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RESEARCH ARTICLE **OPEN ACCESS**

DEVELOPMENT AND EVALUATION OF UHMWPE MICROFIBERS POLYMERIC DIAPHRAGMS FOR ELECTROLYTIC PRODUCTION OF SODIUM HYDROXIDE

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ABSTRACT

The electrolytic process with a polymeric membrane to produce chlorine and sodium hydroxide is still the most used technology in the world. However, the most common material used in the production of diaphragms was asbestos, which was banned due to its toxicity to humans in its use and extraction. Thus, this work aimed to develop and evaluate a new and cheaper polymeric diaphragm using Ultra High Molecular Weight Polyethylene (UHMWPE) microfibers. Therefore, nine Polymeric Diaphragms (PD) were developed with different compositions and evaluated based on measurements of their thickness, permeability, resistivity, and performance during the electrolytic process. The results showed that higher proportions of short-length microfibers produced more promising diaphragms. In addition, the PDG diaphragm had a soda production of 35.68 g/L, a value higher than that presented by the commercial diaphragm, which was 11.04 g/L.

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INTRODUCTION

The chlor-alkali industry is one of the most important segments of the electro-intensive industry due to its commercial technical importance, with chlor-alkali derivatives present in more than 50% of all industrial chemical processes (Wang *et al*., 2014; Schneider and Dotzel, 2002). The three main electrolytic process systems are based on mercury, diaphragm, and membrane cells (Schneider and Dotzel, 2002). According to the Brazilian Association of the Alkali, Chlorine and Derivatives Industry Abiclor (Abiclor, 2021), in 2013, 63% of the Brazilian production of chlor-alkali used diaphragm technology (only 9% with asbestos-free diaphragms), 23% used membrane and 14% used mercury(Abiclor, 2021; Lakshmanan and Murugesan, 2014). A diaphragm is a porous separator located between the anodic and cathodic compartments of the electrolytic cell that significantly reduces the undesirable mixture of products formed in the compartments during electrolysis of the brine. Historically, asbestos was the main material used to construct diaphragms in electrochemical cells, however, its use was gradually banned due to the growing concern with its toxic effects on the human body and association with lung cancer (Schneider and Dotzel, 2002; Millet, 2013).

Membrane cells and polymeric diaphragms are two alternatives to asbestos diaphragm cells. However, in a report to the US Environmental Protection Agency, they estimated that a $ 2 billion capital investment would be needed to convert the nation's diaphragm cells to membranes (Curlin *et al*., 1990). This cost reflects the high price of technology and equipment imports, which increases the cost of production of membrane cells, making it impossible to expand the capacity of cells in large quantities (Guiguar, 1990). Thus, it is more economical to continue the operation of existing diaphragm cells than to convert them to membrane cells. For these reasons, several studies have been carried out with the intention of developing an economical diaphragm to substitute asbestos. For practical applications, a diaphragm must be inexpensive, chemically stable, and offer adequate durability. For optimal performance, it must have properties such as hydrophilicity, permeability, and conductivity, close to that of an asbestos diaphragm. In addition to the polymeric materials used in diaphragm development, it is necessary to use a doping process with inorganic fillers, clays, and oxides, to decrease permeability and increase the conductivity of the diaphragm (Millet, 2013; Cunha, 2015). The Polyramix® by ELTECH Systems and Tephram® by PPG Industries are two mechanically and chemically stable diaphragms, without asbestos in their composition, that has been commercially disseminated. The name POLYRAMIX (PMX) is derived from the wordspolymer and ceramic. It is a patented fibrous material produced from a combination of metal oxide particles and a fluorocarbon resin. The preferred metal oxide is zirconium oxide, although other metal oxides, such as titanium dioxide, can be used, and the polymer used is PTFE. PMX fibers are branched, irregular, and flexible, with lengths of 1000-7000 µm and diameter of 10-100 µm, and a density twice that of asbestos (Curlin, 1990).Polyramix is more energy-efficient and has a longer service life than asbestos diaphragms (Shreve and Brink, 2008). Tephram is a fluoropolymer-based separator composed of PTFE microfibers, Nafion, and a longer, secondary PTFE fiber. The longest fiber, DuPont Teflon, reinforces the diaphragm, but it is too thick to be used as a primary fiber. Microfibrils are prepared by a process patented by PPG Industries and comprise most of the diaphragm material. PTFE fibers form a blanket at the base while Nafion microfibers provide adequate porosity to the diaphragm (Foller *et al*., 1998; Ahmed and Foller, 2003). However, these separators are expensive compared to the regular asbestos diaphragm and, therefore, the cell must operate for 3-4 years to reduce the per-unit cost of production (Hine *et al*., 2005). Although the chlor-alkali industry uses commercially available polymeric diaphragms, the applications of these materials are limited by high market costs. Based on current industry options and needs, the main objective of this research is to develop a polymeric diaphragm, using ultra-high-molecular-weight polyethylene (UHMWPE) microfibers, which are both effective in the production of chlor-alkali and cost-effective.

