Membrane-less Electrolysis for Simultaneous Organic Load Removal and Hydrogen Production from Olive Mill Wastewater

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The olive oil milling, a hallmark of Mediterranean agriculture, generates large volumes of wastewater (OMW). These effluents are acidic and highly concentrated in organic matter, including phenolic compounds, sugars, and fatty acids, which make them particularly challenging to treat with conventional methods. Due to their toxicity and poor biodegradability, uncontrolled disposal of OMW may pose serious risks to soil and aquatic ecosystems. At the same time, the transition towards a low-carbon economy requires innovative technologies to produce green hydrogen from sustainable sources.

In this context, this work investigates a novel dual-purpose electrochemical strategy that combines the treatment of OMW with hydrogen production, using a membrane-less electrolyzer. The aim is to achieve selective oxidation of organic pollutants at the anode—reducing the chemical oxygen demand (COD) and the total organic carbon (TOC)—while producing pure hydrogen at the cathode. This is made possible by exploiting the low oxidation potential of organic compounds naturally present in OMW, which compete with the oxygen evolution reaction (OER), thereby minimizing oxygen production and improving overall energy efficiency. Experimental tests were carried out using a three-electrode batch setup for preliminary screening, followed by continuous-flow electrolysis in a filter-press type membrane-less electrolyzer. The anode was a dimensionally stable electrode (DSA – $Ti/RuO_2–IrO_2$), while the cathode was made of stainless steel. Linear sweep voltammetry, cyclic voltammetry, and galvanostatic electrolysis were used to assess system performance under varying current densities and pH conditions.

COD removal up to 49.7% and TOC reduction of 11.4% were achieved under the optimal conditions, where instantaneous current efficiency (ICE) almost 100% were obtained, which highlights the preferential use of electrons for organic oxidation rather than OER. The proposed electrochemical process offers a sustainable solution for agro-industrial waste valorisation and decentralized hydrogen generation, paving the way for circular economy applications in the olive oil sector.

Keywords: *Membrane-less electrolysis, Advanced oxidation processes (AOPs), Olive mill wastewater, hydrogen*

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