Factors Influencing the Formation of Sodium Hydroxide by an Ion Exchange Membrane Cell

Jimmy Aurelio Rosales-Huamani 1,*†, Juan Taumaturgo Medina-Collana 2†, Zoila Margarita Diaz-Cordova 2† and Jorge Alberto Montaño-Pisfil 2†

1 Multidisciplinary Sensing, Universal Accessibility and Machine Learning Group, National University of Engineering, Lima 1533, Peru
2 Faculty of Chemical Engineering National University of Callao, Juan Pablo II 306 Avenue, Bellavista, Callao 07011, Peru; jtmcdac@unac.edu.pe (J.T.M.-C.); zdiazcz@unac.edu.pe (Z.M.D.-C.); jamontanop@unac.edu.pe (J.A.M.-P.)
* Correspondence: jrosales@uni.edu.pe; Tel.: +51-1-381-5639
† These authors contributed equally to this work.

Abstract: The present study aimed to evaluate the factors that influence the formation of sodium hydroxide (NaOH) by means of an electrolytic cell with ion exchange membranes. To achieve this experiment, the NaOH production cell had to be designed and built inexpensively, using graphite electrodes. The operational parameters in our study were: initial NaOH concentration, applied voltage, and temperature. All experiments were carried out using model NaCl solutions with a concentration of 40 g/L for 150 min. The results of the experiment were that the NaOH concentration, conductivity, and pH presented an increasing linear trend with the electrolysis time. Finally, it was possible to obtain the efficiency level of the electric current in our investigation, which was an average of 80.2%, that indicated good performance of the built cell.

Keywords: sodium hydroxide; electrolytic cell; ion exchange membranes

1. Introduction

The chlor-alkali industry uses brine and electricity for chemical production, like chlorine, hydrogen, and sodium hydroxide [1,2]. Chlorine manufacture made by chlor-alkali electrolysis is the second-biggest industrial electrochemical process, with more than 70 million tons of \( \text{Cl}_2 \) produced yearly and requires more than 200 TWh of power supply [3].

Chlorine and sodium hydroxide are the top 10 chemicals produced worldwide, and are the raw materials for a huge number of products used in everyday life. Soda is employed in the making of detergent soap, fabric, paints, glass, and ceramics [4], in addition to its usage in pH regulation and acid neutralization, caustic soda is employed as a reactant in the production of many chemicals [5].

By applying direct-current (DC) electricity to a pair of electrodes (positive and negative) submerged in aqueous sodium chloride (NaCl), hydrogen (\( \text{H}_2 \)), chlorine (\( \text{Cl}_2 \)), and sodium hydroxide (NaOH, often referred to as “alkali”) are simultaneously produced [6].

Chlor-alkali production requires a lot of electricity consumption that usually represents 40–50% of process expenses in operation; power consumption depends on different technologies used in production [7]. Most of the chlor-alkali is made by electrolyzing a brine (NaCl) solution that requires mercury, diaphragm, and membrane technologies. However, the chlor-alkali process generates polluting emissions that causes a serious impact on the environment, and people. Thus, development of more efficient and cleaner processes is required [8].

European countries willingly accepted to change their mercury cell technology due to environmental protection laws and huge power costs. The Minamata Convention on...
Mercury began to be applied on 16 August 2017, and this agreement requires less usage and emissions of mercury; at the same time, it claims for more research and development of technologies that do not use mercury.

The production of chlorine and sodium hydroxide by membrane technology was introduced into industrial practice in the mid-1970s as an alternative to mercury diaphragm and cathode methods, and in 1990 about 20% of NaOH and Cl₂ were produced by membrane technology. At the end of 2016, membrane technology in Europe accounted for approximately 66% of chlorine production. Lately, membrane technology has been the top preferred process in Europe, having more than 83% of the chlorine yield in the EU 27 and EFTA countries in 2018 [9]. The global reaction in electrolytic cells is shown in Equation (1):

\[ 2\text{H}_2\text{O}^{(l)} + 2\text{NaCl}^{(aq)} \rightarrow 2\text{NaOH}^{(aq)} + \text{Cl}_2^{(g)} + \text{H}_2^{(g)}. \]  

(1)

The top challenge that the chlor-alkali industry has to face is finding efficient processes that use less power supply, and to produce maximum yield. Considering the currently high costs of electric power, the benefits of the industry mainly depend on such new technologies [10].