MATERIALS AND METHODS

In this work, four types of commercial ultra-high-molecular-weight polyethylene (UHMWPE) microfiber (MF) were used in diaphragm production. The lengths and diameter of each microfiberare listed in Table 1. All microfibers were selected according to their physical characteristics and chemical stability. These materials proved to be resistant to pH variations (between 3 and 13 to anodic and cathodic compartments respectively) and temperatures (between 50ºC and 80ºC) i.e., resistant to high concentrations of hypochlorite solution and alkalis according to the work developed by Viana (Viana, 2009; Viana *et al*., 2008).

Table 1. UHMWPE microfibers used in diaphragm formation

Microfibers	Length (µm)	Average Diameter (µm)
MF0.1	100	5
MF0.6	600	1.2
MF0.9	900	15
MF1.6	1600	1.2

To improve microfiber dispersion during diaphragm formation on the cathode (SAE 1020 perforated mild steel plate), this study employed the Kelcocrete thickener, supplied by CPKelc Ind., a mineral clay–Atapulgita (Nunes *et al*., 2019), andzirconium oxide was used to reduce the diaphragm porosity and improve its hydrophilicity.The mineral brine was prepared in the laboratory at a concentration of 320g/L and was used to evaluate the diaphragms during conductivity and electrolysis tests.

Mixture Design: In 1958, Scheffé (1958) introduced the concept of the Simplex-Lattice project for mixing experiments and developed polynomial models that have the same number of terms as existing points in the associated projects. The project consists of the symmetric arrangement of points and is referred to with {p, m} - Lattice (Cornell, 1973). Where p is the number of components and m is the degree of a polynomial.

The experimental space of a mixture with p components is reduced to a s*implex* region limited by the conditions:

$$x_i \geq 0, \quad 1 \leq i \leq p \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$\sum_{i=1}^{p} x_i = 1 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where $x_i$represents the proportion of the *i*-th component. This equation removes a degree of freedom from the proportions. The experimental space, which contains the p components of the mixture, can be geometrically represented by the interior and the limits (vertex, edges, faces) of a regular (p-1) - dimensional simplex (Cornell, 1973). The vertices represent mixtures containing a single component and the interior points result in mixtures with a combination of all components. Figure 1 represents the experimental spaces of a simplex.

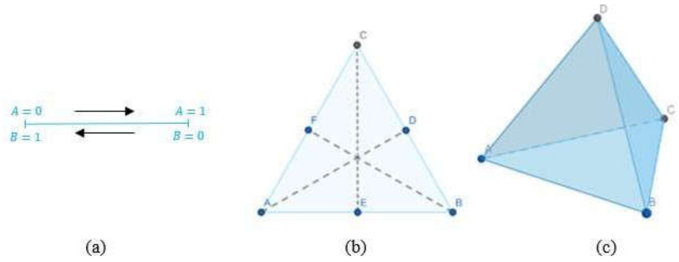


Figure 1.

To propose and evaluate several possible compositions of the polymeric diaphragm, the STATISTICA 10 software was used, 9 random experiments were generated via Simplex - Lattice mixture planning for the 4 UHMWPE microfibers, with a degree 1 polynomial and added interior points and fixed central point.Table 2 shows the experimental planning generated with their respective microfiber (MF) proportions. The diaphragms developed in this study were called Polymeric Diaphragms (PD). The compositions of PDs are presented according to the increasing concentration of microfibers.

Table 2. Simplex-Lattice experimental design for 4 components

Diaphragm	MF0.1	MF0.9	MF0.6	MF1.6
PDA	25.0%	25.0%	25.0%	25.0%
PDB	62.5%	12.5%	12.5%	12.5%
PDC	100%	0%	0%	0%
PDD	12.5%	62.5%	12.5%	12.5%
PDE	0%	100%	0%	0%
PDF	12.5%	12.5%	62.5%	12.5%
PDG	0%	0%	100%	0%
PDH	12.5%	12.5%	12.5%	62.5%
PDI	0%	0%	0%	100%

Deposition of Diaphragms: A dispersion was prepared with Kelcocrete, clay, and microfibers (in the proportions indicated in Table 2) and deposited on the cathode with the aid of a programmable vacuum pump (Buchi V-7000). After this procedure, the formed diaphragm was dried in an oven (Solab SL 102) at a constant temperature of 120 ºC for 90 minutes.

