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Effect of Operating Parameters on the Production of Hydrochloric acid and Sodium Hydroxide by Bipolar Membrane Electrodialysis

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In the present research work, a laboratory-scale bipolar electrodialysis unit (EDBM) for the production of hydrochloric acid and sodium hydroxide was constructed and put into operation. In order to evaluate the effect exerted by the cell operating parameters on both acid and base concentrations, Taguchi metrology with an orthogonal L9 matrix was used. Four factors were selected at three levels, initial sodium chloride concentration (5, 20 and 50 g/L), electrical potential (5, 10 and 15 V), flow rate (400, 600 and 800 mL min^{-1}) and initial acid and base concentration (0 , 0.025 and 0.05 M). Using Minitab analysis, it was determined that the most influential factor on the concentration of hydrochloric acid and sodium hydroxide was the electrical voltage applied to the EDMB cell. The most suitable operating parameter levels to achieve a higher concentration of hydrochloric acid and sodium hydroxide were electrical voltage (15 V), flow rate (400 mL min -1), sodium chloride concentration (50 g/L) and initial concentration of NaOH and HCl (0.05 M). The results reveal that the constructed EDMB prototype has a high capacity to convert inorganic salts into their respective acidic solutions and hydroxides, which constitutes a valuable green technology for industry.

1. Introduction

The chlor-alkali industry is responsible for the world's largest production of sodium hydroxide NaOH (99.5%) through the mercury cell, membrane and diaphragm processes. However, their production presents major environmental problems, as the use of mercury or asbestos leads to significant ecological risks. Therefore, the membrane cell process has gained popularity in the chlor-alkali industry due to its distinct advantages, such as low chemical dosage, absence of secondary contamination and high product yield (Brinkmann et al., 2014). The industrial production of hydrochloric acid requires the synthesis of gaseous hydrogen chloride (HCl) and its subsequent absorption in water to form an aqueous solution. Generally, this process starts with the production of chlorine gas (Cl_2) by electrolysis of brine (sodium chloride), mainly with ion exchange membrane cell technology. However, the high temperatures and pressures associated with the synthesis of HCl gas could produce very unstable conditions leading to an explosion of the reactants. Electrodialysis (ED) in a process using ion exchange membranes, when an electrical potential difference is applied, causes the transport of ions across the membrane. The main components of the ED system include cation exchange membranes (CEM), anion exchange membranes (AEM) and electrodes (anode and cathode at the ends of the cell) (Liang et al., 2024). Electrodialysis with bipolar membrane (EDBM) allows the generation of acid (HX), alkaline substances (MOH) and desalination of a salt solution, under the application of an external current field without the addition of any chemical reagents (Bunani *et al.,* 2017). EDBM has found various applications such as the production of organic acids (Ma et al., 2019) and inorganic (Li et al., 2024) and bases (Song et al., 2021) and in the valorisation of brine (León et al., 2022). The bipolar membrane is composed of an anion exchange layer, a cation exchange layer and an intermediate layer that allows water dissociation (Pärnamäe *et al.,* 2021). Bipolar membranes (EDBM) are not permeable to ions, but promote the dissociation of water, forming hydrogen ions (H^+) and

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hydroxide ions (OH^-) when placed in an electric field (Strathmann, 2010) . Subsequently, the protons and hydroxyl ions generated initiate chemical reactions with other species (anion and cation) present in the aqueous solution, thus producing the acids and bases mentioned above.Electromembrane technologies, such as electrodialysis (ED) and electrodialysis with bipolar membranes (EDBM), have been widely proposed for the treatment and valorisation of concentrated SWRO streams, the so-called brines, which contain NaCl in high concentration and can therefore be considered as hypersaline streams (Reig *et al*., 2016)(Herrero-Gonzalez et al., 2020). New sustainable sources, such as concentrated brines, which are often considered waste, are currently being investigated for the production of sodium hydroxide by electrodialysis with bipolar membranes (EDBM) (León et al., 2024). EDBM technology applied to brine produces acids (HCl) and bases (NaOH) with only two inputs, electrical power and brine. In this way, self-sufficiency of reagents could be achieved (Cassaro *et al.,* 2023).This study focuses on the evaluation of the influence of the operating parameters of the electrodialysis cell incorporating a bipolar membrane on the effect of the resulting concentrations of acids and bases produced, as well as the electrical current efficiency. For its evaluation, a design of experiments was carried out using the Taguchi methodology**.**

2. Materials and Methods

2.1. Chemical products

Chemicals used during the study: hydrochloric acid (HCl), sodium chloride (NaCl), sodium hydroxide (NaOH) and sodium sulphate (Na_2SO_4). All chemicals used are of high purity and of the Merck brand.