Mercury cells were widely used in the United States; they represented 20% of full chlor-alkali yield in the 1980s, but they have become banned because of mercury pollution laws, including the National Emissions Standards for Hazardous Air Pollutants [11,12]. The process consists of two principal steps, the electrolyzer and the decomposer [4].

A simplified diagram of the production process is shown in Figure 1. Then the brine enters the electrolytic cell from the side near the anode, and the diluted brine exits the other end of the cell. At the anode, which is the positively charged electrode, the chloride ion oxidizes to chlorine gas. The reaction is shown in Equation (2).

Oxidation at the anode:

\[ 2\text{Cl}^-{(aq)} \rightarrow \text{Cl}_2^{(g)} + 2e^- . \]  

(2)

Reduction at the cathode: At the cathode the sodium ion is reduced and produces an amalgam with the mercury, and the reaction is shown in Equation (3):

\[ \text{Hg}^{(l)} + \text{Na}^{+{(aq)}} + 2e^- \rightarrow \text{NaHg}^{(l)}. \]  

(3)

The sodium amalgam then reacts with the water in a separate reactor called a decomposer where gaseous hydrogen, ordinary hydroxide solution, and mercury are produced, which is recirculated to the electrolytic cell. The reaction is shown in Equation (4):

\[ 2\text{NaHg}^{(l)} + 2\text{H}_2\text{O}^{(l)} \rightarrow 2\text{NaOH}^{(aq)} + 2\text{Hg}^{(l)} + \text{H}_2^{(g)}. \]  

(4)

At the outlet of the decomposer, the sodium hydroxide holds a 50% purity.

![Figure 1. Mercury cell process.](image)

The mercury cell process is known to produce the highest-quality caustic soda, but its major drawback is that its products have some mercury present [13].
Because of incidents of mercury contamination in Minamata and Niigata in 1972, Japan began changing to membrane cells, and today there are mercury-free cells operating [4,14]. Membrane cell technology is a clean, feasible technique for the reuse of these wastes, but simultaneously, it relies on many aspects, like brine purity, flow density, and pH factor [15].

The anode and cathode are isolated by an ion exchange membrane. This membrane avoids the transit of chlorine ions (negatively charged) but permits sodium ions (positively charged) to move freely through the cell [11]. In this process, sodium chloride brine is added to the cell through the anode compartment [16], while the water moves along the cathode compartment. The continuation of the reactions occur at the anode and the cathode [3]. These are shown in Equations (5) and (7).

Anode:

\[ 2Cl^-_{(aq)} \rightarrow Cl_2(g) + 2e^- . \]  

(5)

In addition to the release of chlorine gas, the evolution of unwanted oxygen gas is mainly due to the oxidation of water:

\[ 2H_2O(l) \rightarrow 4H^+_{(aq)} + O_2(g) + 2e^- . \]  

(6)

In the cathode, water is electrolyzed into \( OH^- \) and hydrogen gas.

Cathode:

\[ 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-_{(aq)}. \]  

(7)

A cation-exchange membrane divides the anode and cathode solutions, but is permeable to \( Na^+ \). The sodium ions merge with hydroxyl ions and form sodium hydroxide [17]. The reaction is shown in Equation (8).

\[ Na^+_{(aq)} + OH^-_{(aq)} \rightarrow NaOH_{(aq)}. \]  

(8)

The full electrolysis reaction of \( NaCl \) to \( NaOH \) and \( Cl_2 \) can be seen below [18], and the reaction is shown in Equation (9).

\[ 2NaCl_{(aq)} + 2H_2O(l) \rightarrow Cl_2(g) + 2NaOH_{(aq)} + H_2(g). \]  

(9)

In this method, sodium chloride solution is poured into the cell through the anode compartment, while the water moves through the cathode compartment. The by-product of hydrogen is frequently employed to supply heat by combustion [13]. In addition, other usages can be found in the future, such as use in fuel cells [19]. A typical membrane electrolysis cell is shown in Figure 2. On the anode, chloride is oxidized to chlorine gas, and then dissolved in the anolyte [20].

