GENERATION OF GREEN HYDROGEN FROM OIL PRODUCTION WATER

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Dedication

To my beloved wife, whose love, patience, and unwavering support have been the light that illuminated my path in the most challenging moments. Her presence has been a constant source of inspiration and joy in this journey.

To my mother and grandparents, whose stories and teachings have been an integral part of my life. Their example of perseverance and endless love have guided me at every step of this adventure.

To my brothers, invaluable companions at every stage of my life, whose fraternal support and sincere advice have been essential in the achievement of my goals.

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Por último, he sometido esta disertación a la herramienta de integridad académica, definida por la universidad.

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Ever Herrera Ríos

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Resumen

GENERACIÓN DE HIDRÓGENO VERDE A PARTIR DE AGUA DE PRODUCCIÓN PETROLERA

El principal objetivo de este estudio es evaluar el efecto del contenido de aceite del agua de producción de campos petroleros sobre la producción de hidrógeno verde por electrólisis en presencia de puntos cuánticos de carbono (CQD). Para ello, se utilizaron diversas técnicas electroquímicas, como la voltametría de barrido lineal (LSV), la voltametría cíclica (CV) y la potenciometría, para identificar el efecto del petróleo crudo durante la producción de hidrógeno. Los resultados muestran que el uso de CQD afecta la eficiencia faradaica, la cual aumenta del 78% al 83% con la incorporación de CQD. En presencia de CQD, los efectos generados por la presencia del petróleo se inhiben a bajas concentraciones de petróleo. Por el contrario, la producción de hidrógeno aumenta un 10,0% (0,1 ml/min) con una eficiencia Faradaica del 83% y una eficiencia de media celda del 41%, frente al récord obtenido con la máxima concentración de crudo emulsionado (400 mg/ L). Se emplearon análisis termogravimétricos (TGA), espectrometría de masas (MS) y espectroscopía infrarroja por transformada de Fourier (FTIR) para discernir la adsorción de petróleo crudo en los electrodos, cuantificar las fracciones de gas generadas durante el proceso e identificar los grupos funcionales presentes en la conclusión del procedimiento, respectivamente. El tamaño de las gotas iniciales de la emulsión fue de 3,4 µm, al final de la prueba hubo evidencia de rotura completa de la emulsión debido al efecto del campo eléctrico aplicado. Según las pruebas, no se observa evidencia de adsorción de petróleo crudo en electrodos de grafito durante la electrólisis. Se ha demostrado que la producción de hidrógeno verde a partir del agua de producción de petróleo crudo es factible debido a la propuesta de un electrolito disruptivo en el agua producida que inhibe el efecto del contenido de aceite en la emulsión O/W. Esto permite la implementación de una nueva iniciativa de producción de energía verde alineada con el objetivo global de lograr cero emisiones netas (NZE) para 2050. La investigación actual presenta una alternativa prospectiva para aprovechar el potencial de energía eléctrica de 18 kW empleado en los procesos de ruptura de emulsiones dentro de un Campo colombiano para tratamiento alrededor de 1000 bblopd. Esta alternativa ofrece un potencial teórico para la producción de hidrógeno, de aproximadamente 7,6 kW, lo que representa una oportunidad prometedora para el despliegue práctico en el campo.

Palabras clave: Agua de producción, CQDs, Electrólisis, Grafito, Hidrógeno.

Abstract

GENERATION OF GREEN HYDROGEN FROM OIL PRODUCTION WATER

The main objective of this study is to evaluate the effect of the oil content of oilfield production water on the production of green hydrogen by electrolysis in the presence of carbon quantum dots (CQDs). For this purpose, various electrochemical techniques, such as linear sweep voltammetry (LSV), cyclic voltammetry (CV), and potentiometry were used to identify the effect of crude oil during hydrogen production. The results show that the use of CQDs affects the Faradaic efficiency, which increases from 78% to 83% with the incorporation of CQDs. In the presence of CQDs, the effects generated by the presence of the oil are inhibited at low oil concentrations. On the contrary, hydrogen production increases by 10.0% (0.1 ml/min) with a faradaic efficiency of 83% and a half-cell efficiency of 41%, compared to the record obtained with the maximum concentration of emulsified crude oil (400 mg/L). Thermogravimetric analysis (TGA), mass spectrometry (MS), and Fourier-transform infrared spectroscopy (FTIR) were employed to discern the adsorption of crude oil onto the electrodes, quantify the gas fractions generated during the process, and identify the functional groups present at the conclusion of the procedure, respectively. The size of the initial emulsion droplets was 3.4 µm, at the end of the test there was evidence of complete breakage of the emulsion due to the effect of the applied electric field. No evidence of adsorption of crude oil on graphite electrodes during electrolysis is observed based on the tests. It has been shown that green hydrogen production from crude oil production water is feasible due to the proposed of a disruptive electrolyte in the produced water which inhibite the effect of the oil content in the O/W emulsion. This allows the implementation of a new green energy production initiative aligned with the global goal of achieving net zero emissions (NZE) by 2050. The current investigation presents a prospective alternative for harnessing the 18 kW electrical energy potential employed within emulsion-breaking processes within a Colombian field for treatment around of 1000 bblopd. This alternative offers a theoretical potential for hydrogen production, approximating 7.6 kW, thus representing a promising opportunity for practical field deployment.

Keywords: Crude oil; CQDs; Electrolysis; Graphite; Hydrogen; Produced water

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Introduction

Hydrogen is currently used in various applications, such as refining, steel, ammonia, and methanol production [1, 2]. Several types of hydrogen production can be categorized into different colors depending on the kind of energy used. These categories include gray, blue, and green hydrogen, among others.

Green hydrogen production involves the use of renewable energies and is achieved through the process of electrolysis. In contrast, gray and blue hydrogen use fossil fuels for H_2 production, with the difference that blue hydrogen uses CO_2 capture mechanisms. Another variety called aqua Hydrogen is produced from fossil fuels but inhibits CO_2 emissions [3-5].

To improve the efficiency of hydrogen production, different strategies have been developed that focus on using different electrode materials and different electrolytes to optime their designs [6-11]. However, one of the challenges in this process is the type of water used since it requires high purity to avoid blockage and deterioration of the electrodes. Currently, some studies focus on using seawater for hydrogen production. Nevertheless, the possibility of sustaining the oxygen evolution reaction (OER) versus the chlorine evolution reaction (ClER) at the anode is challenging due to corrosive processes [12, 13].

An alternative water source is found in the oil and gas industry, which oil wells can produce huge amounts of water. For instance, about 1.7 MMbbl/day of water can be produced in a field in Colombia [14]. However, the produced water from oilfields may contain different contaminants that would affect hydrogen production, such as Mg and Ca salts that adhere to the electrode surface and emulsified crude oil. Several studies have investigated the use of industrial wastewater or vegetable oil as feedstock for electrolysis, and have found that the presence of vegetable oils can extend the life of electrodes by creating a protective layer on their surface, which prevents corrosive processes [15, 16].

Hence, new alternatives and novel technologies should be developed to improve the efficiency and reduce the associated problems during hydrogen production. The material used to produce hydrogen should have a large active surface area to aid in the kinetics of electron transport. This is easily accessible in carbon-based zero-dimensional (0D) and two-dimensional (2D) materials. Particularly for 0D materials, such as carbon quantum dots (CQDs), the surface electric potential is strong, the surface area is vast, the solution dispersion is excellently uniform, lowering the intermediate dissociation energy, and surface functional groups such as -COOH, -OH, -C=O results in the enhancement of kinetics of electrocatalysis [17, 18].

However, to the best of our knowledge, there are no studies reported in the specialized literature that evaluate the production of green hydrogen by electrolysis using produced water from oil wells or making use of electrolytic nanofluids such as CQDs. Therefore, the main objective of this study is to evaluate the effect of the oil content in the produced water for production of green hydrogen and hence provide a baseline scenario with this technology. Additionally, the use of CQDs in produced water like a disruptive nanoelectrolyte will be analyzed considering its conductivity and Hydrogen Evolution Reaction (HER) favoring properties to improve the studied system.

This document is comprised of four chapters, delineating the theoretical foundations, research methodology, results obtained, and the conclusions and recommendations arising from the study.

Chapter 1: Foundations

Introduction to green hydrogen generation and its significance in the current energy context.

Overview of produced water in Colombian oil fields.

Fundamentals of Carbon Quantum Dots (CQDs) and their application in chemical processes.

Chapter 2: Methodology

Detailed description of the experimental methodology employed in the research.

Procedures for the preparation of crude oil and produced water emulsions.

Setup and calibration of equipment for hydrogen generation and measurement.

Chapter 3: Results

Presentation and analysis of data derived from the experiments.

Assessment of the impact of emulsified crude content on the efficiency of hydrogen production.

Chapter 4: Conclusions and recommendations

Interpretation of the findings in relation to existing literature.

Discussion on the effectiveness of CQDs in enhancing green hydrogen generation.

Summary of the key discoveries of the study.

