, also has a significant effect because it favors the conductivity within the system and the electron transfer in the system, Ghalwa et al., mention that sodium chloride has the best performance in the process of sodium hypochlorite synthesis (Ghalwa et al., 2012). Time has been shown to be proportional to the concentration of active chlorine produced, however, the temperature of the system can increase, favoring the volatility of active chlorine (Al-Hamaiedeh, 2013). In the same study, he determined that the optimum time to obtain hypochlorite was 60 minutes.

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Other parameters studied are the spacing between the plates that make up the electrode (Ronco et al., 2007), materials (Nurul Aniyyah et al., 2022) and voltage (Hsu et al., 2017). In the present investigation, the performance of a batch electrolytic system for the production of a sodium hypochlorite disinfectant solution using graphite electrodes in a volume of 22 liters is evaluated.

2. Materials and Methods

Electrolysis system used

The electrolysis reactor was constructed including a control board allowing to modify current intensity and graphite electrodes with an anodic area of 1865 cm^2, spacing of 8 mm between four graphite sheets of 4 mm thickness, the electrodes are immersed in the tank containing an electrolyte in solution with a capacity of 22 liters, the concentration of chlorides varied according to the design of experiments.

Design of experiments evaluated

Chloride concentration (X_1), current intensity (X_2) and time (X_3) were used as independent variables to be studied within a design of experiments, using as levels 100 to 150 g $Cl^-.l^{-1}$, 30 to 120 minutes and 70-80 Amps. The design of experiments was evaluated using Statgraphics Centurion XVI software, in order to identify the levels that maximize the production of sodium hypochlorite, the effect of each variable and the mathematical model that describes the behavior of the process.

Free chlorine characterization methods

The determination of the final sodium hypochlorite concentration in each experiment was quantified using the iodometric method 4500 Cl-B standard methods, ASTM D2022 (Baird et al., 2017) and for chlorides the technique used was Mohr ASTM D1411-09.
Energy efficiency of the sodium hypochlorite production process.
Faraday's law allows calculating the energy efficiency due to the fact that it explains that the ratio between masses released by the electrolyte solution, by the current intensity modifies the ions present in the solution (Khalid et al., 2018; Saha and Gupta, 2017).
Equations 1 and 2 explain energy efficiency analysis:

$$Total\ chlorine\ [mg] = Chlorine\ experimentally\ produced\ (mg.l^{-1}) * Electrolysis\ volume\ (l) \quad (1)$$

$$Energy\ efficiency\ \ mg\ Cl_2.kJ^{-1} = \frac{Total\ chlorine\ (mg)}{Electrical\ energy\ consumed\ (kJ)} \quad (2)$$

3. Results

Table 1 shows the combinations for the execution of the design of experiments, and the results on hypochlorite concentration and energy efficiency.

Table 1: Design of experiments, hypochlorite production and energy efficiency.

Experiment	X_1	X_2	X_3	Hypochlorite concentration [$g.l^{-1}$]	Energy efficiency [$mgCl_2.(kJ)^{-1}$]
1	150	70	120	4.30	47.00
2	100	80	120	4.37	41.72
3	100	80	30	2.10	80.39
4	100	70	30	1.43	62.63
5	100	70	120	3.38	36.89
6	150	70	30	1.94	84.84
7	150	80	30	2.52	96.25
8	150	80	120	4.42	42.58

Chlorides concentration $mg.l^{-1}$ (X_1), Current intensity (A) (X_2) y time (minutes) (X_3)

The effect of the variables described in Figure 1, Pareto diagram, shows that the variables evaluated are statistically significant and have a proportional relationship with the concentration of sodium hypochlorite, with time being the variable with the greatest influence and chloride concentration the factor with the least incidence.