Diaphragm Doping: The diaphragms deposited on the cathode were doped with a dispersion composed of Atapulgita and zirconiumoxide in the proportion 1:3, respectively. Then, the doped diaphragm was submitted to sintering in a muffle furnace (Furnace 47900 – Barnstead Thermolyne) according to the curve shown in Figure 2. This procedure aims to decrease the permeability and porosity of the diaphragms as well as to give them greater hydrophilicity. After the heat treatment, their average thickness was determined using an Elecktrophysik Minitest 4100 model ultrasound thickness gauge.

Permeability Tests: The permeability coefficient (k) is determined by the amount of brine that percolated the diaphragm under the cathode within a given time interval, based on Darcy's Law (Equation 3). The tests were performed using experimental system shown in Figure 3.

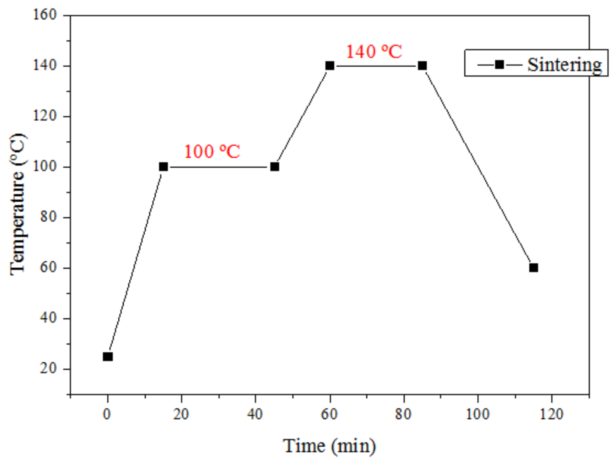


Figure 2.

$$k = \frac{\nu L Q}{A g \Delta h} \quad (3)$$

where, Δh is the height of the liquid column, ν is the brine kinematic viscosity, L is the diaphragm thickness, Q the permeation flow rate, g the constant of gravity and A is the transversal area (64.0 cm^2).

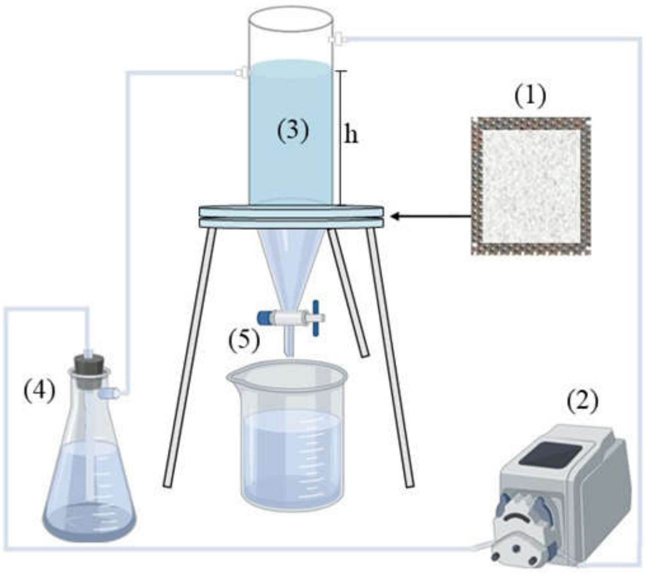


Figure 3.

Conductivity Tests - MacMullin Number (N_{Mac}): The conductivity cell and the instrumental configuration were elaborated based on the work of Poush (1983). A frequency generator (Agilent 33210A) was used to apply a sinusoidal signal of 1.4 kHz with an amplitude of 5.0 V and an offset of 0 V. The current (I) and potential (E) were recorded separately using two high-impedance multimeters (ICEL MD-9000R). First, only the brine resistance (R_o) was determined and then the electrolyte resistance plus the diaphragm (R), both using the first Ohm's law (Equation 4).

$$R = \frac{E}{I} \quad (4)$$

The relationship between electrolyte resistivities (ρ_0) and electrolyte with diaphragm (ρ) were determined by Ohm's second law (Equation 5).The dimensionless number of MacMullin was determined using Equation 6.

