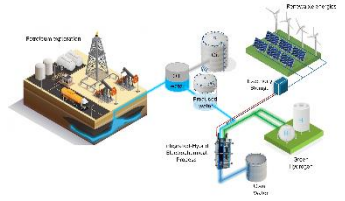
Replacing oxygen evolution reaction in water splitting process by produced water electrolysis with co-generation of green hydrogen: From wastewater to the future of the energetic industry

ORAL
Ph.D. Student: N
Journal: JECE

Danyelle M. de Araujo[1], Herbet L. Oliveira[1], José E. L. Santos[1], Jussara C. Cardozo[1], Amanda D. Gondim[1], Livia N. Cavalcanti[1], Fabíola Correia de Carvalho[2], Jose H.O. Nascimento[3], Carlos A. Martínez-Huitle[1,4], Elisama V. dos Santos[1,4]. (1) Renewable Energies and Environmental Sustainability Research Group, Institute of Chemistry, Federal University of Rio Grande do Norte, Campus Universitário, Av. Salgado Filho 3000, Lagoa Nova, CEP 59078-970, Natal, Rio Grande do Norte, Brazil, (2) Instituto SENAI de Inovação em Energias Renováveis, Avenida Capitão Mor Gouveia, 2770, Lagoa Nova, CEP 59063-400, RN, Brazil. (3) Research Group on Innovation in Micro and Nanotechnology, Department of Textile Engineering, Federal University of Rio Grande do Norte, Campus Universitário, Av. Salgado Filho 3000, Lagoa Nova, CEP 59072-970, Natal, RN, Brazil,(4) National Institute for Alternative Technologies of Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactives (INCT–DATREM), Institute of Chemistry, UNESP, P.O. Box 355, 14800 900 Araraquara, SP, Brazil. carlos.alberto.mh@ufrn.br



A proton-exchange membrane cell (PEM) featuring a BDD anode and a 316-Ni-Fe mesh as the cathode, energized by a solar source of energy through a photovoltaic (PV), was used as an integrated-hybrid approach to guarantee the decontamination of the effluent at the anodic compartment, while produces green H_2 at the cathodic one, both with a volume of 0.04 L. The electrolysis was performed by applying approximately 7, 13 and 26 mA cm^{-2} for up to 600 min. The study demonstrates that anodic oxidation achieves almost total mineralization of organics in various tested scenarios. Higher current densities are found to optimize green H_2 generation, yielding a theoretical value of 1.27 L of dry H_2 per 0.5 L of produced water (PW) treated over 10 h with favorable current efficiency (specifically 18.6 mA cm^{-2}). Overall, PW treatment and simultaneous green H_2 generation emerge as a promising solution, mitigating cost barriers associated with industrial effluents while promoting carbon-neutral energy, cleaner industries, decarbonized transportation, and resilient energy solutions.

Introduction

Approximately 630 million m^3 of oil and gas (O&G) are produced in Brazil per day [1], appearing among the world's 10-leading oil producers. However, this huge amount of O&G can lead to the production of up to 10 times of this value in produced water (PW), depending on the age of the oil well, which represents an astounding average value of 5670 million m^3 day^{-1} [2]. This exploration has a bigger concern mainly when it happens on shore, once the high-saline effluent must be properly treated and discharged to avoid polluting clean water bodies and other nearby ecosystems [3]. This research endeavors to overcome the complexities surrounding the treatment of PW in the sector, aiming to shed light on decreasing the involved costs in its treatment by developing an innovative technique. Production systems based on coupling water electrolyzers with solar and wind sources are promising solutions soon for the utilization of surplus power from these sources. Taking advantage of this aspect, the use of divided electrochemical cells coupled with membranes to simultaneously produce H_2, while treating real and synthetic wastewater, is efficient [3]. In the present work, the simultaneous production of green H_2 and the electrochemical treatment of PW was demonstrated using an integrated-hybrid approach with a PEM-type cell equipped with a boron-doped diamond (BDD) electrode as the anode, a Ni-Fe mesh as the cathode, and with 0.25 M of NaOH in the cathodic compartment. The proposed technology uses a photovoltaic array to power the operation of the designed cell, establishing a promising, efficient, and sustainable alternative to produce high-value-added green H_2, and second advance is related to the energy transition towards zero carbon emissions (SDG 7) [4].

Material and Methods

The effluent sample used in the study was sourced

from a northeastern onshore Brazilian oil plant, specifically from the effluent stream without undergoing any prior treatment. The proton-exchange membrane cell (PEM or wastewater||H_2 cell) used in this work and all the prototype apparatus with a solar source of energy through a photovoltaic (PV) cell placed on the roof of the building where the laboratory operates. The effect of the EO of 0.5 L of the raw PW in the anodic compartment (circulated at a constant flow rate of 39 mL min^{-1}) on the production of green H_2 in the cathode was evaluated by applying approximately 7, 13 and 26 mA cm^{-2}, without adding any supporting electrolyte during 600 min. Organic matter removal was evaluated by the COD decaying during electrolysis by using smartphone-based protocol. Removal of specific organic compounds was demonstrated and described.

