# The synergistic effect of $H_2$ injections and applied potential on biogas production during the treatment of industrial potato processing wastewater in a Microbial Electrolysis Cell-assisted Anaerobic Digestion system

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**Abstract:** This study deals with the synergistic effect $H_2$ supply and applied potential, during the treatment of industrial potato processing wastewater in a Microbial Electrolysis Cell-assisted Anaerobic Digestion (MEC-AD) system, in order to enhance the quality of the produced biogas. The MEC-AD reactor was equipped with carbon felt electrodes and operated for 80 d at a constant Hydraulic Retention Time of 15 d. The results showed that when $H_2$ was supplied in excess, the MEC-AD reactor failed, due to the inhibition of hydrolysis, acid accumulation, pH increase and enrichment of hydrogen sulfide producing bacteria. Nevertheless, when $H_2$ was supplied through saturating the feed, the reactor operated stably, leading to a COD removal of 92.6% and exhibited enhanced biogas quality, producing a $CH_4$:$CO_2$ ratio of 2.9, relative to 1.1 when no $H_2$ was supplied. Overall, the combined effect of hydrogenotrophic methanogenesis and electromethanosynthesis represents a promising strategy for enhancing biogas quality, while simultaneously enabling the synergistic integration of bioelectrochemical and anaerobic processes to mitigate failure mechanisms associated with elevated $H_2$ partial pressures.

**Keywords:** Applied potential; Bio-electrochemical systems; Electromethanosynthesis; Hydrogen; MEC-AD

## 1. Introduction

Hydrogenotrophic methanogenesis has emerged as an appealing biological alternative for biogas upgrading to methane. In this concept, $CO_2$ and $H_2$ can be biologically converted to $CH_4$ by the action of hydrogenotrophic methanogens without any additional energy input (Fu et al., 2021). While $H_2$ supply can enhance hydrogenotrophic methanogenesis for biogas upgrading, excess $H_2$ disrupts AD by inhibiting degradation pathways, causing acid accumulation and pH increase through bicarbonate consumption, as $H_2$ partial pressure strongly influences fermentation and methanogenesis (Cuff et al., 2020). Low gas-liquid mass transfer rate of $H_2$ limits its availability for methanogens, reducing the efficiency of the system (Basani et al., 2016). Cazier et al. reported that at elevated $H_2$ partial pressures, overall substrate degradation declined, indicating selective inhibition of hydrolysis, while co-supplied $CO_2$ prevented this effect (Cazier et al., 2015). Cuff et al. found that, during $H_2$ injection in AD, a shift toward propionate caused intermittent suppression of acetoclastic methanogenesis, lowering biogas yield (Cuff et al., 2020). Application of an electric potential in Anaerobic Digestion (Microbial Electrolysis Cell-assisted Anaerobic Digestion – MEC-AD) has also been recently proposed as a means to enhance biogas production, while also securing a more robust operation. By introducing electrodes in conventional AD and applying a small potential, the oxidation of organic compounds on the bioanode is promoted and the $CH_4$ production is boosted through electromethanosynthesis on the biocathode (Kanellos et al., 2024).

In this context, the present study aims to evaluate the combined effect of hydrogenotrophic methanogenesis and electromethanosynthesis, in order to facilitate the enrichment of microbial communities and enhance the quality of the produced biogas, during the treatment of an industrial potato processing wastewater (IPPW).

## 2. Materials and Methods

### *2.1. Reactor setup*

The MEC-AD reactor consisted of a 2 L tubular glass vessels, equipped with a plastic tube used for feeding and sampling and a biogas outlet. A stainless steel sintered sparger was integrated into the reactor, to facilitate $H_2$ injection and diffusion within the bulk. The reactor was constantly stirred and the working volume was 1.8 L, while it was kept at a constant temperature of 35 $^oC$. A total of six electrodes (3 cm × 10 cm x 1 cm each), made from carbon felt, were inserted in the MEC-AD reactor. Three of them served as the bioanode and the other three served as the biocathode. Titanium wire was connected to the electrodes as the current collector and a DC power supply (DC PS-1502DD) was used to apply a constant voltage of 1 V.

