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Preliminary study of the efficiency of alkaline water electrolysis for hydrogen production using an ultrasonic electrode

Estudo preliminar da eficiência da eletrólise alcalina da água para produção de hidrogênio utilizando eletrodo ultrassônico

Estudio preliminar de la eficiencia de la electrólisis alcalina del agua para la producción de hidrógeno utilizando un electrodo ultrasónico

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Abstract
This study presents research on increasing the efficiency of alkaline water electrolysis for green hydrogen production using ultrasonic electrodes. The aim of the work was to investigate the efficiency of alkaline water electrolysis using ultrasonic electrodes, focusing on green hydrogen production and environmental sustainability. The methodology involved the use of a stainless steel electrolytic cell, 316L stainless steel electrodes, and a 30% (w/w) KOH electrolyte solution. A 20W, 40kHz ultrasonic generator was used, applying ultrasound directly to the electrode. The hydrogen produced was collected through a water displacement system. The experimental design followed a full factorial design, with data analysis by analysis of variance (ANOVA) and mean comparison (Tukey). It was shown that the application of ultrasound directly to the electrode can significantly improve the efficiency of electrolysis, reducing overvoltage and resistances, and accelerating the formation of hydrogen microbubbles, resulting in up to a 28% increase in hydrogen production. The importance of optimizing parameters such as ultrasonic frequency and intensity and electrolyte concentration is highlighted, offering a promising approach to make green hydrogen production more viable and economical. It is suggested to explore different electrode materials and integrate this technology into renewable energy systems for future research.
Keywords: Galvanic cell; Overpotential; Benchtop prototype; Renewable energy; Ultrasonic cathode.

Resumo

Este estudo apresenta uma pesquisa sobre o aumento da eficiência da eletrólise alcalina da água para produção de hidrogênio verde, utilizando eletrodo ultrassônico. O objetivo do trabalho foi investigar a eficiência da eletrólise alcalina da água utilizando eletrodos ultrassônicos, com foco na produção de hidrogênio verde e na sustentabilidade ambiental. A metodologia envolveu a utilização de uma célula eletrolítica de aço inoxidável, eletrodos de aço inoxidável 316L, e solução eletrolítica de KOH a 30% (p/p). Foi utilizado um gerador de ultrassom com potência de 20W e frequência de 40kHz, aplicando-se ultrassom diretamente ao eletrodo. A coleta de hidrogênio produzido foi realizada através de um sistema de deslocamento de água. O planejamento experimental seguiu um delineamento fatorial completo, com análise dos dados por meio de variância (ANOVA) e comparação de médias (Tukey). Foi evidenciado que a aplicação de ultrassom diretamente no eletrodo pode melhorar significativamente a eficiência da eletrólise, reduzindo a sobretensão e as resistências, e acelerando a formação de microbolhas de hidrogênio, resultando em um aumento de até 28% na produção de hidrogênio. Destaca-se a importância de otimizar parâmetros como a frequência e intensidade ultrassônica e a concentração do eletrólito, oferecendo uma abordagem promissora para tornar a produção de hidrogênio verde mais viável e econômica. Sugere-se a exploração de diferentes materiais de eletrodos e a integração desta tecnologia em sistemas de fontes renováveis de energia para futuras pesquisas.
Palavras-chave: Célula galvânica; Sobretensão; Protótipo de bancada; Energia renovável; Cátodo ultrassônico.

Resumen

Este estudio presenta una investigación sobre el aumento de la eficiencia de la electrólisis alcalina del agua para la producción de hidrógeno verde utilizando electrodos ultrasónicos. El objetivo del trabajo fue investigar la eficiencia de la electrólisis alcalina del agua utilizando electrodos ultrasónicos, centrándose en la producción de hidrógeno verde y la sostenibilidad ambiental. La metodología implicó el uso de una celda electrolítica de acero inoxidable, electrodos de acero inoxidable 316L y una solución electrolítica de KOH al 30% (p/p). Se utilizó un generador ultrasónico con una potencia de 20W y una frecuencia de 40kHz, aplicando ultrasonido directamente al electrodo. El hidrógeno producido se recogió a través de un sistema de desplazamiento de agua. El diseño experimental siguió un diseño factorial completo, con análisis de datos mediante análisis de varianza (ANOVA) y comparación de medias (Tukey). Se demostró que la aplicación de ultrasonido directamente al electrodo puede mejorar significativamente la eficiencia de la electrólisis, reduciendo la sobretensión y las resistencias, y acelerando la formación de microburbujas de hidrógeno, resultando en un aumento de hasta el 28% en la producción de hidrógeno. Se destaca la importancia de optimizar parámetros como la frecuencia e intensidad ultrasónica y la concentración del electrolito, ofreciendo un enfoque prometedor para hacer la producción de hidrógeno verde más viable y económica. Se sugiere explorar diferentes materiales de electrodos e integrar esta tecnología en sistemas de energía renovable para futuras investigaciones.
Palabras clave: Célula galvánica; Sobretensión; Prototipo de bancada; Energía renovable; Cátodo ultrasónico.