1. Foundations and Key Concepts: An Introduction

As the global population continues to escalate, so does the demand for energy. This surge in energy demand has significantly impacted climate change, as higher energy consumption correlates with increased greenhouse gas emissions, further exacerbating global warming. In 2018, global energy consumption rose by 2.3% compared to 2017, along with a 1.7% increase in CO2 emissions, totaling 33.1 Gigatonnes (Gt) [19]. The Energy Institute reports that over the past decade, global energy consumption has been escalating at an average annual growth rate of 1.4%. The emissions of greenhouse gases, including methane, carbon dioxide, and nitrous oxide, are notably high due to the combustion of fossil fuels. With the current trajectory of industrial and urban development, these emissions are projected to continue their upward trend. The existing and anticipated levels of these gases, barring a shift in energy sources, are likely to lead to a range of environmental and health repercussions, such as shifts in climate patterns, rising sea levels, ecosystem disturbances, and severe health issues. The environmental impacts and health hazards associated with fossil fuel consumption pose a substantial threat to humanity [20-22].

Hence, hydrogen has garnered special interest as a viable energy alternative, attributed to its high calorific value. Currently, hydrogen finds diverse applications in refining, steel, ammonia, and methanol production [1, 2]. Various hydrogen production methods can be categorized into different 'colors' based on the type of energy utilized. These categories include gray, blue, and green hydrogen. The production of green hydrogen entails the utilization of renewable energies, achieved through electrolysis. In contrast, gray and blue hydrogen are produced from fossil fuels, with the distinction that blue hydrogen incorporates CO_2 capture mechanisms. Another variety, termed aqua Hydrogen, is derived from fossil fuels but inhibits CO_2 emissions [3-5].

To enhance the efficiency of hydrogen production, various strategies have been developed focusing on utilizing diverse electrode materials and electrolytes to optimize their designs [6-11]. However, a challenge in this process is the type of water used, as it necessitates high purity to prevent blockage and deterioration of the electrodes. An excessive energy expenditure for water treatment prior to electrolysis would be counterproductive, especially considering the projected increase in the global urban population facing water scarcity from 933 million (one-third of the world's urban population) in 2016 to 1.693-2.373 million (one-third to nearly half of the world's urban population) by 2050 [23].

Recent studies have focused on utilizing seawater for hydrogen production. Nonetheless, sustaining the oxygen evolution reaction (OER) versus the chlorine evolution reaction (CER) at the anode poses a challenge due to corrosive processes [12, 13]. An alternative water source is found in the oil and gas industry, where oil wells can produce vast amounts of water. For instance, a field in Colombia can produce around 1.7 million barrels/day of water [14]. However, the produced water from oil fields may contain various contaminants that could affect hydrogen production, such as Mg and Ca salts adhering to the electrode surface and emulsified crude oil. Several studies have investigated the use of industrial wastewater or vegetable oil as feedstock for electrolysis, finding that the presence of vegetable oils can prolong electrode life by creating a protective layer on their surface, preventing corrosive processes [15, 16].

Thus, new alternatives and innovative technologies should be developed to enhance efficiency and mitigate associated problems during hydrogen production. The material used for hydrogen production should possess a large active surface area to aid in the kinetics of electron transport, which is readily available in carbon-based zero-dimensional (0D) and two-dimensional (2D) materials. Specifically for 0D materials, such as carbon quantum dots (CQDs), the surface electric potential is strong, the surface area vast, the solution dispersion uniformly excellent, lowering intermediate dissociation energy, and surface functional groups like -COOH, -OH, -C=O result in enhanced electrocatalysis kinetics as they provide more favorable anchoring sites and active sites for the preparation of high-performance multicomponent composite materials, additionally heteroatom-doped CQDs (N, S, P, B, etc.) with multicomponents could also promote the electrocatalytic properties of the compounds by enhancing electron transfer through internal interactions [17, 18, 24]. Supported nanoparticles on working electrodes such as those based on graphene oxide and CQDs have been used, as they increase electrical conductivity and have a great capacity to absorb energy, due to their good characteristics such as large surface area, multiple active edge and defect sites, rapid electron transfer, and electron reservoir properties [25-28]. The only reported work in which electrolytic nanofluids are used was performed by Wei et al. [29] using carbon black nanoparticles at a concentration of 0.1% dispersed in the surfactant sodium dodecyl sulfate SDS in the presence of light, increasing the hydrogen production rate from pure water by about 30.4% [29, 30].

However, to the best of our knowledge, there are no studies reported in the specialized literature that evaluate the production of green hydrogen by electrolysis using produced water from oil wells or making use of electrolytic nanofluids such as CQDs. Therefore, the main objective of this study is to evaluate the effect of oil content in produced water for the production of green hydrogen and hence provide a baseline scenario with this technology. Additionally, the use of CQDs in produced water as a disruptive nanoelectrolyte will be analyzed considering its conductivity and Hydrogen Evolution Reaction (HER) favoring properties to improve the studied system.

During the study, the results of hydrogen and chlorine production with and without CQDs were evaluated to identify the effect that crude oil has on the electrolyte and possible associated reaction mechanisms. This study opens a wider landscape of green hydrogen production and the role of the oil and gas industry in the energy transition.

This research addresses a critical gap in current knowledge by exploring the use of produced water, an abundant by-product in the oil and gas industry, as a water source for green hydrogen generation. The use of this water not only represents an opportunity to recycle an industrial waste but can also significantly reduce costs and the environmental footprint of hydrogen production.

Thus, this project not only contributes to the emerging field of green hydrogen but also provides an innovative perspective on the management of industrial by-products and the use of advanced nanomaterials. The success of this research could pave the way for new strategies in green hydrogen production, marking a significant milestone at the intersection of nanotechnology and energy sustainability.

2. Materials and Methods

2.1 Materials

Deionized water, NaCl (99.5%, LOBA Chemie, India), a Colombian intermediate crude oil with API gravity of 25.7° and Tween 80 (Protokimica, Colombia) were used for the preparation of crude oil in water (O/W) emulsion. The working crude oil has a content of saturates, aromatics, resins and asphaltenes of 48.9%, 24.5%, 24.5%, and 2.1%, respectively. Carbon quantum dots (CQDs) were synthesized according to a previous study [27]. Main properties of the employed CQDs are summarized in Table 1.

Table 1. Properties of CQDs

Property	Value
Maximum emission wavelengh (nm)	453
Maximum excitation wavelengh (nm)	350
Thickness (nm)	0.5-1.0
Mean diameter (nm)	30
Zeta Potential (mV) @pH=7	-3.7
pH point of zero charge	3.0

2.2 Methods

The objective of this study is to explore the feasibility of producing green hydrogen from oil production waters by utilizing carbon quantum dots (CQDs) to mitigate the adverse impact on system conductivity, as outlined in Table 2. CQDs are chosen for their conductive and advantageous properties in the HER, which have been well-documented in existing literature. This work is an initial step towards the development of a viable approach for green hydrogen production in the context of oil production waters. The interest lies in finding an alternative option to produce this energy source using the volumes of water produced in oil fields. To accomplish this, a variety of analytical techniques such as cyclic voltammetry

(CV), linear sweep voltammetry (LSV), potentiometry (P), Fourier transform infrared spectroscopy (FTIR), digital microscopy (DM), thermogravimetric analysis (TGA) and mass spectrometry (MS) were applied in triplicate to gain insight into the reaction mechanisms associated with the system, both in the presence and absence of crude oil.

Efficiency calculations were carried out considering Faraday's first law, which is a consequence of the law of conservation of matter, which states that during electrolysis the released mass is directly proportional to the electric charge transferred. Therefore, if during a time, t, a current flow, I, circulates in the system, the amount of moles of generated hydrogen, N, is:

$$N = \frac{It}{2F} \qquad (1)$$

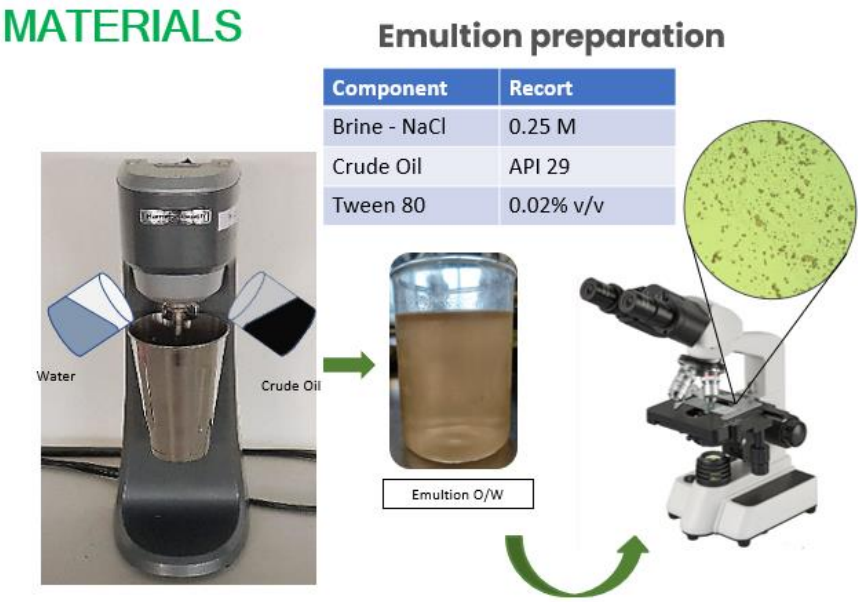
With F=96485 [C/mol]. This amount of hydrogen would produce with a faradaic efficiency of 100%. The determination of faradaic efficiency involves measuring the mass or volume of produced hydrogen and comparing it to the theoretical value derived from the ideal gas equation, considering that hydrogen behaves as an ideal gas under ambient conditions. The calculated theoretical volume can be obtained by applying Equation 2, for the recorded pressure and temperature conditions during the study.

$$V = \frac{nRT}{P} \qquad (2)$$

It was validated with a mass spectrometer (Shimadzu GC-MS, Tokyo, Japan) and provoking combustion. The faradaic efficiency was calculated comparing the actual value with the maximum theoretical value.