### *2.2 Reactor start-up, substrate and operation phases*

Anaerobic Sludge (AS) was obtained from the Municipal Wastewater Treatment Plant of Lykovrisi, in Attica, Greece and served as inoculum. The IPPW was obtained from the factory of PepsiCo Hellas S.A. & Tasty Foods S.A., in Attica, Greece, and it was supplied daily via drawfill operation, at a HRT of 15 d. The physicochemical characteristics of the IPPW were: pH 6.8; alkalinity 0.2 ($eqg_{CaCO3}$/L); soluble COD 2.5 $g_{O2}$/L; total COD 2.8 $g_{O2}$/L. The MEC-AD system operated for 80 d, which were divided into three distinct operational phases. These differentiated based on the quantity and method of $H_2$ supply. Namely, during phase 1, the reactor operated without any $H_2$ addition. During phase 2, $H_2$ injection was used in excess, for purging and filling of the reactor headspace. Finally, during phase 3, the feed was saturated with $H_2$, which was supplied via the influent stream.

*2.3 Analytical methods*

The analytical measurements (pH and soluble COD) were performed according to the standard methods for the Examination of Water and Wastewater. The $CH_4$, $CO_2$, CO, $H_2$ and $H_2S$ content of the biogas was measured using a portable gas analyzer (Gas Data - GFM436).

## 3. Results and Discussion

As shown in Fig. 1, the MEC-AD reactor maintained an average sCOD of 160 mg/L during phase 1, achieving 97% COD removal under stable operation at pH 7.7, effectively treating the IPPW without instability. The $CH_4$:$CO_2$ ratio averaged 1.1, while $H_2S$ and CO concentrations remained low at 30.6 ppm and 10.1 ppm, respectively. During phase 2, excess $H_2$ supply led to a rapid rise in sCOD to 2.4 g/L, reducing removal efficiency to 67.1%. The pH increased from 7.5 to 10, resulting in reactor failure. This outcome was attributed to bicarbonate consumption and acid accumulation, driven by elevated $H_2$ partial pressure that inhibited substrate degradation, as previously reported (Cuff et al., 2020). Despite reactor failure, the $CH_4$:$CO_2$ ratio sharply increased to 42.7, suggesting that although hydrogenotrophic methanogenesis was inhibited, electromethanosynthesis enriched the biogas. This is further corroborated by a rise in $H_2S$ concentration to 162.4 ppm, indicating the proliferation of sulfate producing bacteria antagonistic to methanogens, while CO remained undetected (Mutegoa and Sahini, 2023).

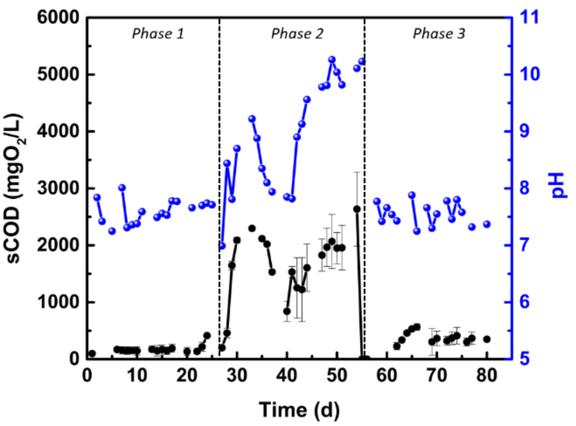


**Figure 1.** The sCOD (on the left) and pH (on the right) of the MEC-AD reactor during all operation phases.

In phase 3, following re-inoculation with AS as in phase 1 and $H_2$ supply via feed saturation, the MEC-AD reactor operated stably with enhanced performance. Although sCOD removal slightly declined to 92.6% due to minor acid accumulation, the system maintained stability at an average pH of 7.7 (Fig. 1). The $CH_4$:$CO_2$ ratio increased to 2.9, demonstrating improved biogas upgrading, while average $H_2S$ levels decreased to 104.7 ppm. Conversely, CO production during phase 3 increased to 57.2 ppm, which could be linked to the activity of CO dehydrogenases (CODHs)—electroactive enzymes that reduce $CO_2$ to CO, despite the thermodynamic favorability of $H_2$ production. The elevated CODHs activity could potentially be attributed to favorable Wood-Ljungdahl pathway, increased selectivity caused by a suboptimal applied potential and increased conversion yields of CO strains (Barbosa et al., 2021; Yuan et al., 2019).

## 4. Conclusions

Overall, the combined effect of hydrogenotrophic methanogenesis and electromethanosynthesis enhanced the quality of the produced biogas when the feed was saturated with $H_2$, whereas supplying $H_2$ in excess led to the inhibition of hydrolysis, acid accumulation, pH increase and enrichment of hydrogen sulfide producing bacteria, resulting in reactor failure.

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