$$R = \rho \frac{L}{A} \quad (5)$$

$$N_{mac} = \frac{\rho}{\rho_0} \quad (6)$$

Diaphragm evaluation from brine electrolysis: Except forthe temperature, the operating conditions of bench-scale electrolysis were very close to those currently used by the chlorine soda industry, i.e.:Brine concentration = 320g/L; the electrodes - perforated plate SAE 1020 were used as cathode and DSA grid (De Nora) as anode. The operational conditions during the brine electrolysiswere performed as following-the galvanostatic process with cathode current density = 0.24A/cm^2 and anode = 0.22A/cm^2, pH of the anolyte and catholyte - 3.5 and 13 respectively. Regarding the different temperature values of45°C and 80°C at the bench and industrial-scalerespectively; The authors make the following assumption: - All diaphragms were evaluated under the same operational conditions. There will certainly be variations in the performance of these diaphragms on an industrial or pilot scale, but it can be assumed that they will occur proportionally. The evaluation criteria established in the laboratory on a semi-pilot scale for choosing the best diaphragm are part of the first step towards pilot testing and are therefore valid. Two diaphragms were simultaneously evaluated during 8 hours of electrolysis. Each cell consisted of two semi-cells (anodic and cathodic) separated by the diaphragm. The first anodic semi-cell was fed with brine and its percolation through the diaphragm to the adjacent semi-cell was maintained by controlling the hydrostatic pressure drop between them during electrolysis. The experimental system used and the main reactions that occur during electrolysis are shown by the Figures 4 (a) and (b) respectively. Basically, the system consisted of a Tectrol AC-CC 30V-30A TCA OBR1A stabilized current source, a Novus field logger, two BL931700 model pH meters from the pH controller, two Cole-Parmer OPVOW/ATC PH probes and an HMI interface.

The concentrations of sodium hydroxide, sodium chloride, and sodium chlorate were determined using standardized titration methodologies. These concentrations were determined every 30 minutes and from their accumulated masses at the end of the electrolysis. In the electrolysis process, the diaphragms were evaluated from the current and energy efficiencies, E.C and E.E respectively, related to their caustic soda production. Equations 7 and 8 obtained from Gallone (1973) were used to calculate these efficiencies.

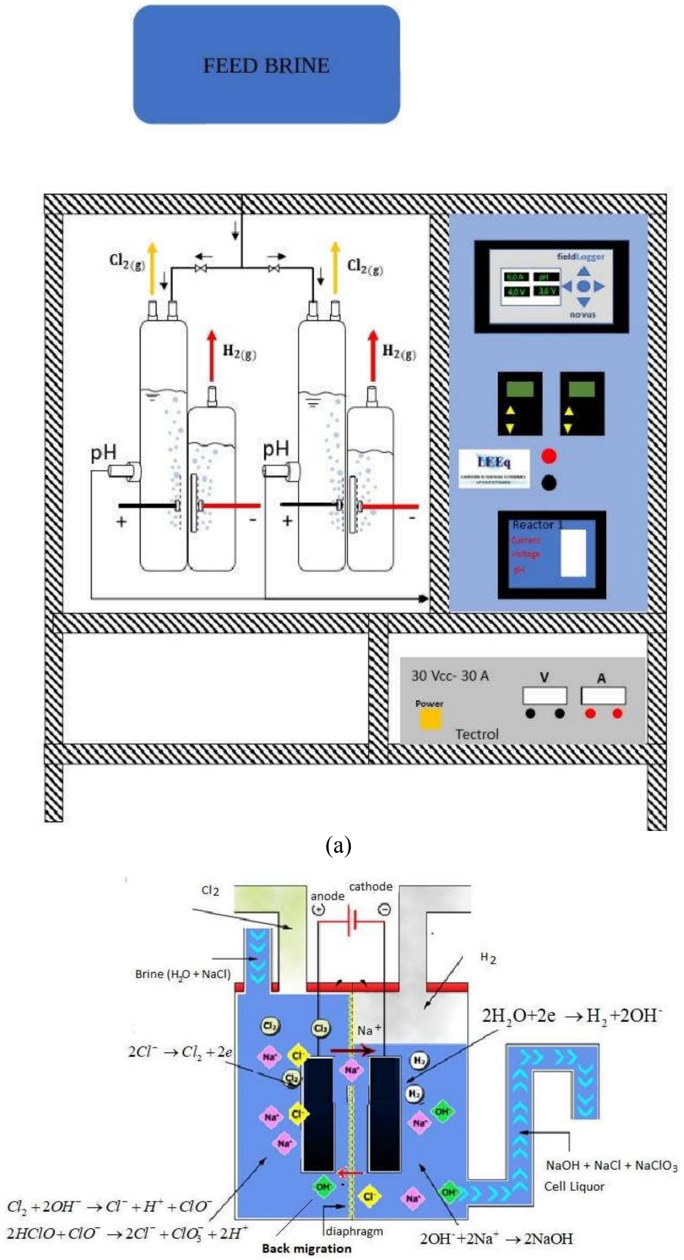
$$EC = \frac{M_{NaOH}\,produced}{M_{NaOH}\,theoretical} \cdot 100 \quad (7)$$