2.2.1 Emulsion preparation

For emulsion preparation Figure 1, firstly, a 0.25 M NaCl brine was prepared with deionized water with continuous stirring at 600 rpm. The crude oil-in-water (O/W) emulsions were prepared by mixing the brine and crude oil at 16000 rpm for 30 minutes for different oil concentrations of 10, 100, and 400 mg/L. Emulsion stability was ensured by monitoring through microscopy (Motic BA310) every 24 hours, removing the supernatant, and finishing with filtration every 48 hours [14].



Component	Recort
Brine - NaCl	0.25 M
Crude Oil	API 29
Tween 80	0.02% v/v

Figure 1. Preparation of working emulsion with Colombian crude oil and representative brine.

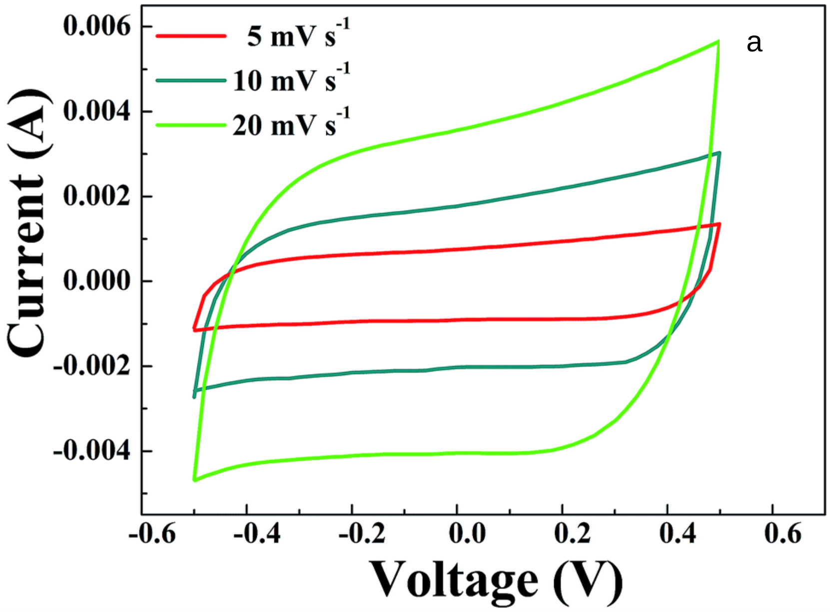
2.2.2 Experimental Setup

The experimental setup was designed in a sterile glass container, using an Ag/AgCl reference electrode (Gamry Instrumentals, Warminster, USA) and an INTERFACE 1000 potentiostat (Gamry Instrumentals, Warminster, USA). Considering the content of Na^+ and Cl^- ions in the electrolyte, an inert electrode is required. For this reason, given its good conductivity and low cost, parallel graphite electrodes were used. Each electrode exposes an effective geometric area of 22.5 cm^2, with a separation of 3.5 cm between electrodes. The assembly and reference electrode were validated with the results reported by Quan et al. [31]. The cyclic voltammetry curves for graphite electrodes in NaCl 1 M solution were obtained at 2, 5 10, 20, and 50 mV/s. In addition, the sweep speed in the study was set at 20 mV/s with a working potential of -2 V. The CQDs were synthesized using a microwave-assisted carbonization methodology, adapted from that reported by Franco et al. [27].

The gases were collected and characterized using a mass spectrometer (Shimadzu GC-MS, Tokyo, Japan), additionally, FTIR (Shimadzu GC-MS, Tokyo, Japan) analysis was performed on the working electrolyte before and after each test to identify if there was any change in the composition of the electrolyte as a consequence of the reaction mechanisms present in the system during the electrolysis. Flow rate, pH, conductivity, and temperature were recorded before the process to evaluate the repeatability of the system.

2.3 Validation system

The assembly and reference electrode validation were conducted in accordance with the findings of Xueping Quan et al. [31]. As depicted in Figure 2.a, the results of Xueping Quan and Figure 2.b of the validation system, for the graphite electrode immersed in a 1 M NaCl solution, was employed scan rates of 2, 5, 10, 20, and 50 V/s. The cyclic voltammetry readings were in concordance, demonstrating a deviation of merely 2%. The profiles of the voltammograms exhibited symmetrical shapes, devoid of any distinct oxidation or reduction peaks.



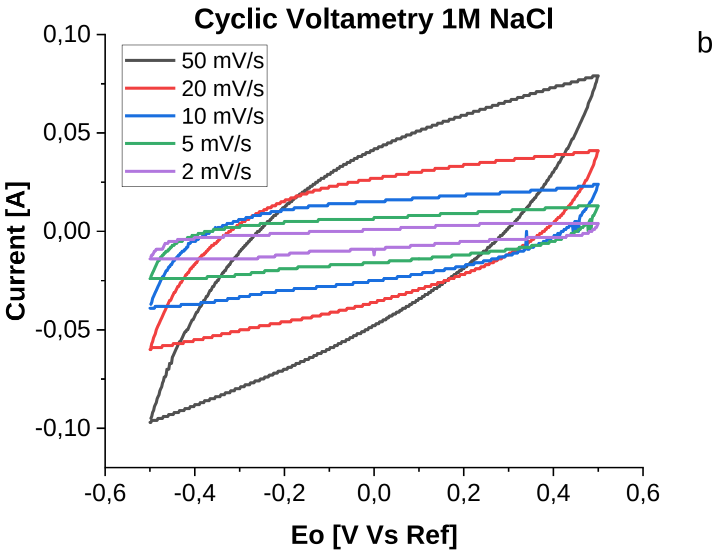


Figure 2. Cyclic Voltammetry curves graphite electrode in NaCl 1 M solution at five rate scans (a) Taken from [31], (b) Own elaboration.

3. Results

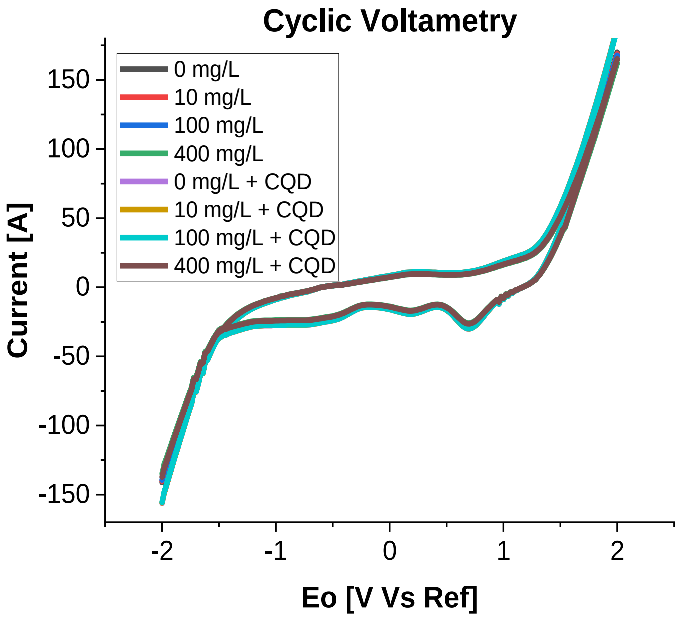
The chronoamperometry test times were set in periods of 21 hours for crude concentrations of 0, 10, 100, and 400 mg/L. Three test voltages of 2, 3, and 4V were previously evaluated, and the one that provided a sufficient gas bubble production and showed the system's least heating was selected. For this case, a fixed potential of -2V was used, since it allowed abundant production of bubbles above the reaction initiation potential, where the temperature increase inside the cell at the end of the test was approximately 1.0 °C. Thus, the formation of water vapor that could cause deviations in the quantification of the gases produced was reduced. The conductivity, pH, droplet size, and temperature at the beginning of the tests are summarized in Table 2.

Table 2. Starting Conditions Table for the oil in water emulsions in the presence and absence of CQDs.

Parameter	**Crude oil content (mg/L)**				**Crude oil content (mg/L) +100 (mg/L) CQDs**			
	0	**10**	**100**	**400**	**0**	**10**	**100**	**400**
Conductivity (mS/cm)	26.35	26.35	26.08	25.66	26.56	26.54	26.48	26.45
pH	6.0	6.0	6.0	6.0	6.0	5.8	5.8	5.8
Droplet Size (µm)	0	3.4	3.4	3.4	0	3.4	3.4	3.4
Temperature (°C)	23.2	23.1	23.2	23.3	23.3	23.2	23.2	23.2

The efficiency of the system during the hydrogen evolution reaction (HER) and chlorine evolution reaction (CER) was analyzed using chronoamperometry and Faradaic Efficiency. Tafel curves were obtained to identify the overpotential required to reach a reference current density that is present in all four evaluated systems to recognize the effect of crude oil during the process. Figure 3a shows the CV curves for the studied crude oil concentrations with and without CQDs. The scan rate was fixed at 20 mV/s because it was observed that at low speeds there are no significant changes in the scanning of the system and in this way loss of information is ruled out for lower scanning speeds, the initial potential (Eo) was -2 V, the cathodic cut-off potential (Ec) was -2 V, and the anodic cut-off potential

(Ea) was 2 V. The systems (with and without CQDs) present an oxidation peak of 0.71 V, which corresponds to the theoretical potential for H_2O_2 production (Eo = 0.695 V) [20]. Since the durability of the electrodes is always an important step in the development of new processes such as the one implemented in this work, Figure 3b presents the response in the potentiometry during 21 hours for the graphite electrodes and the four concentrations of crude oil worked with and without CQDs, an increase in the current values over time can be appreciated, this is because the worked solution is not fed back and taking into account that the electrolyte is becoming richer in OH - anions as the electrolysis progresses the response in conductivity favors the passage of current. This allows inferring that for the worked concentrations of crude oil, there is no considerable impact on gas production. In the presence of carbon quantum dots (CQDs), there is evidence of an improvement and decrease in the reduction and oxidation reactions, respectively.