![Figure 2. Membrane cell process.](image)

Table 1 shows the main advantages and disadvantages of mercury cells and membranes, adapting and modifying from [2].
Table 1. Advantages and drawbacks of electrolytic chlor-alkali technologies

| Technology | Advantages | Drawbacks |
|------------|------------|-----------|
| Mercury    | Low standard requirements for raw material solution. | Mercury utilization. |
|            | Top product quality. | High power demand. |
| Membrane   | Low power demand. | High expenses of environmental procedures. |
|            | Safety raw materials. | Top quality standards for raw material solution. |
|            | Good NaOH quality. | Poor chlorine quality. |
|            |                        | Elevated thermic energy consumption. |
|            |                        | High expensive of membranes. |

Because the capital investment, operating costs, and power consumption expenses are lower than that of diaphragm and mercury technology [21], membrane cell technology is used in all new chlor-alkali plants. Another technique for NaOH production is by the diaphragm cell, which operates at a lower voltage than mercury cells, the discharge is free from mercury problems and requires less brine purity than membrane cells, which reduces the brine pretreatment charge [22]. Because of the separated formation of Cl₂ and NaOH, the mercury cell generally produces a purer product than do the diaphragm and membrane cells but with higher energy consumption because of the increased cell voltage for electrolysis [23].

The main objective of our study was to evaluate the operational factors that influence the reached concentration of sodium hydroxide in the chlor-alkali membrane cell using experiments with synthetic brine. The initial NaOH concentration, electric potential, and temperature factors were studied in a laboratory scale experiment.

The present work is divided up as follows: in Section 2 the experimental procedure to be used is shown, in Section 3 we present the results, and finally, in Section 4 the conclusions obtained from the present study are presented.

2. Experimental Procedure

2.1. Materials

The chemicals used in our research were analytically pure, such as sodium chloride (NaCl), sodium hydroxide (NaOH), and hydrochloric acid (HCl). For the analysis, deionized water was used, supplied by a Chiwatec Water Treatment Technology brand for electroionization equipment. The glass materials used were burettes to carry out the titration operation. A heating system with an rpm and temperature indicator was also used.

2.2. Chemical Analysis

The changes in the sodium hydroxide concentration were determined by an acid-base titration with a calibrated solution of HCl of 0.01 N using phenolphthalein as an indicator. The NaOH concentration was calculated using Equation (10).

\[ C_{NaOH} = \frac{C_{HCl} \times V_{HCl}}{V_{NaOH}} \]  

\( C_{HCl} \text{(mol/l)} \): concentration of the calibrated HCl solution.  
\( V_{HCl} \text{(l)} \): volume of the acid.  
\( V_{NaOH} \text{(l)} \): volume of NaOH used for titration.

The conductivity of the hydroxide was evaluated using the ADW 310 conductimeter, and the pH of the NaOH using the AD 12 pH meter.

2.3. Characteristics of the Ion Exchange Membrane

A cation exchange membrane type FTCM-E (Fumatech Bwt GmbH, Bietigheim-Bissingen, Germany) [24] was used in this study. According to the manufacturer, this is a high-durability membrane for electrolysis application. The membrane has a thickness
of (0.17–0.19 mm) and a very low specific area resistance (2.5–3.5 $\Omega \cdot \text{cm}^2$) at 0.5 M NaCl and 25 $^\circ$C and an ion exchange capacity of 1.5–1.8 meq/g. For good functioning of the membrane, it is first immersed in distilled water for a period of 24 h and then in a 0.25 N aqueous solution of NaCl for the other 24 h.

When conducting the experiments, there are factors that could affect the membranes. The paper [21] mentioned that the application of depolarized cathodes with oxygen in the cell affects the membrane, reducing the consumption of electrical energy in the chlor-alkali process. Then in [25] it was mentioned that the membrane is susceptible to being contaminated with ions such as $\text{Mg}^{2+}$ and $\text{Cd}^{2+}$ in the brine, which shortens its useful life. Regardless, [26] mentioned that calcium and magnesium in precipitated form decrease efficiency and increase energy consumption. Furthermore, the high pressure gases in the electrolytic cell exacerbate the degradation of the membrane.

