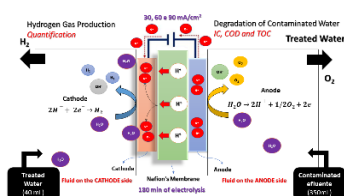


Retreatment of contaminated water with simultaneous production of green hydrogen by hybrid electrochemical oxidative process

ORAL
Ph.D. Student: N
Journal: JECE7.7

Mayra Kerolly Sales Monteiro^{1,3}, Jussara Câmara Cardozo¹, Amanda D. Gondim¹, Lívia N. Cavalcanti¹, Carlos A. Martínez-Huitle^{1,3}, Marco A. Quiroz², Elisama V. Dos Santos^{1,3}

¹Renewable 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 ²National Institute for Alternative Technologies of Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactives (INCT-DATREM), UNESP, Araraquara 14800-900, Brazil ³Human Resources Program of the National Agency for Petroleum, Natural Gas and Biofuels – PRH-26-ANP, Graduate Program in Chemical Engineering - PPGEQ, Lagoa Nova, Natal/RN, 59078-970, Brazil.



This study aims to optimize an integrated-hybrid process that simultaneously produces green H₂ from the reuse of pre-treated water in the anode compartment and removes organic matter from an effluent. This process is expected to be a viable environmental alternative for converting water into energy with reasonable cost requirements and higher efficiency. The generation of green hydrogen gas (H₂) in the cathodic compartment while wastewater is being electrochemically oxidized (EO) in the anodic compartment was investigated for the first time in a PEM-type electrochemical cell powered by a photovoltaic (PV) energy source. In a second moment, the treated water was reused in the cathode compartment for a new hybrid process. EO of wastewater was carried out on a Nb/BDD anode at different current densities (30, 60 and 90 mA/cm²), while a stainless steel (SS) cathode was used for green H₂ production.

Introduction

Pollution is the direct or indirect introduction into water or soil, through human activity, of substances, vibrations, heat or noise, which may have harmful effects on human health or the quality of the environment and may also cause harm to material goods or deteriorate or impair the enjoyment or other legitimate uses of the environment. An example of this is the search for a source of energy through natural resources such as fossil fuel [1].

Currently, hydrogen production is a subject of great scientific and technological interest, among other reasons because it is one of the most important energy alternatives to the use of fossil fuels. However, obtaining it at the best cost is still a great challenge, and all possible options should be considered. Hydrogen is the natural product in the oxidation process of aqueous organic pollutants, as it is produced in the complementary cathodic reaction of the liquid electrochemical treatment process [2]. Therefore, the development of a hybrid process to remove organic matter in an effluent and simultaneously produce green H₂ is a viable environmental water-to-energy alternative with higher efficiency and reasonable cost requirements [3].

The new simultaneous generation based on the electrochemical processing of wastewater combined with the valuable by-product produced (green H₂) is showing economic and environmental advantages: direct oxidation on the surface of the anode is possible at lower applied current densities in the

hybrid process, where as in the cathodic reaction of the hybrid process, a lower cost compared to other cathodes, such as Pt, is achieved with the use of SS proving to be efficient for the production of H₂ [4]. However, more attention is needed for each step of the electrolysis process. Not all water pollutants can disperse in water and therefore require a co-solvent, which, however, can change the redox potential [5]. In this work, the influence of EO on the degradation of wastewater to obtain green H₂ was investigated in relation to the behavior observed in drinking water. Simultaneously with the decontamination of the water (anode compartment), the production of H₂ was quantified at different current densities with the presence, in the cathode compartment, of an electrolyte solution prepared with distilled water or with water previously treated in the same system. In fact, the results should establish that it is not necessary to use clean water for the desired production of H₂ to be achieved.

Material and Methods

The electrochemical reactor consisted of two electrodes of dimensions (10.0 cm² BDD and SS), protected inside an acrylic box (10.0 x 7.5 x 1.7cm), with pre-drilled holes for the entry and exit of the solution, and connections electrical (Figure 1). The experiments were carried out in the flow reactor with a mass transfer coefficient of 5.11x10⁻⁵ (m/s). The two-compartment cell was separated by a type 350 Nafion[®] membrane with the opaque side facing the catholyte solution (known as a PEM cell). Each

compartment has a volume of 0.04 L with a space of 3.4 cm between the electrodes. The electrolysis of 350 mL of solution in 0.1 M Na₂SO₄ as supporting electrolyte was performed by applying 30, 60 and 90 mA.cm⁻² for 180 min in a glass tank thermoregulated at 25 °C and circulated through the cell by a peristaltic pump at a constant flow rate of 39 mL.min⁻¹. The H₂ produced in the cathodic reservoir, concomitantly with the oxidation of residual water in the anode compartment, was collected over distilled water, and the volume measured. The electrochemical experiments for H₂ production were developed by coupling two polycrystalline silicon photovoltaic (PV) modules (Canadian CS6U-325p), connected in series with a total peak power of 640Wp.