1. Introduction

The search for alternative and sustainable energy sources has become a global priority in light of the environmental impacts associated with the use of fossil fuels. In this context, hydrogen emerges as a promising energy carrier capable of replacing traditional sources of thermal energy generation due to the environmental benefits related to its combustion (Nemitallah et al., 2018). An innovative approach to hydrogen production is ultrasonic wave-assisted water electrolysis, a process that has the potential to transform how we access clean and sustainable energy.

Water electrolysis is an electrochemical process in which electricity is used to separate water into its constituent components: hydrogen and oxygen. The process requires the application of an electric current through an electrolytic solution to break the H-O-H bonds. The passage of ultrasonic waves with frequencies ranging from 20 to 1000 kHz through a tank containing a biomass suspension causes a phenomenon known as acoustic (ultrasonic) cavitation, i.e., the formation, growth, and implosive collapse of microbubbles containing dissolved gases and water vapor. Practically all the physicochemical effects of ultrasound in liquid media originate from cavitation. The rapid collapse (several nanoseconds or microseconds) of cavitation bubbles is almost adiabatic, making each individual bubble a microreactor, within which temperatures of around 4726.85°C and pressures of hundreds of atmospheres occur (Burton et al., 2021).

Electrolysis, a method of hydrogen production, is expensive due to the high energy consumption, typically between 4.5-5 kWh/m³ of H2, with overall efficiency below 40% (Kumar et al., 2018). To make it more viable, it is necessary to reduce the

energy costs or the energy requirements of the process. This can be achieved by reducing system resistances, such as electrical and electrochemical resistances, and through innovations in electrode materials and cell geometry (Rashid et al., 2015). Ohmic losses, often caused by the adhesion of gas bubbles on the electrodes and in the electrolytic solution, are a major challenge.

Alkaline water electrolysis, which uses sodium or potassium hydroxides to increase water conductivity, is a common technique. Potassium hydroxide is preferred for its corrosion resistance, and nickel-based electrodes are chosen for their cost-effectiveness and activity (Grigoriev et al., 2020). Introducing ultrasound into the process, an area known as sonoelectrochemistry, can improve the energy efficiency of electrolysis. Studies have shown that ultrasound can increase hydrogen production efficiency by 5%-18% at high current densities (Sazali, 2020; Islam, Burheim, & Pollet, 2019). Hydrogen is produced on the surface of the electrodes through electrochemical reactions, and the microbubbles of hydrogen formed are a crucial aspect of the process. The aim of this study is to investigate the efficiency of alkaline water electrolysis using ultrasonic electrodes, evaluating the impacts on green hydrogen production and the environmental sustainability of the technology.

2. Material and methods

2.1 Materials

The electrolyte used was sodium hydroxide (NaOH). Sodium hydroxide solutions were prepared by diluting P.A. grade NaOH, Synth brand, with 98% purity, in deionized water produced by a reverse osmosis system, model OS20 LX, Gehaka brand. Initially, a study was conducted on the conductivity of sodium hydroxide solutions at temperatures close to the operating temperature of the galvanic cell. According to Bousfield and Lowry (1905), the maximum specific conductivity at temperatures of 18-50°C was at mass concentrations of 15% and 19% (4.35 and 6.08 mol/L), respectively. To evaluate the effect of the conductivity of sodium hydroxide solutions on hydrogen flow, an intermediate concentration within the range provided by these authors and two concentrations lower than this value were adopted. Thus, sodium hydroxide solutions at concentrations of 2.0, 3.5, and 5.0 mol/L were analyzed.

The electrode material was chosen based on its nickel content and stability in an alkaline medium. The selected material was 304 stainless steel with a diameter of 0.12±0.01 cm and an active length of 4.05±0.01 cm, a carbon-iron alloy with the addition of chromium (19% w) and nickel (9% w), which provide greater corrosion resistance (Callister, 2018).

For conducting this experimental, laboratory, and quantitative research, we used the methodological foundations of Pereira et al. (2018), who detail the methodology of scientific research, and Koche (2011), who addresses the fundamentals of scientific methodology applicable to experimental studies. Additionally, Gil (2017) provides guidelines on the preparation of research projects, complementing the methodological approach adopted.

2.2 Process Analysis

Alkaline water electrolysis in a galvanic cell involves the decomposition of water into hydrogen and oxygen using electric current, with the aid of an alkaline solution to increase the efficiency of the process (Brauns & Turek, 2020). The galvanic cell consists of two electrodes (anode and cathode) submerged in an alkaline solution. An electric current is applied to the cell, causing water (H_2O) to decompose into its elemental components - hydrogen (H_2) and oxygen (O_2). At the cathode (negative pole), water is reduced, producing gaseous hydrogen (H_2) and hydroxide ions (OH^-).