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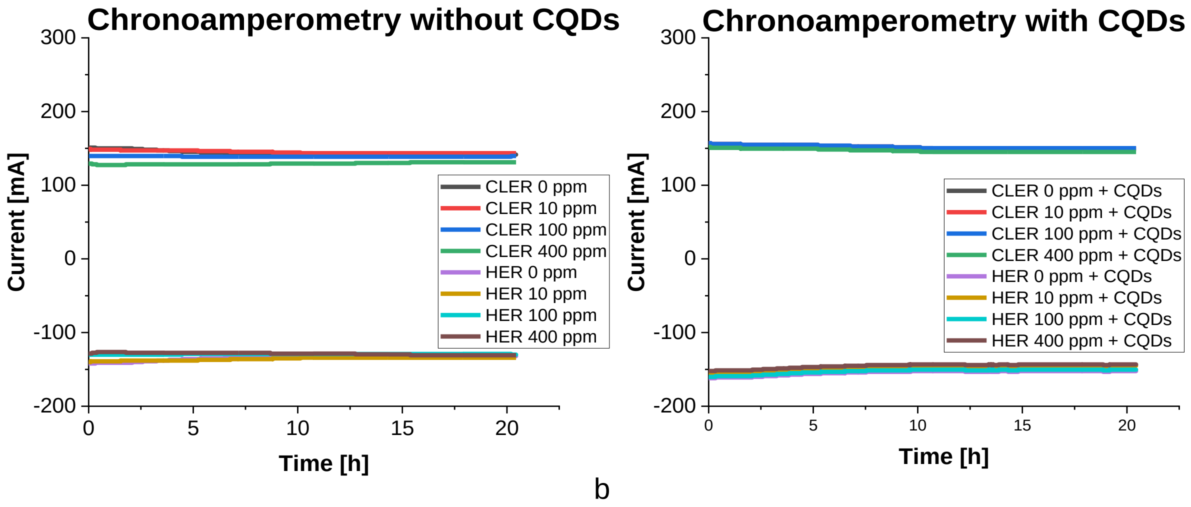


Figure 3. (a) CV cyclic voltammetry for four crude oil concentrations with scanning rate set at 20 mV/s with and without CQDs. (b) Potentiometry for 23 hours to evaluate the behavior of the system including the production flow rate with and without CQDs.

3.1 Chlorine Evolution reaction (CER)

Figure 4.a illustrates the Linear Sweep Voltammetry (LSV) curve within the potential range of 1.0 to 2.0 V for the Chlorine Evolution Reaction (CER). The highest potential recorded in the systems was obtained without crude oil (169.5 mA). With the addition of crude oil, a slight decrease in current was observed for concentrations of 10 mg/L (168.2 mA), 100 mg/L (167.2 mA), and 400 mg/L (161.8 mA) of crude oil, while maintaining the percentage of chlorine produced at 7% in all cases. These results suggest that the presence of crude oil in the systems without CQDs leads to a reduction in conductivity as the concentration of crude oil increases, but it does not influence the fraction of chlorine produced. This behavior is consistent with the conductivity data in Table 2, where higher crude oil concentrations correspond to decreased conductivity or increased solution resistivity [32].

The CER aligns with the theoretical value of chlorine production. The amount of generated gas during the analysis supportthe chosen working potential, as values above 1.8 V resulted in significant gas evolution on the electrodes. The constructed Tafel diagram in

Figure 4.b from the LSV curve demonstrates a slope indicating low kinetics for this type of electrode. Furthermore, the Logarithm of Current Density records for CER at concentrations of 0, 10, 100, and 400 mg/L were 0.877, 0.874, 0.871, and 0.857 Log(mA/cm2), respectively.

Moreover, it is pertinent to highlight that the in-situ production of hypochlorites can be feasibly achieved through the electrolysis of a sodium chloride (NaCl) solution. This process notably requires only NaCl in the feed stream to engender hypochlorous acid (HOCl) and hypochlorite (OCl−) ions. In such scenarios, various researchers advocate for meticulous control over the quantity and concentration of the resultant hypochlorite solution. This precaution is advised owing to the contaminating formation of undesirable and potentially deleterious byproducts, including trihalomethanes and haloacetic acids [33].

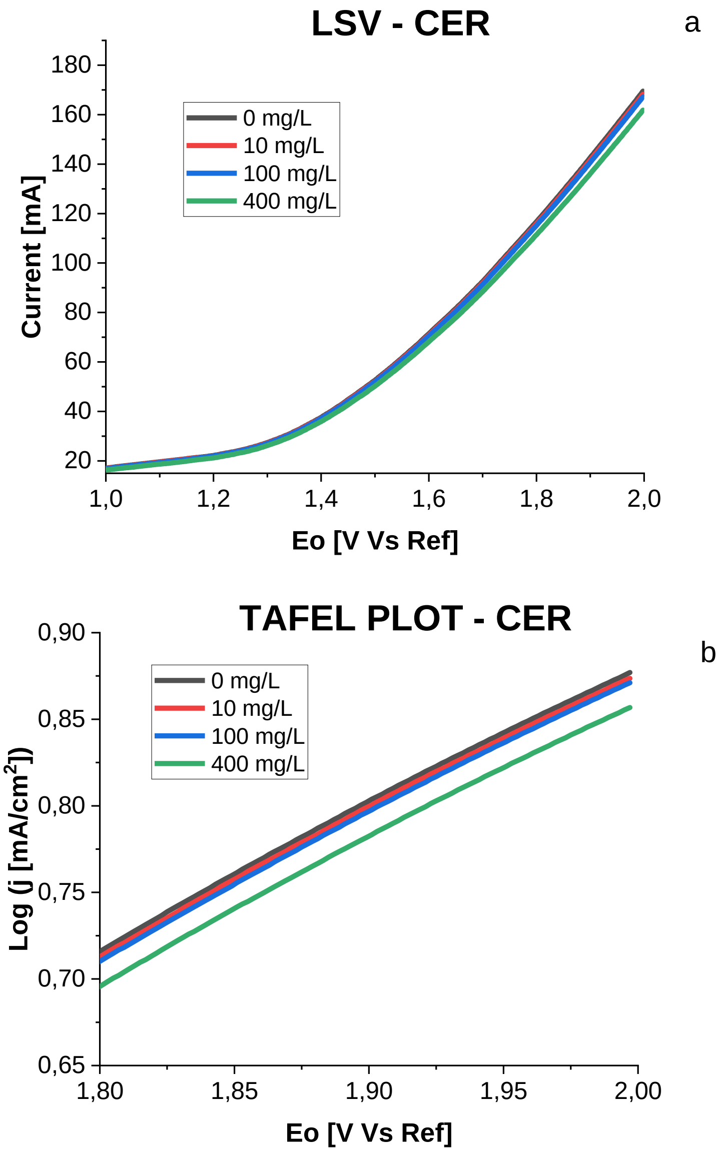


Figure 4. (a) LSV curves in the potential range of 1.0 V and 2 V for the four scenarios studied. (b) Tafel Plot for Chlorine Evolution Reaction (CER).

3.2 Hydrogen Evolution reaction (HER)

In Figure 5.a, the Linear Sweep Voltammetry (LSV) curve is depicted for the potential range from -1.0 to -2.0 V pertaining to the Hydrogen Evolution Reaction (HER). Analogous to the

Cathodic Electrochemical Reaction (CER), current density values exhibit a similar trend to those observed in CER at the working concentrations. The data indicate a lower current density reading for a crude oil concentration of 400 mg/L, yielding -134.8 mA, and a higher current density for 0 mg/L of crude oil, with -141.2 mA. This behavior elucidates that the presence of crude oil in the system engenders an unfavorable response in terms of the system's conductivity as the concentration increases. Furthermore, the Tafel plot, derived from the LSV curve presented in Figure 5.b, delineates a slope value that is indicative of sluggish kinetics for this type of electrode. The rate-determining step and the kinetic velocity for HER are observed to fluctuate between 0.80 and 0.78 Log(mA/cm²).