$$EE = \frac{EC \cdot 2.24V}{cell\ operating\ potential} \cdot 100 \quad (8)$$

Where 2.24 V in equation (8) corresponds to the standard theoretical potential for sodium chloride decomposition.

RESULTS AND DISCUSSIONS

Physical-chemical characterization of diaphragms evaluated: Table 3 shows the results obtained for the thickness, permeability, and NMac measurements for the commercial diaphragm - Tephram in comparison with the developed diaphragms. From these results, it was possible to verify that the higher proportion of short microfibers favored a greater "packaging" of the diaphragm, increasing its density. This fact can also be observed by Moura Junior *et al.*(2021), where it was possible to observe a strong statistical relationship between the length of the fibers and the properties of the diaphragms, with diaphragms formed by fibers of shorter length having a better performance. This condition reduced its thickness, resistivity, and permeability, which can promote lower potential and a more concentrated soda hydroxide solution during electrolysis. On the other hand, it was reported by Almeida Filho *et al.* (2011) using an asbestos diaphragm that a greater number of long fibers increases the thickness and permeability of the diaphragm resulting in greater cellular potential and greater energy consumption.



(a)

(b)

Figure 4.

Table 3. physical-chemical properties of the developed diaphragms and the Tephram commercial diaphragm

Diaphragm	Thickness (cm)	$Kx10^8$(cm²)	Resistivity (Ω.cm)‡	N_{mac}
Tephram	0.221	8.97	0.84	2.73
PDA	0.248	5.38	0.38	1.22
PDB	0.356	3.86	0.35	1.16
PDC	0.242	0.80	0.34	1.12
PDD	0.228	0.85	0.35	1.14
PDE	0.395	5.80	0.42	1.36
PDF	0.286	5.05	0.42	1.36
PDG	0.219	0.85	0.35	1.14
PDH	0.277	7.35	0.38	1.23
PDI	0.427	13.7	0.42	1.35

‡ Brine resistivity = 0.31Ohm.cm

By analyzing Figure 5, it is possible to predict which of the diaphragms developed will present the best results during electrolysis. For a diaphragm to have a good result, it must have a small thickness because it is directly related to cell potential and energy consumption. It should have low permeability because this parameter will influence the migration of ionic species. The migration of hydroxyl ion to the anodic half-cell favors the formation of sodium chlorate thus decreasing the market value of caustic soda and the efficiency of the process (Lime *et al.*, 2010).

Finally, a diaphragm should have N_{Mac} values close to 1, as this parameter characterizes the resistivity of the diaphragm, and the lower the resistivity of the separator, the lower the overall energy consumption (Caldwell *et al.*, 1982).

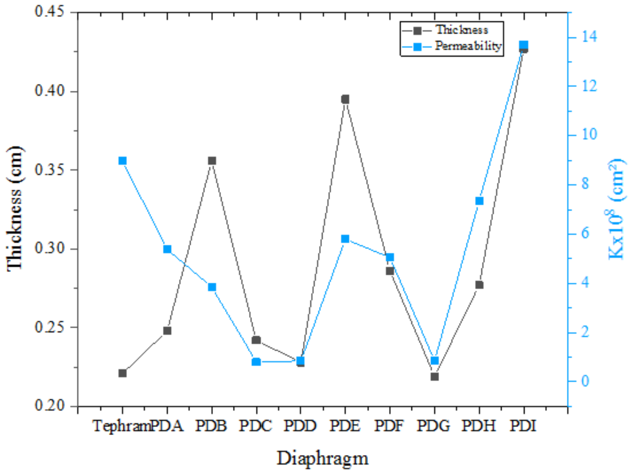


Figure 5.