At the anode (positive pole), oxidation occurs, producing gaseous oxygen (O_2) and hydrogen ions (H^+). The hydroxide ions (OH^-) generated at the cathode move towards the anode, while the hydrogen ions (H^+) move towards the cathode, maintaining the electrical neutrality of the solution. Hydrogen and oxygen are collected in separate compartments to avoid mixing, as their combination can be dangerous (Santos, Sequeira, & Figueiredo, 2013). Hydrogen is collected at the cathode,

and oxygen is collected at the anode. The alkaline solution facilitates ion movement and helps reduce overvoltage, making the process more efficient. The aforementioned authors have demonstrated that the efficiency of alkaline water electrolysis depends on several factors, such as the electrolyte concentration, solution temperature, water purity, and the intensity of the applied current. At the anode, water (H2O) undergoes oxidation. The reaction can be described by the chemical equation presented in Equation 1 (Ursúa & Sanchis, 2012):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (1)$$

Water molecules lose electrons (oxidation). Each water molecule loses two electrons. By losing electrons, water molecules transform into gaseous oxygen (O2), which is released. Besides oxygen, the oxidation of water also produces hydrogen ions (H+). These hydrogen ions (H+) do not remain free in the solution. They react with hydroxide ions (OH-) present in the alkaline solution, maintaining chemical equilibrium. This reaction is important as it is the source of the gaseous oxygen produced during water electrolysis. Thus, the loss of electrons at the anode is balanced by the gain of electrons at the cathode, where reduction and the formation of gaseous hydrogen (H2) occur.

The main reaction at the cathode, the negative electrode where reduction (gain of electrons) occurs, can be simplified as presented in Equation 2:

$$2H_2O + 2e^- \rightarrow H_2 + OH^- \quad (2)$$

At the surface of the cathode, the hydrogen ions (H+) present in the water gain electrons (reduction). They transform into gaseous hydrogen (H2), which is released. As a result of the reaction, hydroxide ions (OH-) are also formed, which remain in the solution. This production of hydroxide ions (OH-) at the cathode helps maintain chemical equilibrium in the alkaline solution.

The efficiency of an alkaline galvanic cell for hydrogen production can be defined as the proportion of electrical energy effectively used to produce hydrogen relative to the total energy consumed by the process (Sakas et al., 2022). This efficiency is influenced by factors such as electrode overvoltage, internal resistance of the cell, temperature of the electrolyte solution, and electrolyte concentration. To experimentally quantify the efficiency, the amount of hydrogen produced and the electrical energy consumed are measured. This is typically done by collecting data on the amount of gas produced (measuring the volume of hydrogen) and comparing it to the theoretical amount expected based on the amount of electricity applied (calculated using Faraday's law). The efficiency is then calculated as the ratio between the hydrogen generated and the theoretically expected hydrogen for the amount of electricity supplied, according to Equation 3 (de Groot, Kraakman, & Barros, 2022):

$$\eta(\%) = \frac{V_{real}}{V_{ideal}} \cdot 100 \quad (3)$$

In which Equation 3 is the comparison of the actual hydrogen gas produced to the ideal value. (Vreal) is the hydrogen gas produced per unit of time measured experimentally and (Videal) is the ideal volume of hydrogen gas generated, which can be calculated using the ideal gas equation under the given conditions. The ideal volume can be calculated using Equation 4:

$$V_{ideal}(cm^3) = \frac{Sit}{nF} \cdot \frac{RT}{P} \quad (4)$$

Where SSS is the stoichiometric coefficient, iii is the applied current, ttt is the operating time, nnn is the number of electrons transferred, F is the Faraday constant (96484 C/mol), T is the operating temperature in Kelvin, R is the ideal gas constant (8.314 J/(K·mol)), and P is the atmospheric pressure in Pascals.

For the calculation of gas pressure, the height of the water column from the initial water level was measured at the end of the experiments. According to fluid statics, the pressure inside the half-cell is equal to the pressure exerted at an external point to it, if the same reference point is adopted. Since the system is open, it can be stated that the pressure in the graduated cylinder is equal to the local atmospheric pressure, as at the reference level only atmospheric pressure acts (Çengel & Cimbala, 2012). Thus, the gas pressure can be calculated using Equation 5:

$$P_{gás} = P_{atm} + \rho_{água} g h_{água} \quad (5)$$

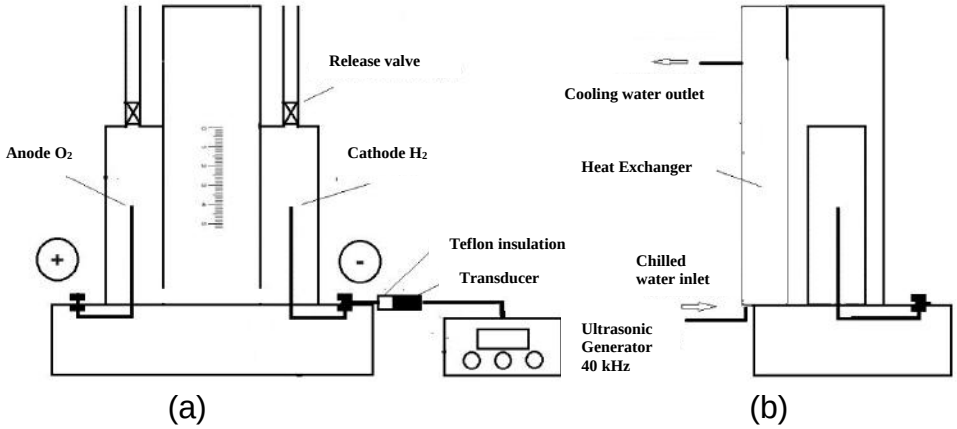
In Equation 5, Patm is the local atmospheric pressure, ρ_água is the specific mass of water, g is the gravitational acceleration, and hágua is the vertical distance between the initial water height and the remaining height in the half-cell.

Several precautions were observed during the experiments. Alkaline solutions are very corrosive, so it was necessary to use appropriate clothing and gloves when handling the reagents. The reactor outlets had clamps to prevent the ducts from coming loose during the experiments. Additionally, the experiments were conducted away from ignition sources due to the explosive nature of hydrogen (Park et al., 2022).

2.3 Experimental Arrangement

Figure 1 shows a schematic diagram of the electrolytic cell assembled for the experiments, with and without the insertion of an ultrasonic field. The cell was made of transparent colorless acrylic plates and aluminum, with an average thickness of 0.22±0.01 cm and 0.09±0.01 mm, respectively. Three blocks with a square cross-sectional area were used, one central block with an internal side of 2.6 cm and two lateral blocks with an internal side of 1.6 cm. The lateral blocks, both with a height of 7.7 cm, serve as containers for the cell's electrodes (cathode and anode). The central block, with a height of 10.7 cm, allows the formation of a hydraulic seal to separate the O2 and H2 gases produced by the alkaline water electrolysis. For this purpose, two lower openings measuring 8.00 mm by 16 mm connect the internal spaces of the chambers containing the electrolyte.

Figure 1 - Galvanic cell used for hydrogen production from water electrolysis: (a) Front view of the galvanic cell and ultrasonic generator; (b) Side view of the galvanic cell highlighting the heat exchanger for electrolyte temperature control.



Source: Prepared by the authors (2024).

Figure 1 shows the electrolytic cell made of acrylic and aluminum, with three blocks: two lateral blocks for the electrodes (cathode and anode) and one central block taller to separate the O2 and H2 gases. The lower openings connect the internal chambers containing the electrolyte, allowing the formation of a hydraulic seal. The front view highlights the cell and the ultrasonic generator, while the side view emphasizes the heat exchanger.

The central block is open to the atmosphere at its top and has about 6.5 cm on one of its sides, specifically from the back of the electrolytic cell, made of aluminum, to allow heat exchange of the electrolyte with cooling water circulating through a fourth block of 2.6 cm wide by 1.5 cm thick and 10.7 cm high, made entirely of aluminum. The lateral blocks have gas retention valves on their tops for the gases formed at each electrode. As there is a scale on the front surface of the central block, this favors the quantification of the volumes of gases formed by electrolysis in both half-cells, based on the principle of communicating vessels established between the three blocks described above. The volumes are quantified with the aid of the differences in the heights of the electrolyte columns between the central block and the lateral blocks. The three blocks that make up the electrolytic cell were installed on a single horizontal block, also made of acrylic, which serves as a base structure for the assembly and allows the cell's electrodes to be installed from the base of the lateral blocks. This allows for lateral connectors to be installed and to receive the electrical connections and an ultrasonic transducer coming from an ultrasonic wave generator. The total volume of electrolyte in the cell is 5.64 cm^3.

2.4 Continuous Voltage Source

The direct current voltage source used to simulate the feeding of the electrochemical cell consists of a kit with 4 Sanyo Ur18650 batteries, 3.7 V, 2600 mA.h and with terminals. With this source, feedings from 3.7 V to 14.8 V can be configured.

The negative terminal of the source was connected to the electrode for hydrogen production (cathode) and the positive terminal to the electrode for oxygen production (anode). The electric current was measured with the aid of a multimeter connected in series with the experimental unit, the reaction temperature was measured by a thermocouple, and the direct current voltage source provided the necessary voltage for the experiment through manual adjustment. The experiments were conducted at ambient pressure and temperatures.