2.4. Electrolytic Cell

An electrolytic cell was constructed with compartments divided by a 90 cm$^2$ fumartch-type cationic membrane (FTCM-E) [24] section, as shown in Figure 3, where the volume of the cells was 200 ml for each compartment, electrodes of 10 cm $\times$ 10 cm graphite, and the space between the electrode and the membrane was 5 mm. The reactor was connected to a power supply with a voltage of 30 volts and a current intensity of 5 A.

The anolyte compartment was connected to a 1 L container containing a NaCl solution and the catholyte compartment was connected to a 1 L capacity sodium hydroxide reservoir. Both compartment reservoirs were connected to a pump with silicone rubber tubing.

The electrolysis cell is of the filter press type was built with acrylic material on which a cationic membrane with a mesh-shaped turbulence promoter was assembled and secured with eight cross bars with nuts to avoid leaks, mixing, or spilling of the liquid. Rubber gaskets were placed between each frame and membrane, which allows for sealing and maintenance of the uniform distribution of flow within the cells, and two acrylic plates were also placed at the ends, each one with an inlet and outlet for the flow of solutions. The external acrylic plates allowed the system to be kept under pressure, providing stability and resistance to the set of cells. Two 1.5 cm-thick acrylic frames were used, into which the electrodes were inserted, each with an inlet and outlet through which the sodium hydroxide and sodium chloride solutions entered.

![Figure 3. Membrane cell process.](image)

2.5. Procedure

The experiences were made in a batch system for the formation of sodium hydroxide. The sodium chloride solution enters the cell through the anode compartment through a submerged pump from a container containing 1.0 L capacity. Silicone tubing was used to
recirculate the brine solution evenly, while dilute sodium hydroxide solution was fed to the cathode side by means of a submerged pump from 1.0 L capacity.

Electrolysis occurs when a direct current passes through anodes and cathodes inside the electrolyte electricity solution. During electrolysis, \( \text{Cl}_2 \) gas is absorbed by a 2 M sodium hydroxide solution in a 2 L container, and hydrogen is simultaneously generated at the cathode and collected in a similar manner. After each experiment the setup was rinsed completely with distilled water, and the electrolysis run time was 150 min. The feed tanks were heated with jacketed heaters and a digital thermometer monitored their temperature. A direct-current power supply was also used.

In our experiment, the operating time was 150 min. This was not an optimal value chosen. In Franco et al. [27] mentioned that the potential and electric current in an industrial chlor-alkali membrane electrolyzer is a tool used to evaluate the progress of its operating efficiency over time. The authors also analyzed the performance of an industrial electrolyzer as a function of its service time for approximately 8 years, recording variations in cell potential and current density.

3. Results and Discussion

As a hypothesis in our research, we tried to verify how certain operating parameters affected the concentration of NaOH produced in the membrane cell. In our experiments, these parameters were: cell temperature, initial concentration of NaOH (N), and the applied electric potential. How these evaluated parameters have a significant influence on the conductivity and pH of the NaOH solution in 150 min was also verified. For all the experiments carried out, the concentration of the NaCl solution was kept constant at 40 g/L, and the feed flow of the NaOH and NaCl solution at 400 mL/min.

Figure 4 shows the effect of the variation of the initial concentration of NaOH at three different concentration values, such as 0.01 N, 0.05 N, and 0.1 N. Operating conditions were maintained at 6.5 V and 35 °C.

![Figure 4](image.png)

**Figure 4.** Effect of NaOH Concentration at 6.5 V and 35 °C.

Figure 5 shows the effect of the voltage variation applied to the initial concentration of NaOH at three different voltage values, such as 5.0 V, 6.5 V, and 7.5 V. Operating conditions were maintained at 25 °C and 0.01 N.
Figure 5. Effect of applied voltage on NaOH concentration at 25 °C and 0.01 N.

