**Bioelectrochemical Hydrogen Production in a Three-Chamber MEC: Integrating OF-MSW Treatment and Renewable Energy Recovery**

Angela Marchetti*a*, Francesco Valentino *b*, Adele Tuci *b*, Marco Gottardo *b*, Marco Zeppilli *a*

*a* Department of Chemistry Sapienza University of Rome, Italy

*b* Department of Environmental Sciences, Informatics and Statistics Ca’ Foscari University of Venice, Italy

E-mail: *angela.marchetti@uniroma1.it*

Hydrogen is widely regarded as a clean energy carrier due to its emission-free combustion; however, most of its current production (96%) still relies on fossil fuels through energy-intensive steam reforming, contributing significantly to CO₂ emissions. Among alternative methods, alkaline water electrolysis is promising but requires substantial energy input. Microbial Electrolysis Cells (MECs) offer a more energy-efficient and sustainable alternative by leveraging electroactive microorganisms to oxidize organic substrates, significantly lowering the voltage required for hydrogen production. This study investigates a novel three-chamber MEC configuration designed to enhance energy efficiency and hydrogen yield by optimizing electron transfer from a bioanode to two flanking cathode chambers. The system was tested using two different feeding solutions: a synthetic medium and a real substrate derived from the acidogenic fermentation of organic fraction of municipal solid waste (OF-MSW). Both substrates were fed under identical organic loading rates (OLR equal to 4 gCOD/L·d) and hydraulic retention time (0.3 d), with continuous feeding in the anodic chamber and batch operation in the cathodic chambers.

Key performance indicators—such as coulombic efficiency at the anode and cathode, hydrogen purity, and energy efficiency—were assessed. Hydrogen was the sole gas produced in both cases, with gas purity near 100%. The synthetic substrate yielded higher current generation (~95 mA), with energy efficiency reaching 110 ± 11%, while the real substrate showed reduced performance (ηE = 55 ± 4%). This was due to a lower conductivity of this substrate (1.0 mS/cm) compared with the conductivity of the synthetic one (6.1 mS/cm), thus increasing the system resistance (ΔV = -2.58 V). Nevertheless, the real fermented substrate still enabled substantial hydrogen production, supporting the system’s suitability for waste valorisation.The findings demonstrate that the proposed MEC design effectively couples organic waste treatment with clean hydrogen generation. The study advances the field of chemical engineering by providing a sustainable pathway for integrating bioelectrochemical systems into energy and waste management infrastructures. By addressing both environmental and energy challenges, this research contributes to the broader transition toward circular and carbon-neutral technologies.

**Keywords**: Microbial Electrolysis Cells (MECs); Sustainable Hydrogen Production; Waste Valorisation