2.2. Chemical analysis

Variations in the concentrations of the sodium hydroxide and hydrochloric acid solutions were determined by acid-base titration using standardized solutions of 0.01 N of HCl and 0.01 N of NaOH, using phenolphthalein as the pH indicator. The conductivity values were measured using a portable digital multimeter HQ40D.

2.3. Membranes

Three types of membranes have been used in the tests: cation exchange membranes (CEM), anion exchange membranes (AEM) and bipolar membranes (BM), supplied by the company (Fumatech Bwt GmbH, Bietigheim Bissingen,Germany).To achieve a good performance of the membrane, it was immersed in a 0.25 N NaCl aqueous solution for the other 24 h; the main characteristics of the membranes used in the test are shown in table 1.

Table 1: Characteristic of cation, anion, and bipolar membranes used in the experiments

Membranes	CEM	AEM	BM
Electric resistance ($\Omega.cm^2$)	2.50–3.50	2.50–3.50	<3
Exchange capacity (meq/g)	1.50–1.80	1.40–1.70	…………..
Thickness (mm)	0.17–0.19	0.16–0.18	0.13–0.16

2.4. Bipolar electrodialysis system (EDBM)

A laboratory-scale bipolar membrane electrodialysis apparatus, recently constructed by the author, was used in this investigation.

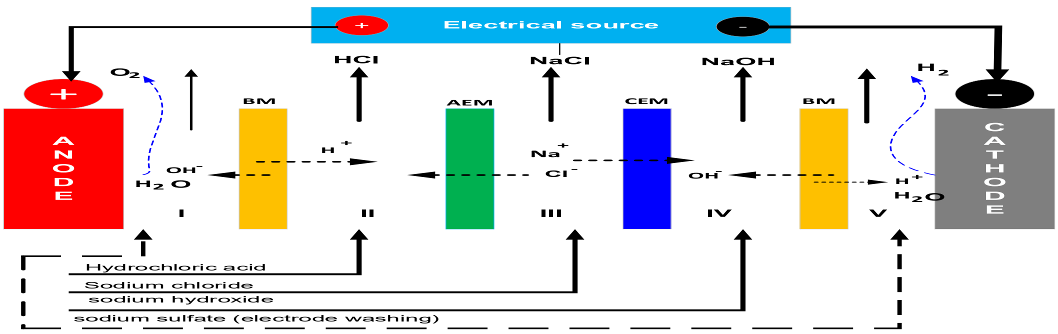

Figure 1: Graphical representation of the arrangement of membranes inside the cell used during the experiment

Figure 1 shows the cell configuration comprising two bipolar membranes, a cationic and an anionic one, corresponding to the notation (BM +CEM +AEM +BM), which allows to obtain three compartments: acid cell(II), basic cell(IV) and salt cell(III). In addition, two electrode cleaning compartments (anodic and cathodic chambers).The effective membrane area was 90 cm^2. The anode and cathode were titanium-based electrode plates of dimensions (5x10 cm). Sodium sulphate was selected as electrode washing solution with a concentration of 0.25 M on the basis of previous studies.

2.5. Photograph of bipolar electrodialysis cell (EDBM)

The electrodialysis cell is constructed analogous to a filter press, the internal architecture contains acrylic plates, on which two ion exchange membranes are placed, together with two bipolar membranes, with their respective turbulence promoters and two electrodes that are fixed to acrylic plates. The external structure consists of two plates that are fixed and secured by eight crossbars with nuts to prevent possible leakage, mixing or spillage of the liquid, as illustrated in Figure 2. The electrolyte reservoirs are connected via segments of blue high-density polyethylene (HDPE) tubing to the pumps, which facilitates continuous recirculation of the solutions.

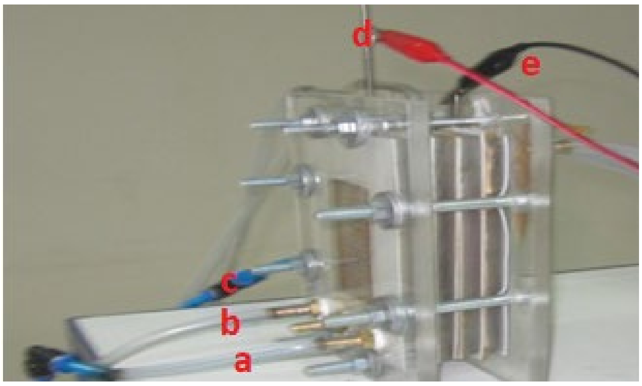

Figure 2: Photography of electrodialysis cell with bipolar membrane. input of solutions, a: acid, b: salt, c: base and d: anode and cathode.