For the most promising diaphragm, Table 3 shows that the values for the N_{Mac} were relatively close, but the PDC, PDD, and PDG diaphragms showed lower values. However, when the criteria of lower thickness and permeability were associated, the PDD and PDG diaphragms were the most promising. Figures 5, 6, 7, 8, and 9 show that the results of electrolysis for these diaphragms confirmed the analysis of the established criteria.

Diaphragm evaluation in brine electrolysis: Table 4 shows the results obtained in the electrolysis tests. The diaphragms evaluated produced concentrations of NaOH close to or even higher than the Asbestos diaphragm. It is important to note that the concentration of chlorates is also relevant because it can define its market price. It is interesting to note that PDD and PDG diaphragms, for example, under the operating conditions used produced 19 and 35.68 g/L of NaOH with 0.66 and 0.1g/L of chlorate, respectively. These diaphragms had practically the same characteristics of thickness, permeability, and N_{Mac} (See Table 3). However, despite the different compositions, these diaphragms have a higher content of very similar short fibers - MF0.6 (100%) and MF0.9 (62.5%) for PDG and PDD, respectively. It can be assumed here that short fibers are important in the composition of a diaphragm because they give it low permeability and thickness. But did PDC with 100% of the shortest fiber (0.1mm) - MF0.1, did not produce satisfactory results. Well, it is known that during diaphragm formation sintering between fibers and between fibers and mineral particles (doping process) will determine its porosity, permeability, thickness, resistivity, and structural integrity. However, these properties may change during electrolysis through fiber accommodation, disbanding, change in porosity, and other modifications.

The permeability, for example, can be modified due to convections and micro convections generated by brine percolation and production of chlorine and hydrogen gases respectively, among other factors such as temperature, joule effect, loss of mineral particles, detachment between fibers resulting in loosening of the original matrix. The PDC diaphragm (100% MF0.1) is made up of very short fibers which can considerably weaken the strength of the contact points between them during electrolysis. This may explain the results obtained for this diaphragm where the relaxation of its structure probably favored the dilution of the caustic soda produced and increased chlorate content.

Table 4. Results of brine electrolysis for the nine diaphragms evaluated and Thephram

Diaphragm	Potential (V)	Current[a] (A)	NaOH (g/L)	NaCl[b] (g/L)	NaClO3 (g/L)	NaOH (g)	NaOH[c] (g)	% E.C.	% E.E.
Tephram	3.88	6.00	11.04	134.43	0.250	63.20	72.47	87.21	51.01
PDA	4.37	6.15	7.76	153.14	0.370	61.38	72.23	84.98	45.32
PDB	4.49	6.12	25.12	148.33	0.710	55.46	72.95	76.03	39.24
PDC	3.17	6.13	16.24	118.07	0.410	53.62	73.90	72.56	53.12
PDD	3.23	6.02	18.96	139.11	0.660	61.90	71.63	86.42	60.49
PDE	3.52	6.12	3.20	156.41	0.670	59.49	72.95	81.55	54.69
PDF	4.56	6.09	18.08	153.72	0.550	56.12	73.43	76.43	38.65
PDG	3.10	6.18	35.68	124.50	0.092	65.94	72.71	90.68	65.53
PDH	3.93	6.09	6.64	164.24	0.600	51.06	73.13	69.54	40.99
PDI	3.73	6.16	7.28	161.91	0.530	54.34	72.23	75.29	48.32

The average current was used to calculate the theoretical mass of NaOH [a];non-electrolyzed chloride[b]; theoretical calculated value[c].