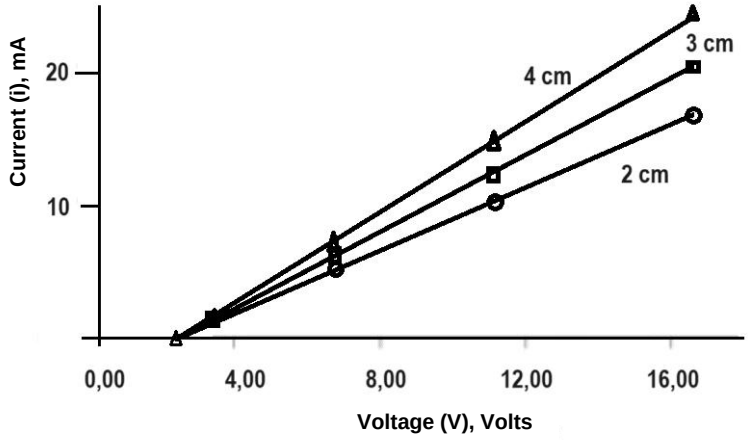
2.5 Produced Hydrogen Collection System

The hydrogen produced is measured directly in the electrolytic cell due to the graduated scale engraved on the central block, initially kept at zero on the scale. As the chemical reaction proceeded, the hydrogen displaced the water column in the lateral blocks downward, providing readings of the volumes of O2 and H2 produced and evaluated with the aid of a digital caliper brand Caliper from MTX®, with a total capacity of 150 mm, resolution of 0.01 mm. This procedure was possible since, under the conditions used, hydrogen has low solubility in water (1.58 ppm at 25°C) (Ansari et al., 2022). Combining it with the experimental time, it was possible to evaluate the average volumetric flow rate of the gases coming from the cathode. The volume of oxygen generated was always half that of hydrogen according to the stoichiometry of the reaction.

2.6 Experiments with Direct Current Voltage Source

The decomposition potential refers to the minimum electrical voltage required to initiate an electrochemical reaction, such as the electrolysis of water. This value is theoretical and gives an idea of the initial amount of energy, in the form of electricity, needed to decompose the electrolytic solution. The decomposition potential can be determined using the current-voltage graph. The quantification of the decomposition potential value of a galvanic cell can be constructed as shown in Figure 2; when y (ordinate value), the current value in mA increases, i.e., departs from the zero value then x (abscissa value), which represents the decomposition potential, gives the value of the decomposition potential.

Figure 1 **-** Current values as a function of voltage for different values of active electrode length for electrolyte concentration of 2 mg/L.



Source: Nefedov et al. (2023).

Figure 2 shows the decomposition potential required to initiate the electrolysis of water, visualized on a current-voltage graph. When the current (y) begins to increase, it indicates that the decomposition potential (x) has been reached. Figure 2 illustrates this relationship for different electrode lengths and electrolyte concentration of 2 mg/L.

The overpotential is the difference between the theoretical decomposition potential and the actual potential observed during an electrochemical reaction. In practice, overpotential is the additional voltage that must be applied to overcome additional resistances in the cell, such as electrolyte resistance, contact resistance, and kinetic factors at the electrode surfaces. It is influenced by various factors, including the nature of the electrode, electrolyte concentration, and temperature. Electrochemical reactions in a system can proceed when various types of overpotentials are overcome.

Full factorial experimental design is a powerful technique for assessing the influence of multiple factors on a response

variable. In this method, all possible combinations of levels of each factor are tested. This allows for the identification of interactions between factors and how each contributes individually to the final outcome. When analyzing the results, it is possible to determine which combinations of factors lead to the best results and optimize the operational conditions. This approach is particularly useful in processes with scientific, industrial, and engineering applications, where efficiency and optimization are crucial. Full factorial provides a comprehensive view of the effects of factors and their interactions, facilitating evidence-based decision-making to improve processes or products.

Additionally, the collected data allows for rigorous statistical analysis, which can reveal non-obvious insights into the relationships between factors and the response variable. In the end, full factorial experimental design can provide crucial information to improve efficiency, reduce costs, and optimize processes.

In the experiments with the DC voltage source, the electrical voltage and electrolyte concentration in the production of hydrogen for the fabricated galvanic cell were initially evaluated. For this, a full factorial experimental design with three levels and two variables (32), as shown in Table 1, was performed. The response variable for verification of the relationships contained in Table 1 was the percentage efficiency of hydrogen production (h[%]).

Table 1 - Full 3^2 factorial design applied to the alkaline electrolysis cell used for hydrogen production without the presence of an ultrasonic field.

Factor/Encoded Values	**-1**	**0**	**+1**
(X_1) Applied Voltage, V	3.7	7.4	11.1
(X_2) Electrolyte concentration - NaOH, moL/L	2.0	3.5	5.0

Source: Prepared by the authors (2024).

For the elaboration of the planning matrix, the electrical voltage (V) was coded as X1, the concentration of [NaOH] as X2.

$$X_1 = \frac{V - 7.4}{3.7} \quad (6)$$

$$X_2 = \frac{[NaOH] - 3.5}{1.7} \quad (7)$$

The experiments at the central point for each electrode type were performed in 3 repetitions, i.e., reproducibility equal to 4. Thus, the aim of this experimental step was to select the operational parameters that would maximize hydrogen production for tests including an ultrasonic electrode (Ratova et al., 2023).