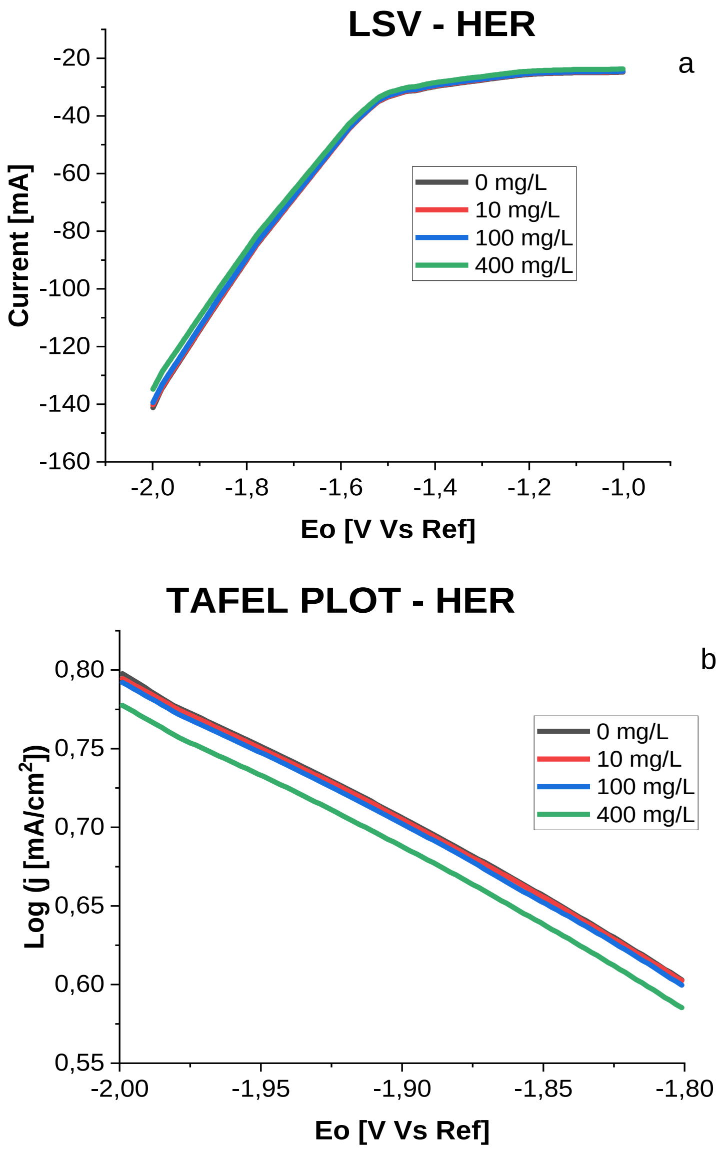
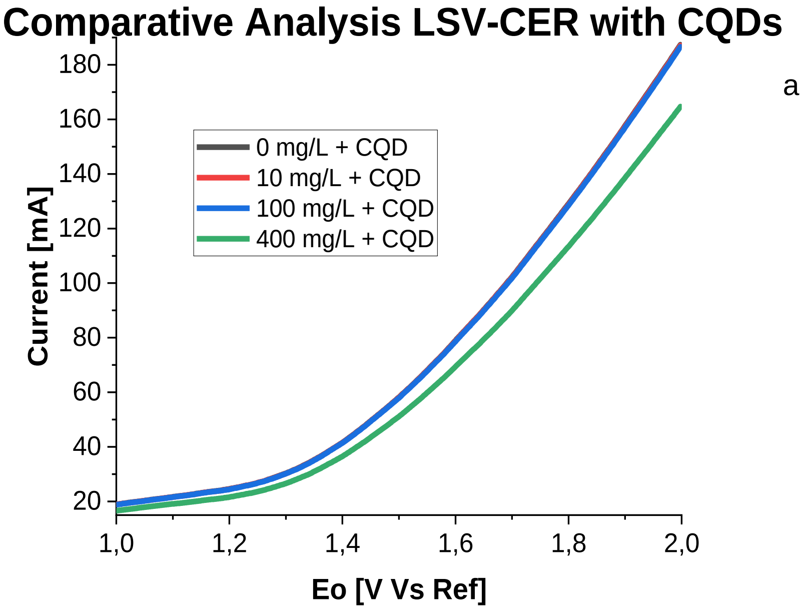


Figure 5. (a) LSV curves for the potential range between -1.0 and -2.0 V for the scenarios studied. (b) Tafel Plot for hydrogen evolution reaction (HER) (without CQDs).

3.3 Effect of the presence of CQDs in Chlorine evolution reaction

With the addition of 100 mg/L of CQDs in each of the evaluated systems, an improvement in the chlorine evolution reaction (CER) can be observed in Figure 6.a This coincides with the analysis carried out in mass spectrometer. The Tafel diagram in Figure 6.b, elaborated from the LSV curve and the registration of the geometric area of the working electrodes, shows a slope value that describes low kinetics for this type of electrode. In addition, it is observed that the speed and the determining step for CER in the concentrations of 0, 10, 100, and 400 mg/L, the Logarithm of Current Density were 0.92, 0.92, 0.92, and 0.86 Log(mA/cm^2), respectively. In the presence of CQD, a greater anodic slope is observed. In future work, it is expected to identify changes in the activity, selectivity, and stability of the reaction due to other reactive species that may additionally be present. [34-37].



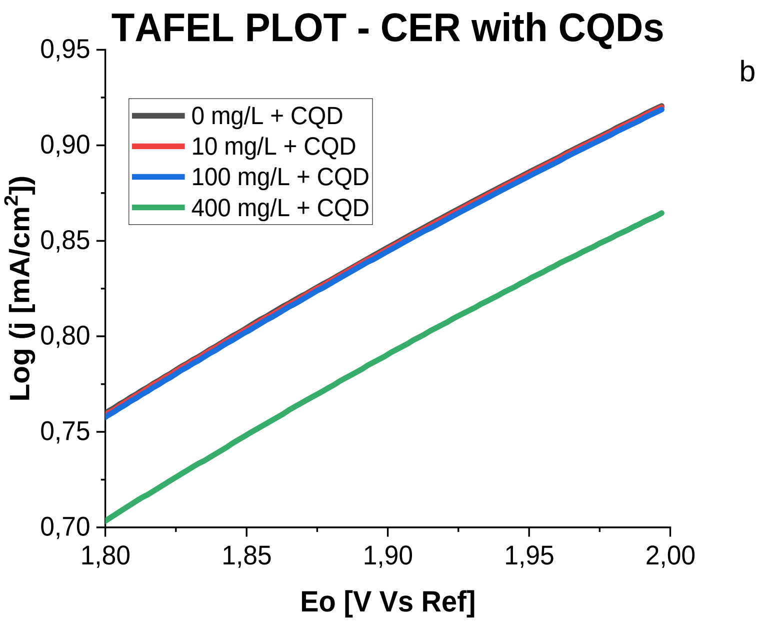
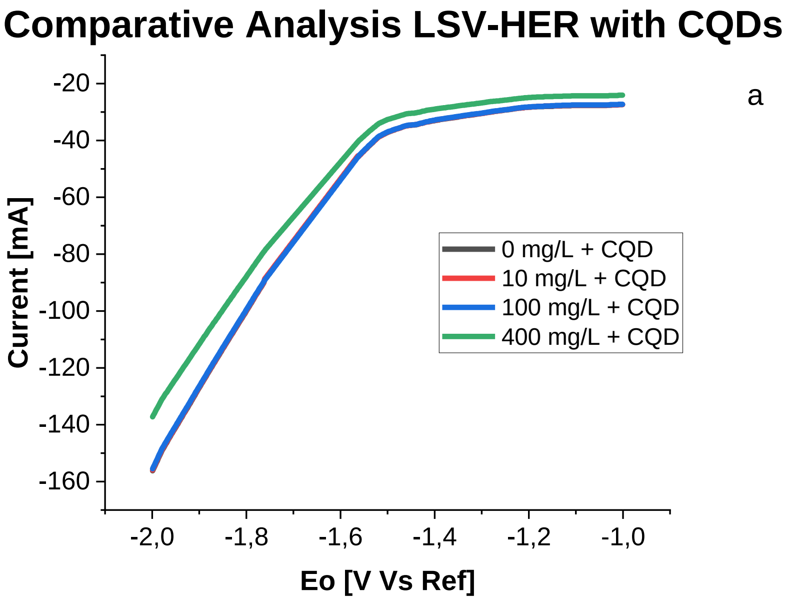


Figure 6. (a) LSV curves for the potential range between 1.0 and 2.0 V for the scenarios studied with CQDs. (b) Tafel Plot for hydrogen evolution reaction (CER) with CQDs.

3.4 Effect of the presence of CQDs in Hydrogen evolution reaction

When the CQDs are added to each of the systems, a favorable response is evidenced in terms of current density for the same work potential, this increase indicates a greater number of species reacting at the cathode. The improvement of the catalytic activity of HER is due to the improvement in the electron transfer rates in solution because the surface of the CQDs is composed of a hydrophobic carbon core which primarily contains C-C bonds, whereas the surfaces contain abundant hydrophilic functional groups such as hydroxyl, carbonyl, and carboxyl groups, the number of H+ ions increases when the CQDs are ionized under acidic conditions, resulting in the acceleration of ion transmission in the solution [38-40].

With the records of the anodic and cathodic reaction of the system, it can be inferred that the concentration of crude oil does not have a considerable implication for the potential of the system Figure 7.a. In addition, in terms of the quantified production efficiency concerning the Hydrogen produced, it was an average of 81%. The results observed with the addition of 100 mg/L of CQDs in the systems show an improvement in the total production of gases and even more in the production of hydrogen according to the measurements of flow and fractions of gases produced, the faradic efficiency shows an improvement of 6% going from 77% in the system with crude oil to 83% in the presence of CQDs, these results show the impact on HER kinetics with the presence of crude oil in the system is inhibited with the presence of CQDs Figure7.b.