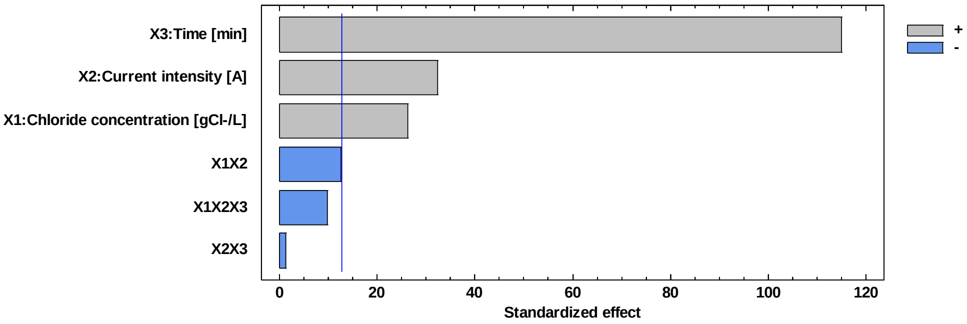

Figure 1. Pareto diagram for hypochlorite production.

Baydum and Sarubbo (2022) reported that chloride concentration in the system increases disinfectant production using an 8-liter electrolyte (Baydum and Sarubbo, 2022). Current intensity was investigated by Hsu et al. using titanium electrodes coated in a 12-liter solution, concluding that intensity has a direct relationship with active chlorine generation (Hsu et al., 2015). In 2012, Salem evaluated the effect of time in an 8-liter electrochemical reactor, obtaining higher hypochlorite concentrations after 50 minutes and after 3 hours this variable is no longer relevant in the process(Saleem et al., 2012).

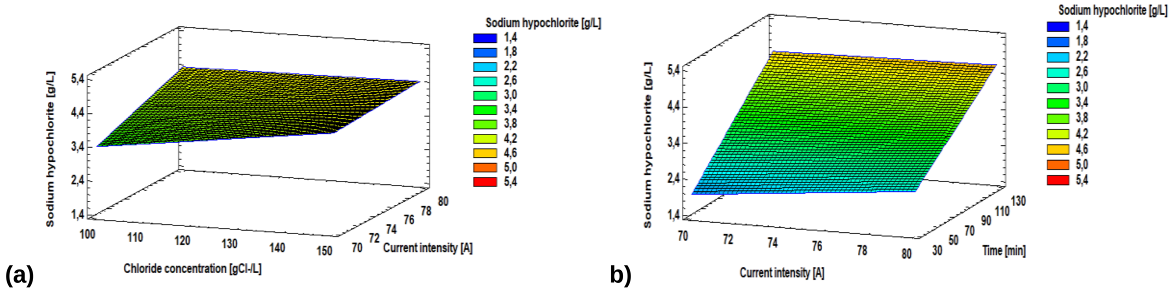

Figure 2: Response surface for hypochlorite production a) As a function of concentration and time. b) As a function of current intensity and time.

Fitted mathematical model for hypochlorite production:

$$Sodium\ hypochlorite\ [g.l^{-1}] = -1.92175 - 0.01257X_1 + 0.0266X_2 - 0.12535X_3 + 0.000297333X_1X_2 + 0.00122333X_1X_3 + 0.00198667X_2X_3 - 0.0000163111X_1X_2X_3 \quad (3)$$

Figure 2 describes the behavior of hypochlorite production as a function of concentration and time; in addition, the current intensity versus time. The analysis indicates that the maximum concentration reached by the system is produced at 80 Amperes, an initial chloride concentration of 150 g $Cl^-.l^{-1}$ and an electrolysis time of 120 minutes, obtaining 4.46 $g.l^{-1}$ of hypochlorite solution.