Figure 6 shows the effect of the temperature variation on the initial concentration at three different temperature values, such as 25 °C, 35 °C, and 45 °C. Operating conditions were maintained at 6.5 V and 0.05 N.

With these three experiments carried out, it was possible to verify how these operational parameters affected the concentration of NaOH produced and how they also increased linearly with time.

To verify the influence of the previously evaluated parameters on conductivity and pH, the following experiments were performed. Figures 7 and 8 show the evolution of electrical conductivity and pH over time at different conditions of concentration, temperature, and voltage.
In both experiments, we found a linear trend between electrical conductivity and pH with time of electrolysis.

To evaluate the influence of current intensity on NaOH production, experiments were carried out at an electric potential of 5.0 V, 6.5 V, and 7.5 V at 25 °C and an initial concentration of 0.05 N of NaOH. This is shown in Figure 9.

In this experiment we appreciate that in the first few minutes the intensity of the current increased, then its value changed, and finally stabilised over time.

Current efficiency is an important parameter in determining the operating range of an electrolytic cell. The current efficiency was calculated based on the concentrations of the final base. It is defined as the ratio of the electrical charge used for the transport of ion to the total electrical current charge [28], and is calculated by (11):

$$
\varepsilon = \frac{zF(C_f - C_i)V_i}{n \int_0^t i dt} \times 100\% \quad (11)
$$

$\varepsilon$: current efficiency.
$F$: Faraday constant (96,500 A.s/ mol).
$C_f, C_i$: initial and final concentration of the NaOH solution mol/L.
$i$: electric current intensity (A).
$\eta$: number of cell pars.
$V_i$: volume of recirculated NaOH solution.
$z$: electric charge.
The efficiency for each experiment was carried out at 25 °C, an initial concentration of 0.01N NaOH, a workflow of 400 mL/min, and a NaCl concentration of 40 g/L. This current efficiency is presented in Table 2.

| Voltage (V) | NaOH Produced (N) | Efficiency |
|------------|-------------------|------------|
| 5.0        | 0.05              | 85.3%      |
| 6.5        | 0.24              | 77.6%      |
| 7.5        | 0.33              | 77.8%      |

The result of the current efficiency obtained can be compared with other work carried out under different operating conditions. In Savari et al. [29] used a flow of 66 mL/min, a NaCl concentration of 58.5 g/L, and a commercial NAFION-117 membrane [30] was also used. In this work, an average efficiency was obtained that was quite similar to our work, equal to 80.1% at different operating conditions. In both cases, the same operating time of 150 min was used. This information is shown in Table 3, adapting and modifying from [29].

| Voltage (V) | NaOH Produced (N) | Efficiency |
|------------|-------------------|------------|
| 10.7       | 0.04              | 93.8%      |
| 16.5       | 0.08              | 60.6%      |
| 23.7       | 0.05              | 85.8%      |

We can conclude that the average efficiency in our research was 80.2%, which represents a good efficiency of our experimental equipment, and a greater quantity of NaOH was also produced. Regarding the economic considerations of our cell to carry out the experiment, we mentioned that the design and construction cost an average of 500 dollars. This cost can be considered quite low compared to other similar research.

4. Conclusions

In the present study, the operating parameters of the electrolysis of a model sodium chloride solution on the formation of NaOH were studied, using graphite electrodes and a cation exchange membrane.

The results obtained in our experiment indicate that the best operating conditions are found at a cell voltage of 7.5 V, an initial concentration in the cathodic compartment of
0.1 N NaOH, and a temperature of 45 °C. Obtained in each case were the highest values of the NaOH concentration after 150 min.

In addition, the average electric current efficiency was obtained at the conditions of 25 °C, initial NaOH concentration of 0.01 N, and voltages of 5.0 V, 6.5 V, and 7.5 V. Its average value was 80.2%.

The applied tension was identified as one of the most significant variables to reach the concentration of sodium hydroxide. This is mainly due to its direct relationship with the consumption of electrical energy. Finally, we mention that the results of the study show that the electrochemistry of the membrane process offers a method that is an interesting economic alternative for the synthesis of NaOH.