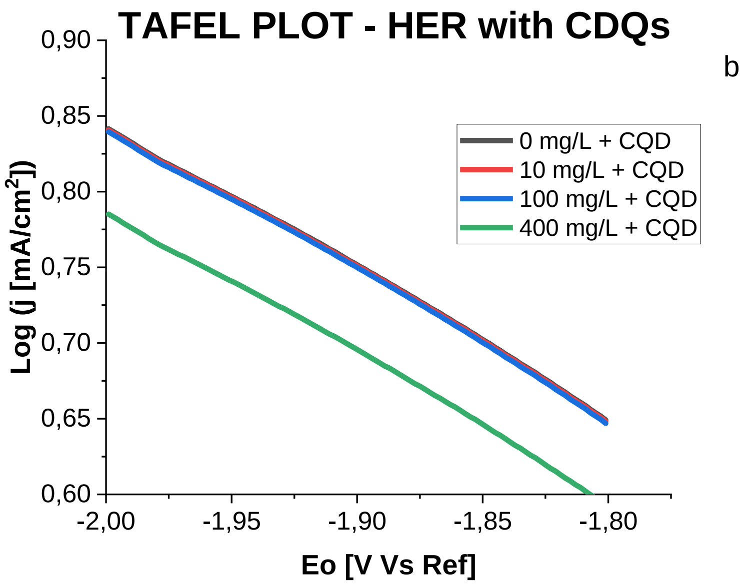


Figure 7. (a) LSV curves for the potential range between -1.0 and -2.0 V for the scenarios studied with CQDs. (b) Tafel Plot for hydrogen evolution reaction (HER) with CQDs.

3.5 Produced gas analysis in the absence and presence of CQDs

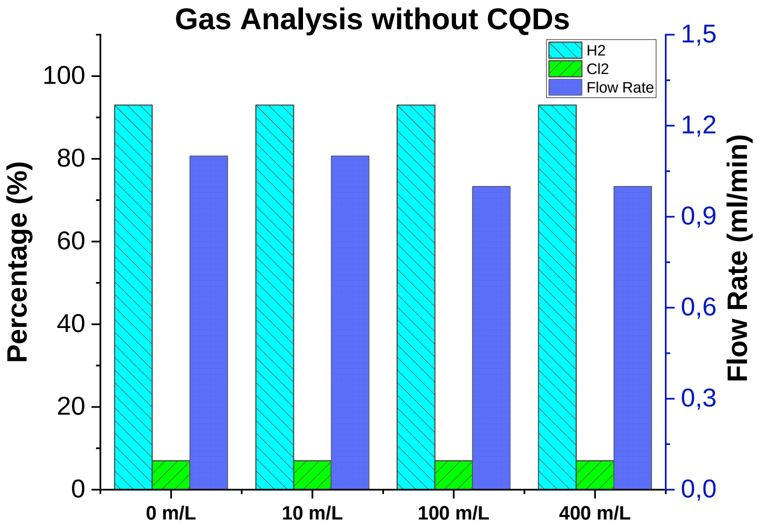
The gases produced were analyzed by a mass spectrometer and the production flow was quantified using a GFM17 mass flow meter (AALBORG INSTRUMENTS & CONTROLS, INC. Canada), no changes in the fractions produced (93% hydrogen and 7% chlorine) are evident with and without crude oil and in the absence of CQDs, but if a 9% reduction in the total flow is observed between the 0 mg/L and 400 mg/L crude system, this is associated with the drop in the system's conductivity with the increase in the crude oil concentration. This allows us to identify that at lower concentrations of crude oil emulsified in water, there is no impact on the total volume of production, nor on the fractions produced. However, with the increase in the concentration of crude oil in the water, there is a reduction in the total volume produced as shown in Figure 8.a With the addition nano-electrolyte of CQDs, changes in both the anodic and cathodic potential as well as the total production can be observed. Figure 8.b, a greater total gas production is obtained with the addition of the CQDs in the systems, showing an inhibitory effect on the part of the CQDs that is more noticeable at low concentrations of crude oil. Future work is expected to identify the reaction

mechanisms and associated byproducts that may be being generated.

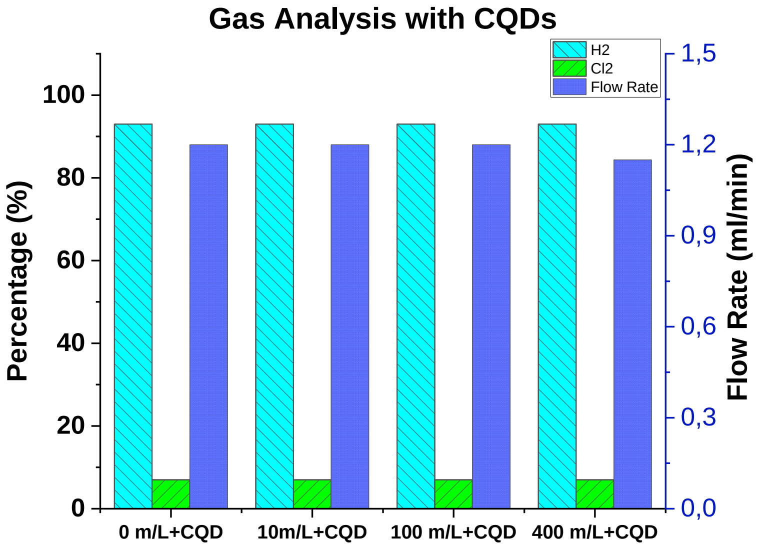
In the context of the HER and CER, cathodic current and anodic current measurements were acquired at a fixed potential of -2.0 and 2.0 V respectively, corresponding to a crude oil concentration of 400 mg/L. This specific potential was intentionally chosen due to its suboptimal performance and is intended to serve as a consistent benchmark across all experimental setups in terms of resistance. The findings, presented in Figure 8.c, Figure 8.d and quantified in terms of electrical resistance, reveal a compelling trend. It becomes apparent that, as the concentration of crude oil within the system increases, a higher overpotential is required to sustain an equivalent current density. This observed phenomenon can be attributed to the decreased electrolyte conductivity resulting from the presence of crude oil. In the presence of CQD, is observed enhanced conductivity exhibited within the system attributed to the inclusion of Carbon Quantum Dots (CQDs) in Figure 8.c and 8.d, it becomes evident that the influence exerted by the presence of crude oil is mitigated, particularly at lower concentrations of emulsified crude oil.

Table 3. Faradic efficiency

Parameter	**Crude oil content (mg/L)**				**Crude oil content (mg/L) +100 (mg/L) CQDs**			
	0	**10**	**100**	**400**	**0**	**10**	**100**	**400**
Faradaic Efficiency Hydrogen(gas)	80%	80%	78%	77%	80%	80%	80%	83%
Faradaic Efficiency Chlorine(gas)	5%	5%	5%	5%	5%	5%	5%	5%


Gas Analysis without CQDs
H2
Cl2
Flow Rate
Percentage (%)
0
20
40
60
80
100
Flow Rate (ml/min)
0,0
0,3
0,6
0,9
1,2
1,5
0 m/L
10 m/L
100 m/L
400 m/L

a


Gas Analysis with CQDs
H2
Cl2
Flow Rate
Percentage (%)
0
20
40
60
80
100
Flow Rate (ml/min)
0,0
0,3
0,6
0,9
1,2
1,5
0 m/L+CQD
10m/L+CQD
100 m/L+CQD
400 m/L+CQD