3. Results and Discussion

3.1 Choices of Experimental Conditions

The benchtop prototype constructed is shown in the photograph of Figure 3. In the center of the unit, the electrolytic cell was placed, and on the sides, to the left, are the instruments for measuring electrical parameters (voltage, current, frequency), and to the right are the power sources, generator, and transducer, responsible for supplying ultrasonic waves to the cathode. This electrode was chosen to directly receive the ultrasonic vibrations since it is responsible for generating gas in greater quantity, that is, the volume of hydrogen is expected to be 2 times the volume of oxygen. At the cathode outlet, a duct can discharge the produced hydrogen to a gasometer built with the adaptation of a 200 cm3 burette. The oxygen was released into the atmosphere, as quantifying it was not the aim of this work. Thus, at the anode outlet, a valve was connected to discharge the oxygen

accumulated by the pressure of the hose at the end of each experimental run. A Minipa M-Scope 60 digital multimeter performed measurements of electrical current, voltage, and ultrasonic frequency. The reaction temperature was measured by a thermocouple with a digital temperature display brand TENMARS, model TM744-R. The experiments were conducted at room pressure and temperature.

Figure 2 - Prototype accompanied by instrumentation in the performance of alkaline electrolysis experiments without and with the action of ultrasonic electrode in the laboratory production of green hydrogen.

Source: Authors (2024).

Figure 3 depicts the prototype of the galvanic cell, which includes a central electrolytic cell, electrical measurement instruments on the left, and power sources on the right. The chosen electrode in the center receives ultrasonic waves, increasing the production of hydrogen. The hydrogen is collected in a gasometer, while the oxygen is released. Measurements of current, voltage, and temperature were taken during the experiments under ambient conditions.

The 3^2 factorial design matrix with associated results is shown in Table 2. It is observed that the electrolyte records efficiencies ranging from 50.23% to 86.12%, depending on the operational conditions of voltage and electrolytic solution concentration. The cell efficiency increases with increasing electrolyte concentration because the higher concentration reduces the concentration polarization effect, increases the ion diffusion rate to the electrode, and increases ionic conductivity (Guo et al., 2023).

However, after an additional 3.7 V, the efficiency decreases again, as observed in Table 2. One explanation for this phenomenon could be the maintenance of the temperature at a constant value. Increasing the temperature maximizes ion diffusion and reduces cell voltage, i.e., it reduces the energy requirements of the system, minimizes cell resistance, improves hydroxyl group conductivity, accelerates the electrochemical reaction rate, resulting in a higher hydrogen gas production rate, and reduces activation overpotential (Buelvas et al., 2014).

Table 2 - Matrix of the complete factorial design applied to the production of hydrogen by alkaline electrolysis of water in this work.

Experiment	X_1 V	X_2 moL/L	h %
1	(-1) 3.7	(-1) 2.0	80.01
2	(-1) 3.7	(0) 3.5	86.12
3	(-1) 3.7	(+1) 5.0	83.21
4	7.4	(-1) 2.0	59.65
5	7.4	3.5	60.3
6	7.4	(+1) 5.0	57.67
7	(+1) 11.1	(-1) 2.0	52.23
8	(+1) 11.1	3.5	56.56
9	(+1) 11.1	(+1) 5.0	50.23
10	7.4	3.5	61.51
11	7.4	3.5	63.45
12	7.4	3.5	59.99

Source: Prepared by the authors (2024).

The preliminary statistical analysis of the data obtained from Table 2 generated Table 3, or the ANOVA table. All terms (linear and quadratic) of the independent variables had their statistical importance confirmed by Fisher factors or confidence level values (p-value < 0.05). The explained variance, which is responsible for explaining the phenomenon by the experimental data, was estimated at 98.39%.

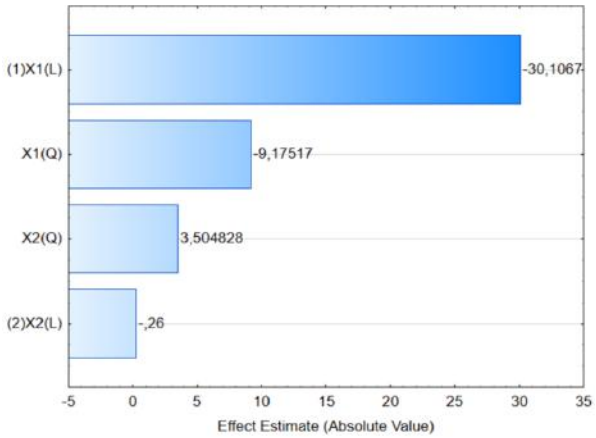
Table 3 - ANOVA table resulting from the analysis of experimental data from the application of full factorial design of hydrogen production by alkaline electrolysis.