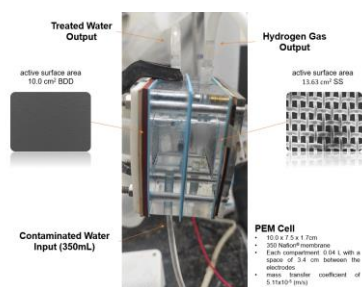


Figure 1. Representation of the electrochemical reactor.

Results and Discussion

These results can be corroborated with the diffractogram performed on the surface of the BDD electrode (Figure 2). The diffraction peak identified for carbon is related to the diffraction plane (002), and for the BDD, used as an anodic electrode, the diffraction of this peak appears shifted to higher values of 2θ approximately equal to 36.5°. This increase in interplanar distance can be caused by the presence of functional groups generated during oxidation ($\cdot\text{OH}$, SO_4^- and $\text{S}_2\text{O}_8^{2-}$) [3,4]. Showing greater charge transfer at high electrical current densities, which favors the formation of hydroxyl radicals on the surface of the electrode. Given these results, it can be inferred that the use of BDD in EO has the capacity to be very promising for the treatment of contaminated effluents [1,2]. Since, the principle of electrochemical decomposition of organic matter in a PEM cell is based on its EO. In this case, the contaminants are oxidized in the anode compartment (through in situ electrogeneration of hydroxyl radicals), generating products such as

carbon dioxide and protons [1,2,3]. These ions manage to cross the membrane and are transported to the cathode compartment, being reduced to molecular H₂ on the surface of the cathode used in the experiments.

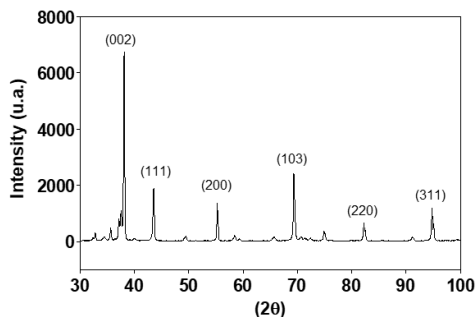


Figure 2. X-ray diffractogram of the DDB electrode.

Conclusions

The mineralization efficiency observed in the anode compartment, due to the results of the advanced integrated-hybrid EO process, occurred as H₂ was produced in the cathode compartment. In this work, the BDD anode used during the degradation of contaminated water was characterized.

References

- [1] SANTOS, J. E. L. et al. Cathodic hydrogen production by simultaneous oxidation of methyl red and 2,4-dichlorophenoxyacetate aqueous solutions using Pb/PbO₂, Ti/Sb-doped SnO₂ and Si/BDD anodes. Part 1: Electrochemical oxidation. *RSC Advances*, v. 10, n. 62, p. 37695–37706, 2020b.
- [2] CÂMARA CARDOZO, J. et al. Photovoltaic Electrochemically Driven Degradation of Calcon Dye with Simultaneous Green Hydrogen Production. *Materials*, v. 15, n. 21, 2022.
- [3] MONTEIRO, M. K. S. et al. Production of chlorine dioxide using hydrogen peroxide and chlorates. *Catalysts*, v. 11, n. 12, 2021. MONTEIRO, M. K. S. et al. Towards the production of chlorine dioxide from electrochemically in-situ produced solutions of chlorate. *Journal of Chemical Technology and Biotechnology*, v. 97, n. 8, p. 2024–2031, 2022.
- [4] CLEMATIS, D.; PANIZZA, M. Solid polymer electrolyte as an alternative approach for the electrochemical removal of herbicide from groundwater. *Electrochimica Acta*, v. 378, p. 138127, 2021.
- [5] MARTÍNEZ-HUITLE, C. A.; BRILLAS, E. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review. *Applied Catalysis B: Environmental*, v. 87, n. 3–4, p. 105–145, 2009.