b

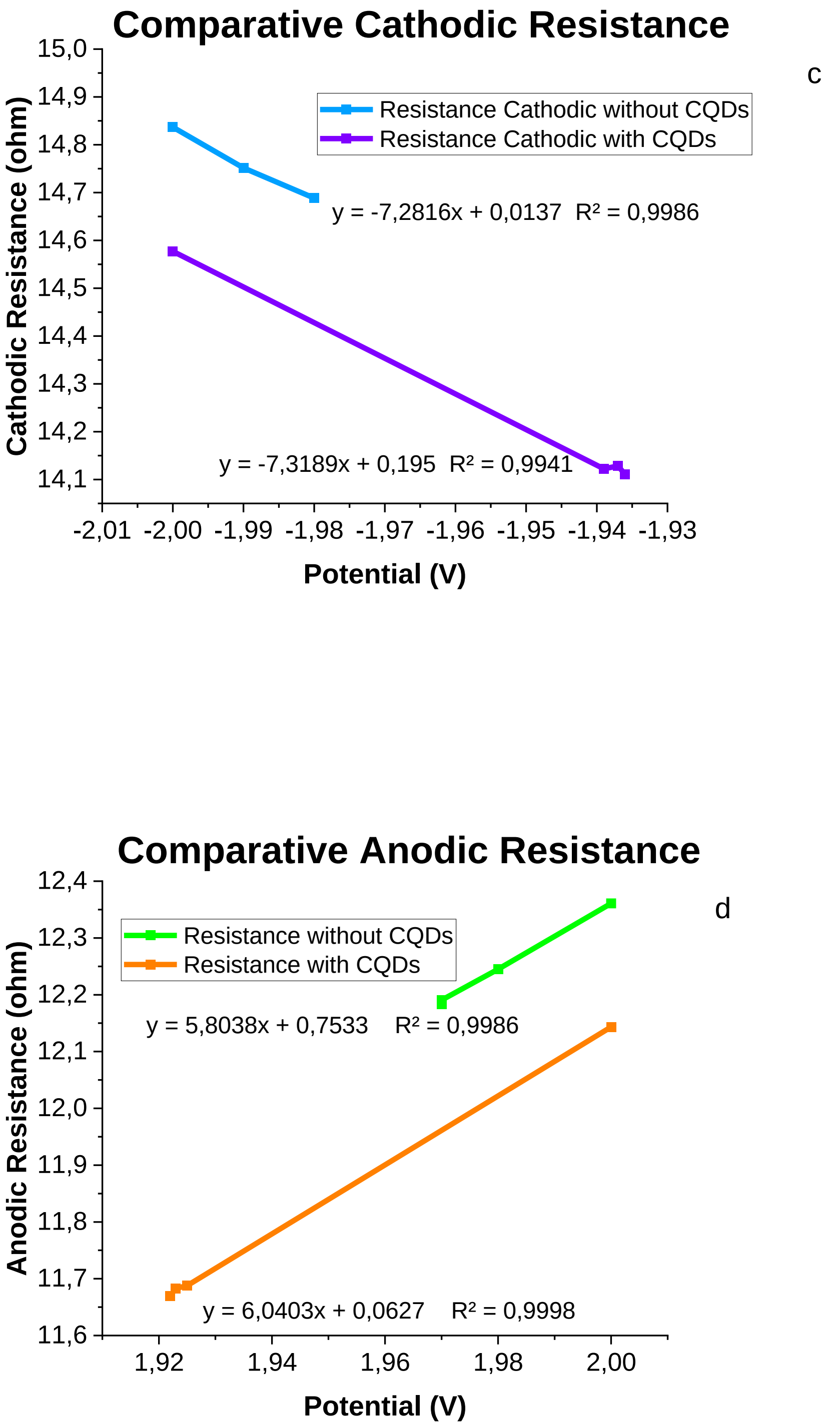


Figure 8. Mass percentage of gases concentrations of 0, 10, 100, and 400 mg/L of crude oil in water without (a) and with (b) CQDs. (c) Cathodic Resistance where the effect of the crude oil can be seen. (d) Anodic Resistance where the effect of the crude oil can be seen.

Table 3 presents a detailed summary of the faradic efficiencies observed. Notably, in the case of Chlorine Evolution Reaction (CER), a markedly low efficiency was observed, as determined through gas collection analysis. It's imperative to note that the feed stream requires only NaCl for the generation of HOCl and OCl− ions; however, these ions were not quantified in the study [33]. The observed low faradic efficiency for chlorine generation implies the occurrence of alternate electrochemical reactions. These reactions may be competing with the Oxygen Evolution Reaction (OER). Additionally, the degradation of hydrocarbons during the progression of the electrochemical reaction was meticulously monitored by quantifying the Chemical Oxygen Demand (COD) of the samples at various time intervals[41]. For a concentration of 400 mg/L of crude oil, the COD values recorded at 0, 3 and 6 hours were 485 mg/L O2, 465 mg/L O2, and 445 mg/L O2, respectively. These results notably indicate the system's low Faradaic efficiency, a phenomenon that warrants further exploration in future studies.

Future research endeavors aim to elucidate and quantify these competing mechanisms, determining whether complete electrodegradation transpires or if the process results in the formation of simpler carbon chains. This investigation is crucial, as indicated by the findings of Sharma et al., in the year of 2020 at Royal Society of Chemistry which suggest that complete electrodegradation is achievable only under specific conditions, such as the application of high potentials (12V) and the use of an oxidizing electrolyte like H2O2[41].

3.6 Material characterization

3.6.1 FTIR Analysis

FTIR analysis of the working electrolyte was performed before and after electrolysis with each of the crude concentrations described above to identify if there is any change in the composition because of the reaction mechanisms present in the system, the only difference was observed in the increase of the peak where the Cl vibration occurs round to 700 cm2 Figure 9.

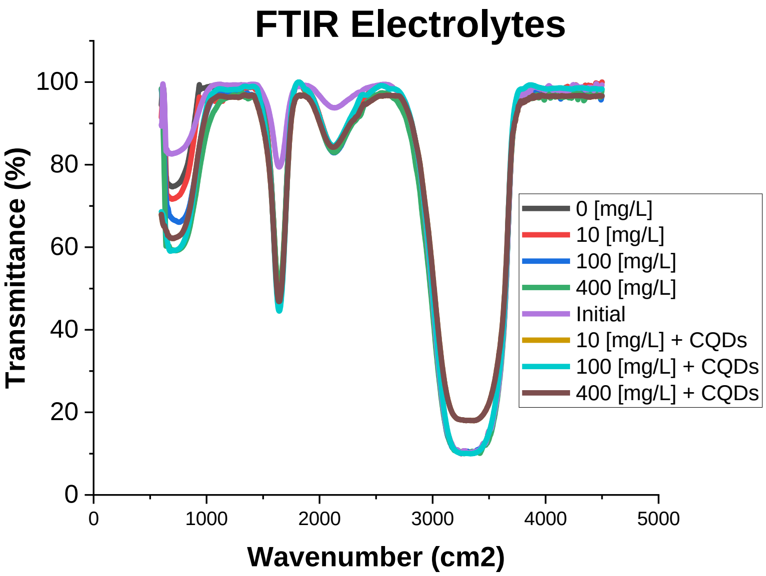


Figure 9. FTIR for concentrations of 0, 10, 100, and 400 mg/L with and without CQDs at the end of each test

3.6.2 Droplet size distribution analysis in emulsions

Additionally, the emulsion droplet size was monitored for the concentrations of 10, 100, and 400 mg/L with and without CQDs, the concentration in each case was obtained from a stock solution of known concentration Figure 10. a, then at the end of 21 hours of work the comparison between the initial solution Figure 10. b, 10. c, and 10.d shows a total breakage of the emulsion the droplet size distribution during the study can be observed in Figure 10. e.

The response in terms of breaking the emulsions is not as efficient as commercial processes that are currently found, this is due to the fact that the separation processes in commercial crude oil in water electrolyzers have numerous designs in which alternating current is used, but they can be useful with high water contents that favor charge transfer at an optimum frequency [42]. The effect of electric current, more precisely direct current (DC) has a significant effect on the breaking of emulsions and this effect depends on factors, such as the nature of the emulsion components, the intensity of the current, and the duration of the current application[43]. Additionally, commercial products are used as surfactants that favor the breaking of the emulsions formed.

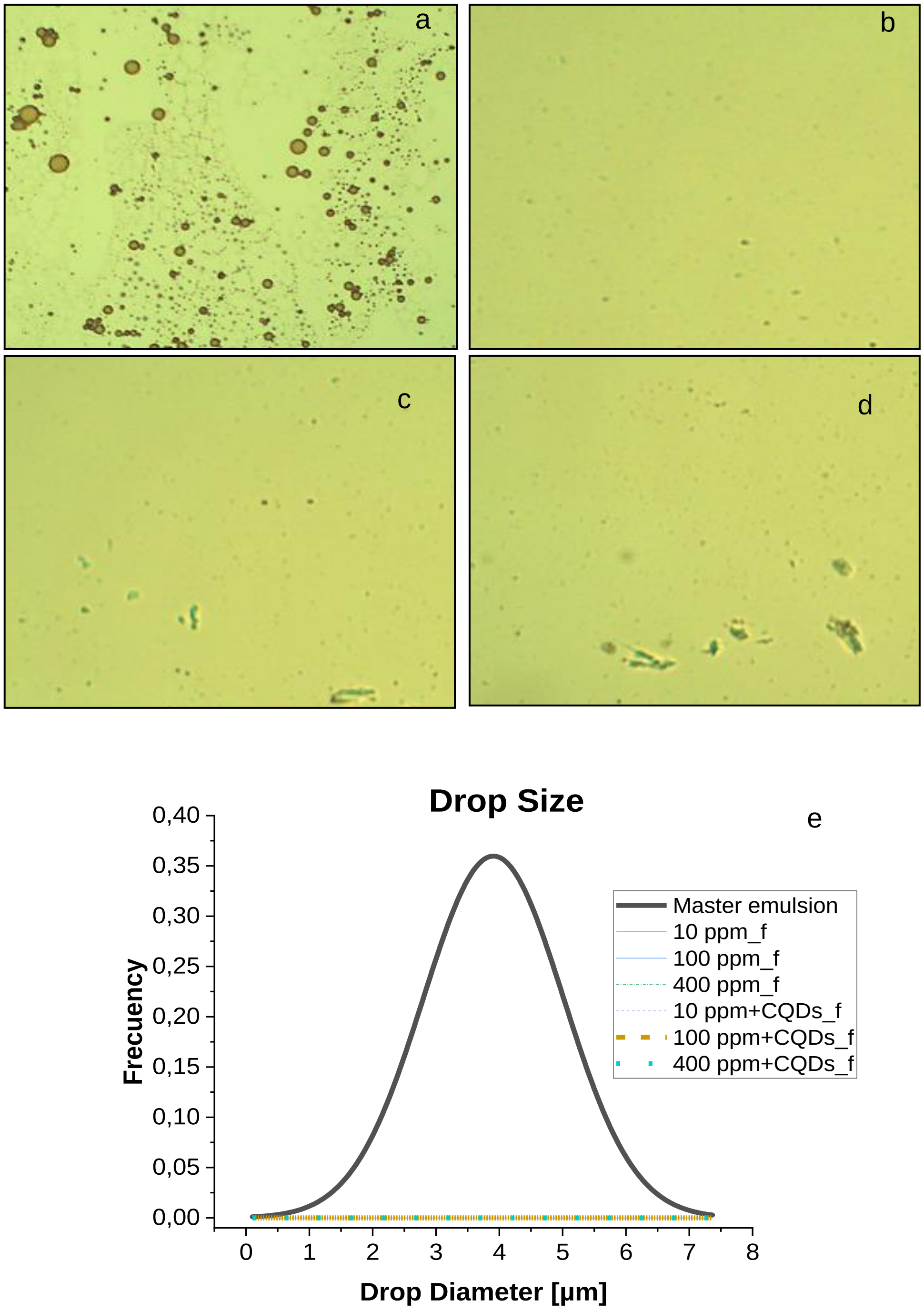


Figure 10. (a) emulsion in a stock solution of known concentration, Figures (b), (c), and (d) correspond to free crude oil in the electrolyte (total emulsion breakdown) after 21 hours for

10, 100, and 400 mg/L crude oil with and without CQDs, figure (e) shows the size distribution curves for each scenario evaluated.