Factor	**Sum Quadratic**	**Degree of freedom**	**Average Quadratic**	**Factor of Fisher**	**Value of p**
X_1	1592.125	2	796.0623	243.6546	0.000000
X_2	34.028	2	17.0141	5.2076	0.035617
Experimental error	26.137	8	3.2672		
Total Sum Squared	1618.364	12			

R2=0.9839; R=0.9756. Source: Prepared by the authors (2024).

Figure 4 illustrates the influences of each factor by quantifying them in the form of a Pareto diagram (Hamali et al., 2023). This figure clearly shows that, statistically, the voltage is much less influential on the process efficiency than the electrolyte concentration, as both effects have negative signs.

Figure 3 - Pareto chart corresponding to the ANOVA Table (Table 3).

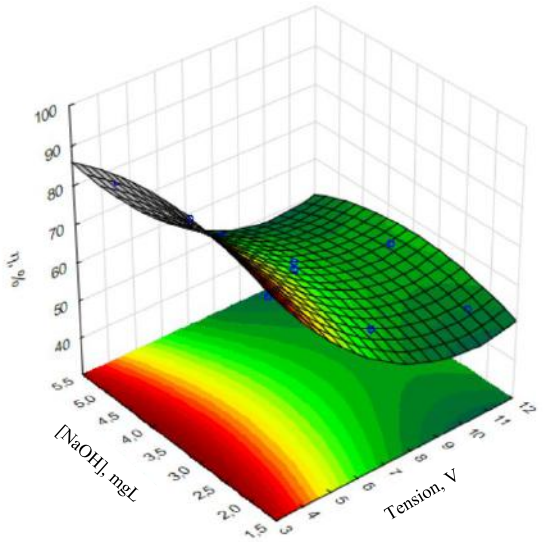


Source: Prepared by the authors (2024).

In Figure 4, this Pareto diagram illustrates the influence of different factors on the efficiency of hydrogen production by alkaline electrolysis. It highlights that the electrolyte concentration has a more significant effect than the voltage, as indicated by the negative effects associated with each factor.

The response surface obtained for the application of the full factorial design to the electrolysis of the prototype used in this work is shown in Figure 5. In this figure, the hydrogen production efficiency is plotted as a function of the factors (voltage between electrodes and electrolyte concentration). As discussed earlier, while maintaining the electrolyte temperature constant, the graph shows an average increase in hydrogen production efficiency with increasing electrolyte concentration (mol/L) and voltage between the electrodes (V). The maximum efficiency value is located for a voltage of 3.7 V and 3.5 mol/L. Therefore, this value was selected for comparison tests between operational conditions without and with an electrode under the influence of an ultrasonic field.

Figure 4 - Graph of the response surface for hydrogen production by alkaline electrolysis (NaOH) with AISI 314 electrodes 4.80 cm apart.



Source: Prepared by the authors (2024).

In this Figure 5, the hydrogen production efficiency is represented as a function of the factors voltage between the

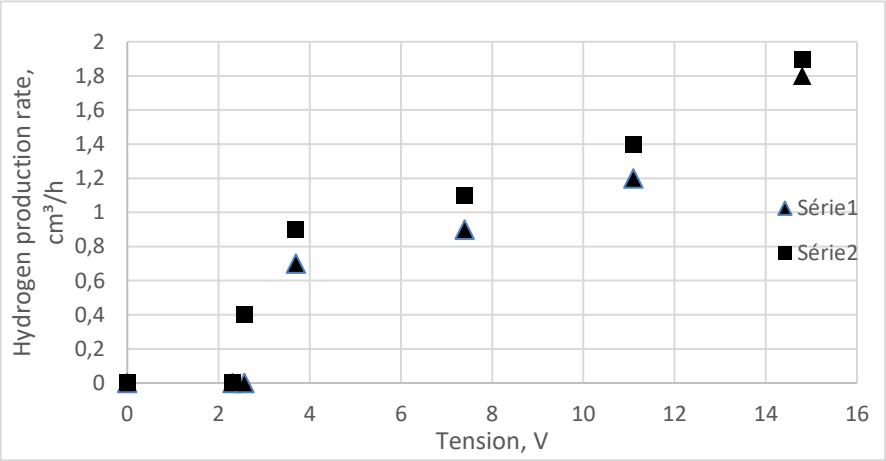
electrodes and electrolyte concentration. As discussed earlier, while maintaining the electrolyte temperature constant, the graph shows an average increase in hydrogen production efficiency as the electrolyte concentration (mol/L) and voltage between the electrodes (V) increase.