2.6. Experimental procedure

After setting up the experimental apparatus, tightness tests (internal and external) were carried out by circulating demineralized water for two hours between each compartment. Nine experiments operated in batch mode were carried out. The tests were conducted over 240 minutes and samples were drawn from the acid and base tanks every 30 minutes. Initial volumes of 1.0 L were used for the acid (HCl) and base (NaOH) compartment, while 1.5 L were used for the salt (NaCl) compartment. For each test, the concentration of hydrochloric acid and sodium hydroxide, pH and conductivity of each solution were monitored over time, while 5 mL samples were taken every 30 minutes from each tank (acid and base) for analysis. The flow rates of salt, acid, base and electrode rinsing solution for the three test levels were kept at constant values of 400 ± 5 mL/min, 600 ± 5 mL/min and 800 ± 5 mL/min. All tests were repeated twice to verify the repeatability of the EDBM unit's performance.

2.7. Taguchi experimental design

For the trials, the Taguchi L9 orthogonal matrix experimental design was applied. Table 2 shows four identified factors, at three experimental levels for each corresponding variable.

Table 2: Taguchi experimental design variables.

Factor	Notation	Units	Levels		
			low	Medium	High
Sodium chloride concentration	X1	g/L	5	20	50
Flow rate	X2	L/min	400	600	800
Electrical potential	X3	V	5	10	15
Initial concentration of acid and base	X4	M	0	0.025	0.05

Initial sodium chloride concentration, solution recirculation flow rate, electrical potential applied to the cell and initial acid and base concentration were selected as controllable factors, and their effect on the achieved hydrochloric acid, sodium hydroxide concentration. Electrical potential has a significant influence on the rate of water dissociation, as well as ion migration and, consequently, the production of acids and bases. The magnitude of the applied electrical potential must be as high as possible in order to achieve greater acid/base production and minimize energy costs. A higher concentration of NaCl in the feed solution generally increases conductivity and ion flow through the membranes, allowing for greater production of acids and bases. Minitab 19 statistical software was used to perform the experimental design.

3. Results and discussions

The production of sodium hydroxide and hydrochloric acid by EDBM involves several variables that are related to each other. The effect of these variables on the final concentration of acid and base achieved in 240 minutes is reported in Table 3.

Table 3: Factorial design matrix and responses

N° test	X1	X2	X3	X4	Acid (HCl)		Base (NaOH)	
					Concentration (M)	pH of the solution	Concentration (M)	pH of the solution
1	5	400	5	0.0	0.004	4.82	0.0035	9.25
2	5	600	10	0.025	0.07	1.67	0.055	13.14
3	5	800	15	0.05	0.114	1.57	0.094	13.49
4	20	400	10	0.05	0.104	1.29	0.076	13.3
5	20	600	15	0.0	0.013	2.42	0.010	13.10
6	20	800	5	0.025	0.045	2.11	0.024	13.16
7	50	400	15	0.025	0.160	1.32	0.132	13.41
8	50	600	5	0.05	0.058	1.83	0.057	13.14
9	50	800	10	0.0	0.0226	2.67	0.018	12.67

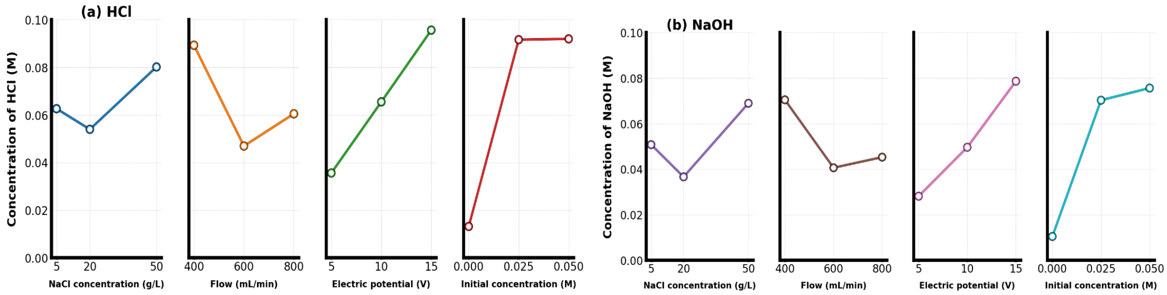

Figure 3: Effect of the operating parameters of the bipolar membrane electrodialysis cell on the concentration of a) hydrochloric acid b) sodium hydroxide

3.1. Voltage effects

Insufficient voltage inhibits the migration of charged ions across the ion exchange membrane and the dissociation of water at the bipolar membrane interface, while excessive voltage can compromise the integrity of the membrane. Figure 3 (a) shows that the concentration of hydrochloric acid and sodium hydroxide increases as the electrical potential applied to the electrodialysis cell. For electrical potentials of 5 and 15 volts, hydrochloric acid concentrations of 0.035 and 0.098 M are achieved.