As future work, we hope to study other operational variables, such as: sodium hydroxide flux, types of membranes and their durability, electrode materials in relation to specific energy consumption, and process efficiency.

Author Contributions: Conceptualization, J.A.R.-H.; methodology, J.A.R.-H.; software, J.T.M.-C.; validation, J.A.M.-P.; formal analysis, Z.M.D.-C.; investigation, J.T.M.-C.; writing—original draft preparation, J.A.R.-H.; writing—review and editing, J.T.M.-C.; supervision, Z.M.D.-C.; project administration, J.A.M.-P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not Applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hou, M.; Chen, L.; Guo, Z.; Dong, X.; Wang, Y.; Xia, Y. A clean and membrane-free chlor-alkali process with decoupled Cl2 and H2/NaOH production. Nat. Commun. 2018, 9, 1–8. [CrossRef] [PubMed]
2. Lakshmanan, S.; Murugesan, T. The chlor-alkali process: Work in progress. Clean Technol. Environ. Policy 2014, 16, 225–234. [CrossRef] [PubMed]
3. Schmittinger, P.; Florkiewicz, T.; Curlin, L.C.; Lüke, B.; Scannell, R., Navin, T.; Zelfel, E.; Bartsch, R. Chlorine, Ullmann’s Encyclopedia of Technical Chemistry; Wiley-VCH: Weinheim, Germany, 2006.
4. O’Brien, T.F.; Bommaraju, T.V.; Hine, F. History of the chlor-alkali industry. In Handbook of Chlor-Alkali Technology; Springer: Berlin/Heidelberg, Germany, 2005; pp. 17–36.
5. Kurt, C.; Bittner, J. Sodium Hydroxide in Ullmann’s Encyclopedia of Industrial Chemistry; Wiley-VCH: Weinheim, Germany, 2003.
6. Lee, D.Y.; Elgowainy, A.; Dai, Q. Life cycle greenhouse gas emissions of hydrogen fuel production from chlor-alkali processes in the United States. Appl. Energy 2018, 217, 467–479. [CrossRef]
7. García-Herrero, I.; Margallo, M.; Onandía, R.; Aldaco, R.; Irabien, A. Environmental challenges of the chlor-alkali production: Seeking answers from a life cycle approach. Sci. Total Environ. 2017, 580, 147–157. [CrossRef] [PubMed]
8. Crook, J.; Mousavi, A. The chlor-alkali process: A review of history and pollution. Environ. Forensics 2016, 17, 211–217. [CrossRef]
9. Euro Chlor, Chlor-Alkali Industry Review 2018/2019. Available online: https://www.chlorineindustryreview.com/ (accessed on 27 January 2021).
10. Lima, P.R.; Mirapalheta, A.; dos Santos Andrade, M.H.; Vilar, E.O.; e Silva, C.L.D.P.; Tonholo, J. Energy loss in electrochemical diaphragm process of chlorine and alkali industry—A collateral effect of the undesirable generation of chlorate. Energy 2010, 35, 2174–2178. [CrossRef]
11. Bommaraju, T.V.; Lüke, B.; O’Brien, T.F.; Blackburn, M.C. Chlorine. In Kirk-Othmer Encyclopedia of Chemical Technology; Wiley Online Library: New York, NY, USA, 2000.
12. Mercury Cell Chlor-Alkali Plants: National Emissions Standards for Hazardous Air Pollutants. Available online: https://www.epa.gov/stationary-sources-air-pollution/mercury-cell-chloralkali-plants-national-emissions-standards (accessed on 27 January 2021).
13. Brinkmann, T.; Santonja, G.G.; Schorcht, F.; Roudier, S.; Sancho, L.D. Best available techniques (BAT) reference document for the production of chlor-alkali. Publ. Off. Eur. Union 2014. [CrossRef]
14. Gochfeld, M. Cases of mercury exposure, bioavailability, and absorption. Ecotoxicol. Environ. Saf. 2003, 56, 174–179. [CrossRef]
15. Melián-Martel, N.; Sadhwani, J.; Baez, S.O.P. Saline waste disposal reuse for desalination plants for the chlor-alkali industry: The particular case of pozo izquierdo SWRO desalination plant. Desalination 2011, 281, 35–41. [CrossRef]
16. Simon, A.; Fujioka, T.; Price, W.E.; Nghiem, L.D. Sodium hydroxide production from sodium carbonate and bicarbonate solutions using membrane electrolysis: A feasibility study. Sep. Purif. Technol. 2014, 127, 70–76. [CrossRef]
17. Rabbani, M.; Dincer, I.; Naterer, G. Efficiency assessment of a photo electrochemical chloralkali process for hydrogen and sodium hydroxide production. Int. J. Hydrogen Energy 2014, 39, 1941–1956. [CrossRef]
18. Du, F.; Warsinger, D.M.; Urmi, T.I.; Thiel, G.P.; Kumar, A.; Lienhard V, J.H. Sodium hydroxide production from seawater desalination brine: Process design and energy efficiency. *Environ. Sci. Technol.* 2018, 52, 5949–5958. [CrossRef]