The response surface analysis indicates that the disinfectant obtained is significantly favored at high chloride concentrations, high current intensities and prolonged times. In addition, the mathematical model has a 99.99% fit and describes the hypochlorite production as a function of the variables proposed in the factorial design of experiments 2^3, it is possible to compare the performance of the prototype with other electrochemical systems, such as that of Baydum, who was able to generate 3.5% m/m of hypochlorite, in 1 hour, with an initial concentration of 4% m/m of chlorides (Baydum and Sarubbo, 2022), In Varigala's research, 120 $mg.l^{-1}$ of active chlorine was obtained in a 22-liter electrolysis cell with recirculation, the conductivity of the system was 2000 µS cm^{-1}(Varigala et al., 2021). Hsu et al., used a volume of 12 liters and 10 Volts, achieved 9 $g.l^{-1}$ of disinfectant (Hsu et al., 2015), while, Salem obtained 6 $g.l^{-1}$ of hypochlorite in a volume of 8 liters (Saleem et al., 2012).

Graphite proved to be efficient in the production of oxidizing solutions, compared to other materials, in the study of graphite electrodes with cerium oxide 0.3 $g.l^{-1}$ of hypochlorite was produced (Alvarado-Ávila et al., 2022), in diamond electrodes the residual concentration of chlorine was 1.6 g.l-1 (Lacasa et al., 2013).

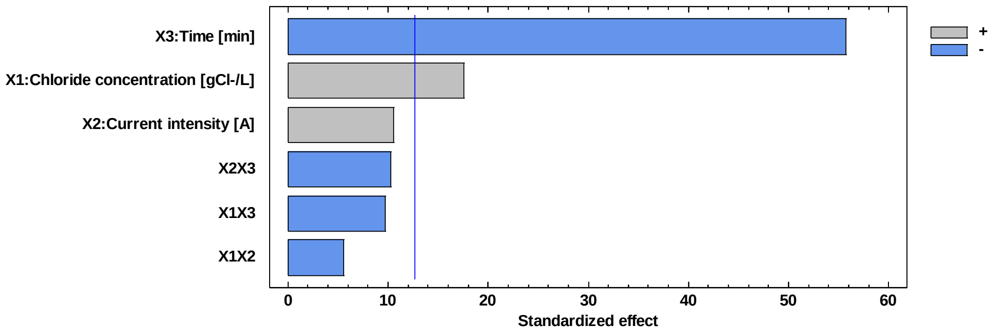

Figure 3. Pareto diagram, energy efficiency in the production of hypochlorite by the prototype.

In the analysis of energy efficiency, the Pareto result rules out the combined interaction of the three variables; however, the variable with the highest interaction in energy efficiency is time X_3, followed by current intensity X2 (Figure 3).

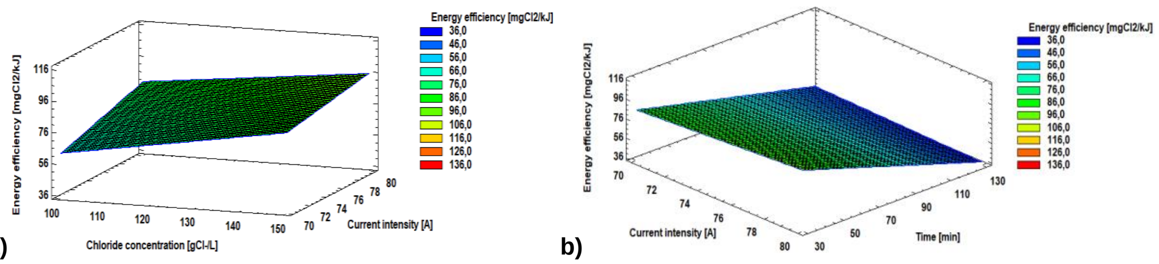

Figure 4: Response surface of energy efficiency in hypochlorite production, a) As a function of concentration and current intensity. b) As a function of current intensity and time.

The response surface (Figure 4) shows that the energy efficiency is significantly affected in relation to time and current intensity. The highest efficiency obtained was 96.25 $mgCl_2.(kJ)^{-1}$ at 30 minutes, 80 Amps and 150 g Cl-.l^{-1}, this is due to the fact that in the shortest operation time a higher efficiency is generated because the energy consumption is reduced, However, the maximum hypochlorite concentration is not achieved, for 30 minutes the concentration was 2.52 $g.l^{-1}$ of disinfectant agent.