3.2. Effect of flow

In Figure 3 (a) and 3(b), the increase in flow rate from 600 to 800 mL/min results in an increase in acid and base concentration. This effect can be attributed to the turbulence that occurs at higher flow rates, as it compresses the membrane boundary layer and reduces the resistance to ion transport*(Li et al., 2016).* In addition, the HCl concentration in the acidic chamber increased from 0.048 to 0.06 M when changing the flow rate from 600 mL/min to 800 mL/min and similar changes in NaOH concentration are observed. Excessive flow rates also prevent water molecules from entering the BPM (Yang et al., 2025). Consequently, 400 L/min results in a higher final HCl concentration in the acid chamber than 600 and 800 L/min. The same trend occurs in the formation of base. However, the comparison between flow rates of 600 and 800 L/min in this study showed minor differences in relation to acid and base contractions.

3.3. Effect of sodium chloride concentration (NaCl)

As can be seen in figure 3(b), an increase in the initial salt concentration resulted in a corresponding increase in the final base concentration. For example, it ranged from 0.035 M to 0.070 M NaOH when the initial salt concentration was increased from 20 g/L to 50 g/L.

3.4. Effect of initial concentration of hydrochloric acid (HCl) and sodium hydroxide(NaOH)

The experimental results are shown in Figure 3(a) and (3(b). A higher initial concentration results in a rather advantageous upward evolution in the final concentrations of both acid and base. For example, it ranged from 0.01 M to 0.08 M NaOH when the initial concentration in the NaOH compartment was increased from 0 to 0.05 M. When the initial concentrations of the HCl and NaOH solutions are 0.025 and 0.05 M they favour the EDMB process by increasing their electrical conductivity in both compartments. We observe, on the contrary, that starting the tests in the two compartments, acidic and basic, using distilled water, results in a very slow increase in the concentration of both solutions. Previous studies have reported that the EDBM technique requires an initial concentration of acid and base and the initial concentrations of acid and base did not significantly affect the overall performance and mention, using the minimum initial concentrations of HCl and NaOH, that the EDBM technique requires an initial concentration of HCl and NaOH (López et al., 2025). In Figure 4(a) and 4(b), it is evident that the voltage level significantly influences the concentration and conductivity of the acidic and basic solutions. As the voltage increases, the conductivity of the hydrochloric acid solution rises, ranging from 8 mS.cm^{-1} (5 V) to 48 mS.cm^{-1} (15 V). Previous studies have reported that increasing the current density leads to an increase in the output acid concentration (from 0.68 M to 0.84 M, when the current density is increased from 200 A m^{-2} to 500 A m^{-2}) (Virruso et al., 2023). Likewise, the sodium hydroxide solution increases the conductivity from 4 (5 V) to 26 mS.cm^{-1} (15 V), at a time interval of 240 minutes. Similarly, as the electrical potential increases the pH level decreases for the acidic solution and increases the pH of the basic solution as a function of time as shown in figure 4 (c). The acidic solution decreases from 6.2 to 2.8 pH at 15 volts and the alkaline solution increases from 9.1 to 13.2 pH. Recent research for(Lugo *et al.,* 2025) has indicated that increasing tension improves ion generation up to a threshold at which membrane degradation phenomena occur. In addition, high flow rates facilitate ion transport.

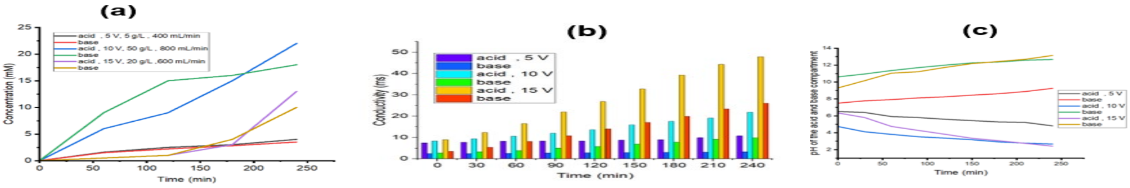

Figure 4: a) Evolution of concentration b) increase in electrical conductivity c) pH evolution of hydrochloric acid and hydroxide solutions as a function of operation time.

4. Conclusions

In this study, a laboratory-scale EDBM unit was examined to investigate the formation of hydrochloric acid and sodium hydroxide, using synthetic feed solutions of sodium chloride. The results indicate that the final acid and base concentration values are a function of the electrical potential applied to the cell, the higher the potential, the higher the final concentration. Similarly, as the electrical potential increases, the pH level decreases for the acidic solution, and the pH of the basic solution rises as a function of time. The factor that contributed least to the variation of acid and base concentrations was the initial concentration of HCl and NaOH, especially when the process was started with distilled water. The findings indicate that the constructed electrodialysis prototype (EDMB) possesses significant capabilities in transforming inorganic salts into their corresponding acid and hydroxide solutions, which offers a remarkable breakthrough in green technology.

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