3.2 Production of Green Hydrogen Without and With the Use of Ultrasonic Electrodes

The experiments were conducted at a constant temperature of 29°C, controlled by the flow of water as a coolant for the electrolyte. The experiments were carried out for the electrolyte at a concentration of 3.5 mol/L, with and without the insertion of an ultrasonic frequency of 40 kHz through a direct connection with the cathode, at a power of 50 W (0.05 kW). Figure 6 presents the curves of hydrogen production rates using alkaline electrolysis without and with the action of the ultrasonic cathode. The figure shows that, as Zadeh (2014) pointed out, the hydrogen generation rate increases with the voltage between the electrodes.

The behaviors of the processes, differentiated by the presence of an ultrasonic field, are identical. The production of hydrogen in alkaline electrolysis with sodium hydroxide improved from about 0.7 to 0.9 cm3/h without and with the presence of an ultrasonic field directly on the cathode.

Figure 5 - Green hydrogen production rate curves without and with the use of ultrasonic electrodes.



Source: Prepared by the authors (2024).

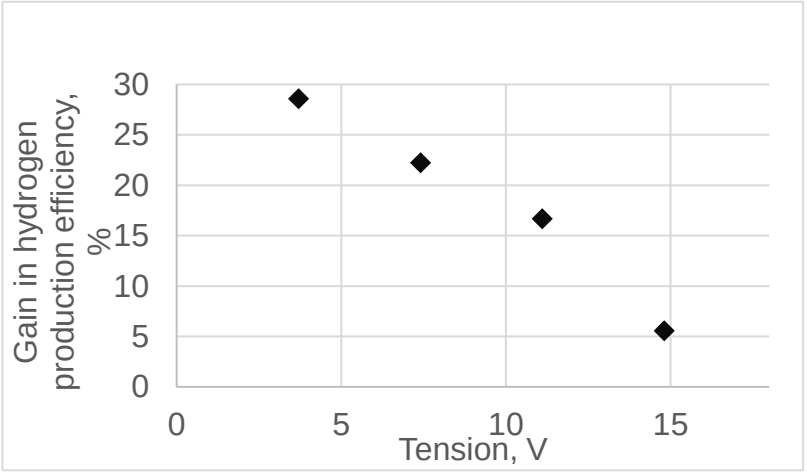
In Figure 6, the curves of green hydrogen production rates are presented both without and with the use of ultrasonic electrodes. The presence of the ultrasonic field directly on the cathode resulted in an increase in hydrogen production, improving from 0.7 to 0.9 cm3/h. This suggests that the application of ultrasound had a positive impact on the efficiency of alkaline electrolysis with sodium hydroxide.

Figure 7 displays the behavior of the percentage difference between the rates of green hydrogen generation without and with the presence of an ultrasonic field directly on the cathode of the galvanic cell. It is also observed that the differences between the hydrogen production rates decrease with the increase in voltage between the electrodes. Sound waves with a frequency of 40 kHz dissipate more energy compared to high frequency, which causes the formation of cavitation bubbles. This is responsible for the cleaning action of the electrode surface with ultrasound as Kumar and Lim (2022) describe, preparing the electrode for more electrochemical reactions, resulting in better hydrogen productivity.

In this work, measurements of specific energy consumption (kWh/m3) for the bench prototype showed that the variation between the two processes (without and with the ultrasonic field) was on the order of ±0.5%, practically the same, despite the higher efficiency caused by the electrode modified by the US. Li, Wang, and Chen (2009) obtained variations of about ±3%.

This difference can be attributed to the use of a higher concentration electrode, that is, 3.5 M, compared to the higher concentration of NaOH used by Li, Wang, and Chen (2009), which was 1.0 M NaOH.

Figure 6 - Efficiency gain between production processes with ultrasound compared to the conventional alkaline electrolysis process.



Source: Prepared by the authors (2024).

In Figure 7, the percentage difference between the hydrogen production rates with and without ultrasound at the cathode is shown. It can be observed that the differences decrease with increasing voltage. The 40 kHz ultrasound increases energy diffusion, forming bubbles that clean the electrode and increase productivity. The efficiency variation between the processes was ±0.5% in terms of specific energy consumption.

4. Conclusion

This study has demonstrated that integrating ultrasonic electrodes into alkaline water electrolysis for green hydrogen production can significantly increase process efficiency. The results indicate an improvement in hydrogen productivity and energy efficiency, evidenced by an increase of up to 28%, with a constant 40 kHz ultrasonic field applied to the cathode, associated with an ultrasonic generator with a specific power of 8.9 W/cm3 of 3.5 M NaOH electrolyte volume.

The role of acoustic cavitation in promoting mass transfer and reducing overpotential is central to these advances. Furthermore, the study highlights the importance of optimizing parameters such as ultrasonic frequency and intensity, and electrolyte concentration. In practical terms, this approach offers a promising path to make green hydrogen production more viable and economical.

For future research, it is suggested to explore different electrode materials and integrate this technology into real systems of renewable energy sources and large-scale hydrogen production, aiming at industrial applicability and environmental sustainability.

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