19. Campanari, S.; Guandalini, G.; Coolegem, J.; ten Have, J.; Hayes, P.; Pichel, A. Modeling, Development, and Testing of a 2 MW Polymeric Electrolyte Membrane Fuel Cell Plant Fueled With Hydrogen From a Chlor-Alkali Industry. *J. Electrochem. Energy Convers. Storage* 2019, 16.

20. Mirzazadeh, T.; Mohammadi, F.; Soltanieh, M.; Joudaki, E. Optimization of caustic current efficiency in a zero-gap advanced chlor-alkali cell with application of genetic algorithm assisted by artificial neural networks. *Chem. Eng. J.* 2008, 140, 157–164. [CrossRef]

21. Moussallem, I.; Jörissen, J.; Kunz, U.; Pinnow, S.; Turek, T. Chlor-alkali electrolysis with oxygen depolarized cathodes: History, present status and future prospects. *J. Appl. Electrochem.* 2008, 38, 1177–1194. [CrossRef]

22. Shim, J.H.; Jeong, J.Y.; Park, J.Y. Effects of operating conditions on improving alkali and electrical efficiency in chlor-alkali diaphragm cell. *Int. J. Electrochem. Sci.* 2015, 10, 6338–6347.

23. O’Brien, T.F.; Bommaraju, T.V.; Hine, F. *Handbook of Chlor-Alkali Technology: Volume I: Fundamentals, Volume II: Brine Treatment and Cell Operation, Volume III: Facility Design and Product Handling, Volume IV: Operations, Volume V: Corrosion, Environmental Issues, and Future Developments*; Springer Science & Business Media: Berlin/Heidelberg, Germany, 2007; Volume 1.

24. Membrane. Available online: https://www.fumatech.com/EN/Membranes/ (accessed on 3 February 2020).

25. Bazinet, L.; Araya-Farias, M. Effect of calcium and carbonate concentrations on cationic membrane fouling during electrodialysis. *J. Colloid Interface Sci.* 2005, 281, 188–196. [CrossRef] [PubMed]

26. Madaeni, S.; Kazemi, V. Treatment of saturated brine in chlor-alkali process using membranes. *Sep. Purif. Technol.* 2008, 61, 68–74. [CrossRef]

27. Franco, F.; Prior, J.; Velizarov, S.; Mendes, A. A systematic performance history analysis of a chlor-alkali membrane electrolyser under industrial operating conditions. *Appl. Sci.* 2019, 9, 284. [CrossRef]

28. Zhou, Y.; Yan, H.; Wang, X.; Wang, Y.; Xu, T. A closed loop production of water insoluble organic acid using bipolar membranes electrodialysis (BMED). *J. Membr. Sci.* 2016, 520, 345–353. [CrossRef]

29. Savari, S.; Sachdeva, S.; Kumar, A. Electrolysis of sodium chloride using composite poly (styrene-co-divinylbenzene) cation exchange membranes. *J. Membr. Sci.* 2008, 310, 246–261. [CrossRef]

30. Nafion. Available online: https://www.fuelcellstore.com/membranes/nafion/ (accessed on 3 February 2020).