Results and Discussion

In this work, seeking to avoid the inclusion of chemicals in the treatment line and make the process less dispendious and easier to operate, the electrolysis was performed directly with the raw PW. The results clearly confirms that lower j is enough to perform effective removal of organic matter, where the most important pollutants were completely eliminated after the electrochemical treatment under specific conditions. The production of heterogeneous free •OH at BDD surface promotes the indirect oxidation of organic matter and it can be intensified by electroproduction of the secondary oxidant species, such as active chlorine, sulfate ion radical and persulfate from the dissolved precursor salts in the PW effluent. On the other hand, it is possible to confirm that green H_2 is efficiently produced as a function of j and time. Despite the significant COD removals in all cases (see pink-color region in Fig. 1a), energetic requerements (see the colored regions in Fig. 1c) depends on the parallel electrochemical reactions (e.g.: oxygen evolution) and effluent conductivity features. Then, higher j implies higher COD removal and H_2 production, but also a higher EC (green region in Fig. 1c). In this way, it is proved that the system achieves significant green H_2 production even with a solution with low conductivity/salinity; and simultaneously, the wastewater treatment occurs. Faradaic efficiency (FE) (see Fig. 1d) typically varied at the first 30–50 min of the electrolysis [5–7], depending on j and the intrinsic factors and afterwards, it always remains above 95% until the end of the process, evidencing the higher efficiency of the hybrid process to produce H_2. According to the obtained values in the previous topic and the linear tendency perceived during green H_2 production (Fig 1b) at all j, if the jlim is used, a value of 1.27 L of dry H_2 is expected to be produced during 10 h of treatment in 0.5 L of PW. Scaling to the average amount of PW daily produced in Brazil (5670 million m^3 day^{-1}), the total green H_2 that can be generated reaches an outstanding value of 14402 million m^3 day^{-1}. Then, taking into account the costs, the hybrid-integrated approach could be economically-sustainable.

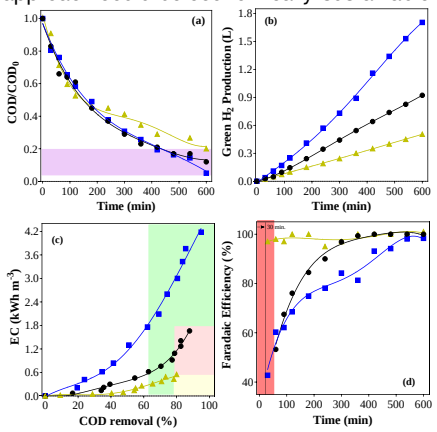


Figure 1. (a) COD decreases as a function of time and j. (b) Volume of green H_2 as a function of j. (c) Energy consumption (EC) as a function of COD removal. (d) Faradaic efficiency (FE) H_2 production as a function of time. FE and EC were calculated. j: 7 (green triangle), 13 (black circle) and 26 $mAcm^{-2}$ (blue square). Symbols: real values; lines: tendency behavior.

Conclusions

In this proof-of-concept investigation, the authors provide insights into novel applications of EO of PW treatment, with a specific emphasis on innovative solutions for a cleaner and more sustainable energy landscape, regarding the generation of green H2, which ushers a new era of eco-friendly and efficient energy production.

Acknowledgments

Financial support from CNPq (408110/2022-8) and from FAPESP (2014/50945-4 and 2019/13113-4), are gratefully acknowledged. Araujo, D.M, Barbosa Segundo, I.D., Cardozo, J.C., and Santos, J.E.L acknowledge the postdoctoral fellowships awarded by CNPq (116925/2022-1, 152760/2022-1, 351605/2022-3, 350643/2023-7 respectively).

References

[1] National Agency for Petroleum NG and B (Brazil). Painéis Dinâmicos de Produção de Petróleo e Gás Natural 2023 (accessed August 2, 2023).

[2] Abdulgani I, Escalona-Durán F, de Araújo DM, dos Santos E V., Barbosa Segundo ID, Martínez-Huitle CA. Journal of Electroanalytical Chemistry 2022;910:116163.
[3] Santos JEL, Da Silva DR, Martínez-Huitle CA, Dos Santos EV, Quiroz MA. RSC Adv 2020;10:37947–55.
[4] Abdin Z, Zafaranloo A, Rafiee A, Mérida W, Lipiński W, Khalilpour KR. Renewable and Sustainable Energy Reviews 2020;120:109620.
[5] Câmara Cardozo J, da Silva DR, Martínez-Huitle CA, Quiroz MA, Dos Santos E V. Materials 2022;15:7445.
[6] Oliveira HL, Barros TM, Santos JEL, Gondim AD, Quiroz MA, Martínez-Huitle CA, et al. Electrochem Commun 2023;154:107553.
[7] Campos da Paixão I, Cardozo JC, Sales Monteiro MK, Gondim AD, Cavalcanti LN, Fabiano de Santana Souza D, et al. RSC Adv 2023;13:35755–65.