Mathematical model of energy efficiency for hypochlorite production in the prototype:

$$Energy\ efficiency\ [mgCl_2.kj^{-1}] = -257.017 + 1.64987X_1 + 3.89367X_2 + 1.13856X_3 - 0.0157X_1X_2 - 0.00302222X_1X_3 - 0.0159222X_2X_3 \quad (4)$$

The mathematical model obtained in Equation 4 describes the behavior of the energy efficiency of the prototype as a function of the three variables manipulated in the process, the adjusted mathematical model has an R2 of 99.97%, It is comparable with results of Hsu, Naderi and Nasseri and Khalid, established that by increasing the operation time and the electric potential (proportional to the current intensity) the energy efficiency is reduced (Hsu et al., 2017; Khalid et al., 2020; Naderi and Nasseri, 2020).

The maximum efficiency obtained for Hsu was 45 mg Cl2.$(kJ)^{-1}$ at 200 min and 6 Volts (Hsu et al., 2017). Similar results have been obtained using a 200 ml system, at conditions of 63.42 g.l-1 chlorides, 15.73 Volts and 15 minutes, where the energy efficiency was 42 mg $Cl_2.(kJ)^{-1}$(Naderi and Nasseri, 2020). The current efficiency evaluated in 1.7 liter anodic and cathodic cells was 4.08 % using titanium electrodes, at 0.68 Amps and 5 Volts (Khalid et al., 2018), indicating that it can achieve higher efficiency with increasing current intensity.

Energy consumption as a function of residual total oxidants (TRO) has been used as an indicator of electrolysis efficiency. In the research of Jung et al. a 300 ml cell and coated titanium electrodes were used, under conditions of 200 $mA.(cm^2)^{-1}$ and 5 $g.l^{-1}$ chlorides, the energy consumption of was 5 $E10^{-3}$ Wh/TRO (Jung et al., 2016) indicating that the amount of energy required for the production of a disinfectant solution is low enough to produce a disinfectant solution. The results obtained allow establishing that electrolytic reactors can respond to the growing need for water disinfection in resource-poor areas due to their low energy consumption and high production yield.

4. Conclusions

The evaluation of the effect of the variables in the production of hypochlorite in a 22 liter reactor, built with graphite electrodes, concludes with the significant statistical correlation between the current intensity and chloride concentration in the medium, allowing to establish that the maximum concentration of hypochlorite was 4.46 $g.l^{-1}$, at conditions of 120 minutes, 80 amperes and 150 $g.l^{-1}$ of initial chlorides.
The energy efficiency analysis showed that the equipment during its maximum efficiency of 96.25 $mgCl_2.(kJ)^{-1}$, during 30 minutes was not able to obtain the maximum concentration, thus foreseeing the need to study the optimization of energy efficiency in electrolysis equipment with graphite electrodes.

Nomenclature

A – amperes, A
cm^2 – square centimeters, cm^2
Cl_2 – molecular chlorine
Cl^- – chloride ion
ClO_2 – chlorine dioxide
$g.l^{-1}$– grams per liter
gCl^-l^{-1}– grams of chlorides per liter
H_2– hydrogen molecular
HClO –hypochlorous acid
kJ – energy consumed
l – liter of cell electrolysis
$mgCl_2.(kJ)^{-1}$ – milligrams of free chlorine per kilojule
$mg.l^{-1}$ -milligram per liter
ml – milliliters
min – minutes
mm – millimeter
NaClO – sodium hypochlorite
TRO - oxidantes totales residuales
Wh - watts-hour
X_1 - chloride concentration in the medium, gCl^-l^{-1}
X_2 – current intensity, A
X_3 – time, min
$\mu S.cm^{-1}$ – microsiemens per centimeter

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