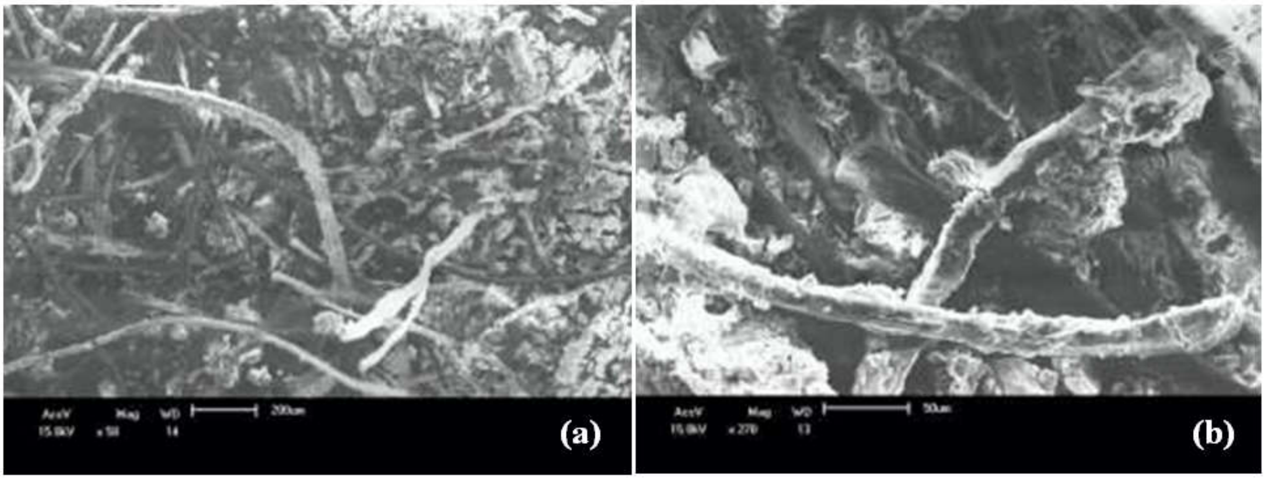


Figure 6.

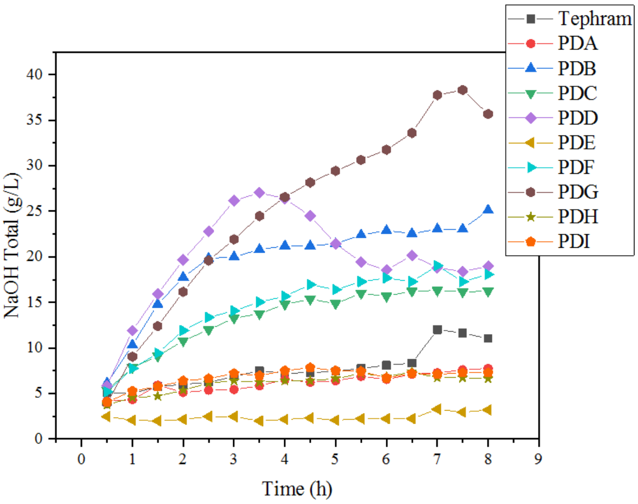


Figure 7.

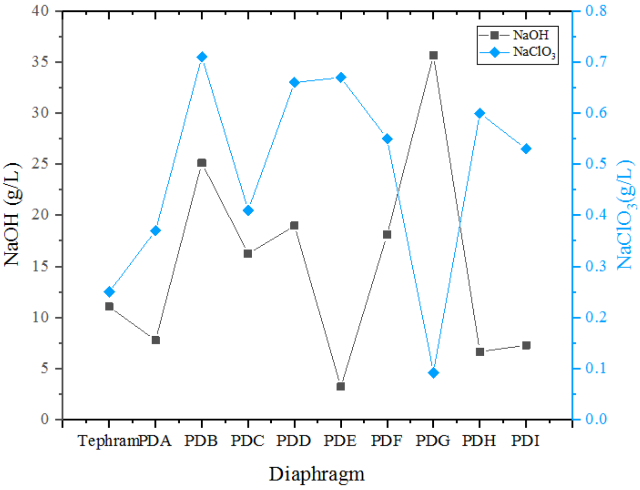


Figure 8.

Considering the PDD and PDG diaphragms one can therefore assume in the first case, the importance of the synergistic effect in the case of using different types of fibers, or the "ideal size" in the case of using only one. Figures 6(a) and 6(b) show as an example SEM images of the PDD diaphragm formed. The different types of microfibers, Kelcrokete thickener, and mineral particles can be observed. Figure 7 shows the variation in sodium hydroxide concentration during electrolysis. The low performance of the PDE diaphragm formed with 100% of MF0.9 fiber can be highlighted. The PDA diaphragm formed with 25% of this same fiber also showed low performance. These results show that this type of fiber did not contribute to preserving the diaphragm's properties during electrolysis, either as the only constituent as in the first case or acting synergistically in the second case. After 4 hours of electrolysis, the PDD diaphragm formed by 62.5% of this fiber showed a marked decrease in sodium hydroxide concentration, probably due to the accommodation of its fibers and a slight increase in its permeability. The concentrations of NaOH and $NaClO_3$ present in the "liquor" produced at the end of the electrolysis are shown in Figure 8. The PDG diaphragm produced a higher concentration of sodium hydroxide with a lower chlorate content. The low sodium chlorate concentration indicates a reduction in the phenomenon known as "back migration", which is the migration of hydroxyl ions from the cathode to the anodic compartment. This phenomenon decreases the efficiency of the process, the quality of the alkali produced, and its market price (Lime *et al.*, 2010). Likewise, Jardim Junior (2006) reported in his work that the formation of sodium chlorate ($NaClO_3$) represents a loss in process efficiency because part of the chlorinated product is consumed in unwanted parallel reactions. The current and energy efficiencies are shown in Figure 9.