3.6.3 Thermogravimetric analysis at working electrodes

Furthermore, thermogravimetric analysis was conducted on the crude oil used in the experiment, which revealed a 96% loss in sample mass at 340°C with a heating rate of 20°C/min. The analysis was also performed on the graphite electrodes before and after the 21-hour potentiometry test, as shown in Figure 11. For the electrodes used in 0 and 10 mg/L solutions, no significant change in mass was observed. However, for the electrodes used in 100 and 400 mg/L electrolytes, evidence of mass change was found, which could be attributed to the crude oil adhering to the electrodes after the test was completed rather than crude oil adsorption during the test. This observation aligns with the results of cyclic voltammetry and mass spectrometry tests, which did not reveal any byproducts during the process.

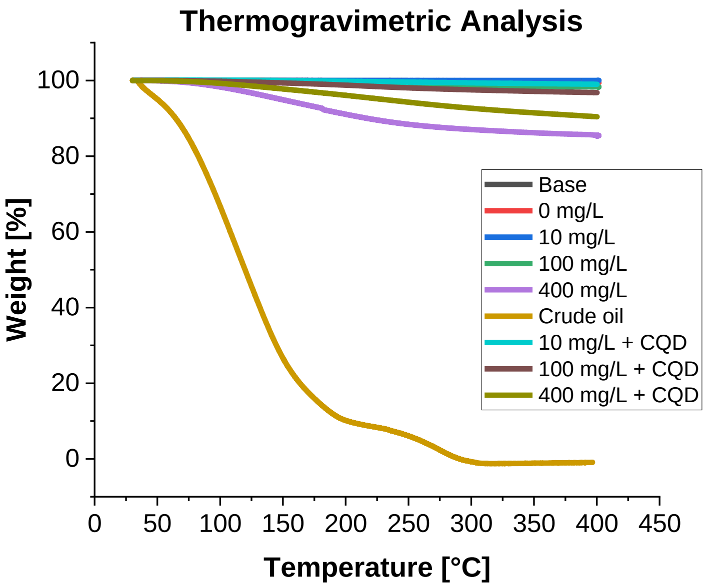


Figure 11. Thermogravimetric analysis for the crude oil and graphite electrodes before and after the 21-hour potentiometry test.

3.6.4 Thermogravimetric analysis at working electrodes

For a Colombian oil field with an approximate crude oil production of 2000 bbl/day, a free water knock-out (FWKO) separator is used in the primary separation process. Subsequently, the reservoir fluids undergo electric charges in an electrostatic separator with steel cells that help break down stronger emulsions and recover more crude oil in the field. This electrostatic separator has an electrical consumption of 18 kW. Comparing this consumption with the results obtained in this study, considering the semi-cell for the worst system, an efficiency of approximately 41% in a process that was not initially designed to be efficient, the schematic of the system installed in the field is shown in Figure 12. In this sense, there is an opportunity to generate green hydrogen in a process that has been used only for crude oil separation in oil fields. This could potentially reduce operating costs by being able to recycle this energy through a fuel cell.

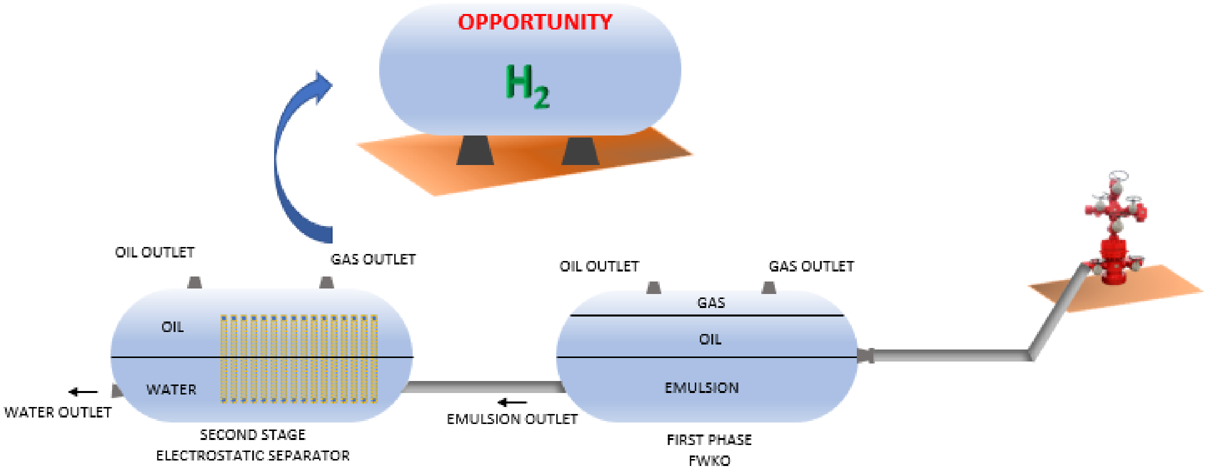


Figure 12. Schematic of separation process installed in Colombian field and Opportunity.

4. Conclusions and recommendations

4.1 Conclusions

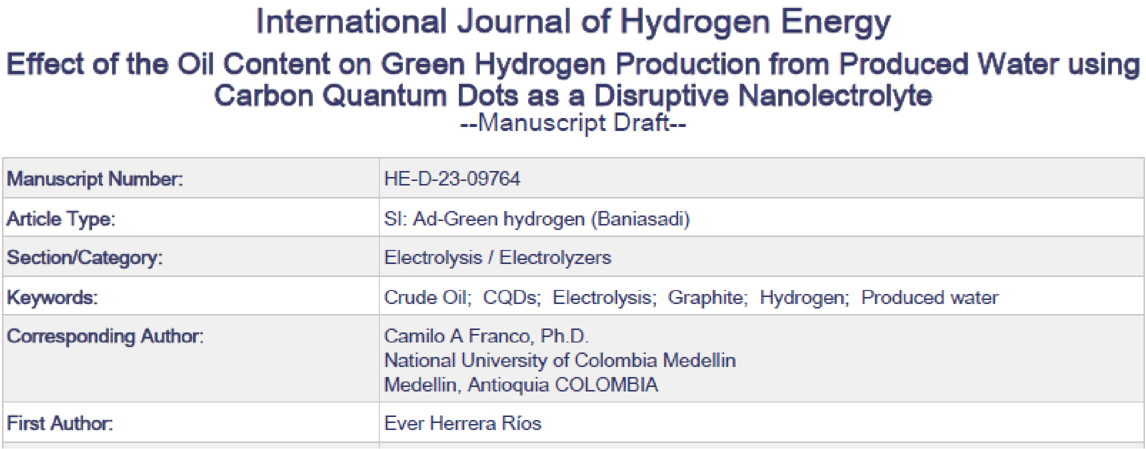
- The results show that the use of produced water in hydrogen generation is feasible and opens a new avenue of work to continue advancing in the improvement opportunities offered using nanoscale materials such as CQDs that were implemented as electrolytic nanofluids.
- The total gas production is reduced by increasing the concentration of crude oil, although no change is evident in the fractions of gases produced. With the addition of the CQDs, favorable impacts are observed in the system, first related to the total flow of gases produced, and second with a favoring of HER during the process.
- The emulsion droplet size decreases as the currents circulate, which ends with a complete breakdown of the emulsions in the system allowing studying in the future the effect of other components in the electrolyte such as different commercial surfactants or the use of dispersed nanoparticles to reduce the interfacial tension and favor coalescence between the raw droplets.
- Owing to the enhanced conductivity exhibited within the system attributed to the inclusion of Carbon Quantum Dots (CQDs), it becomes evident that the influence exerted by the presence of crude oil is mitigated, particularly at lower concentrations of emulsified crude oil.

4.2 Recommendations

Although notable results have been achieved, there are still opportunities for improvement that need to be addressed in the future. The problems and possible solutions are listed below:

(1) Selection of materials with high selectivity. with catalytic properties for HER and inhibition properties for CER that allow for longer electrode life.
(2) Evaluation of reaction mechanisms involved in the oxidation reactions with the presence of CQDs in the electrolyte.
(3) Optimization of the electrolytic cell design, recommendations in the function of the area, space between electrodes, and other crudes considering the compositional variation of hydrocarbons in the production time.
(4) Identify the effect of NaCl concentration or representative ions from other reservoirs in HER and CER.

The article is submitted to the International Journal of Hydrogen Energy with registration number HE-D-23-09764 of November 30, 2023



International Journal of Hydrogen Energy
Effect of the Oil Content on Green Hydrogen Production from Produced Water using Carbon Quantum Dots as a Disruptive Nanolectrolyte
--Manuscript Draft--

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Section/Category:	Electrolysis / Electrolyzers
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