From the results discussed above, it was already expected that the PDG diaphragm would obtain better scores compared to the others. This is certainly related to greater stability during electrolysis of its properties obtained before electrolysis. The results show that its current (90.68%) and energy (65.53%) efficiencies were higher than the 87.21% and 51.0% respectively for the Asbestos diaphragm taken here as a reference.Note that a diaphragm can generally have a higher current efficiency than energy. This is possible because the E.C. depends on the amount of soda produced (Faraday's law) but this product may occur due to a high relative potential. This occurred with Asbestos, PDA, PDB, and PDF diaphragms. The opposite situation occurred with PDC and PDH diaphragms. In the first case, undesirable parallel reactions to produce sodium chlorate contributed to an E.C. value below E.E. In the second case, although PDH produced fewchlorates, the average potential was relatively high.

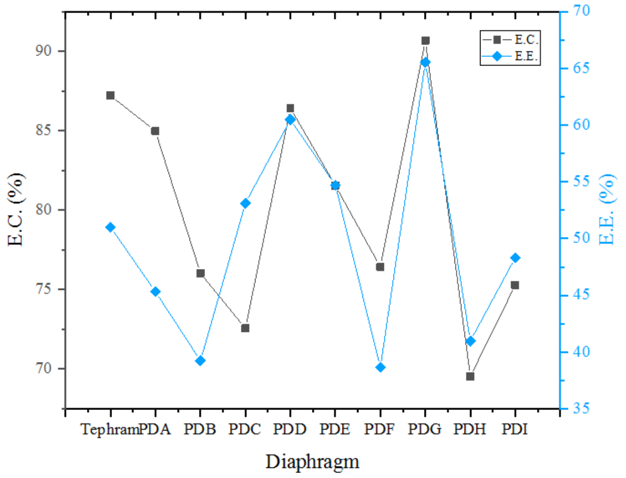


Figure 9.

The relationship between cell potential and diaphragm thickness is shown in Figure 10. We can see, as expected, that for larger thicknesses we will have a greater potential, and therefore a greater consumption of energy during electrolysis. For this, we can highlight the PDC, PDD, and PDG diaphragms as the most efficient in this regard.

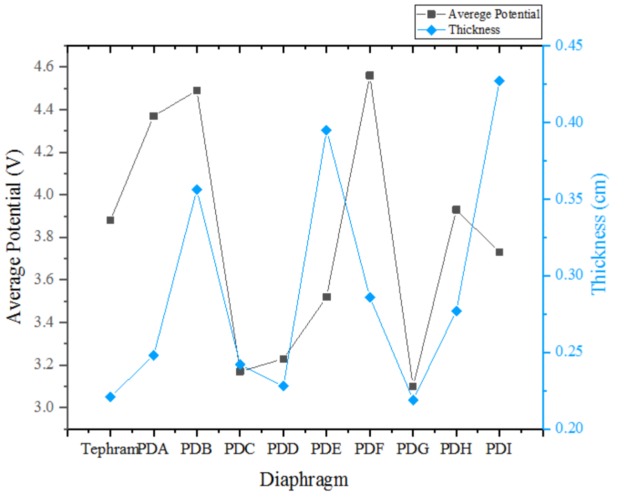


Figure 10.

CONCLUSIONS

Using the experimental planning of the mixture, it was possible to determine the composition of four microfibers of UHMWPE to produce 9 (nine) diaphragms and evaluate them for electrolytic production of sodium hydroxide. The Asbestos diaphragm was used as a reference to compare all the results analyzed. Among the diaphragms produced with higher proportions of short microfibers - PDD, PDC, and PDG, these showed the best results in terms of thickness, permeability, and resistivity due to greater compaction of their matrix, forming diaphragms with higher density and greater retention of mineral particles. Some of the diaphragms developed showed promising results in the production of sodium hydroxide. The PDG diaphragm stands out here where it produced a concentration of 35.68 g/L of NaOH with a current efficiency of 90.65% and low chlorate content of about 0.092 g/L. It is worth noting here that it would be premature to draw any definitive conclusions from the results obtained as complementary studies are still needed to assess, for example, the useful life of the best evaluated PDG, PDD and PDC diaphragms.

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