Batch vs semi-continuous operation for ammonium removal and hydrogen production in a two-chamber microbial electrolysis cell

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Introduction

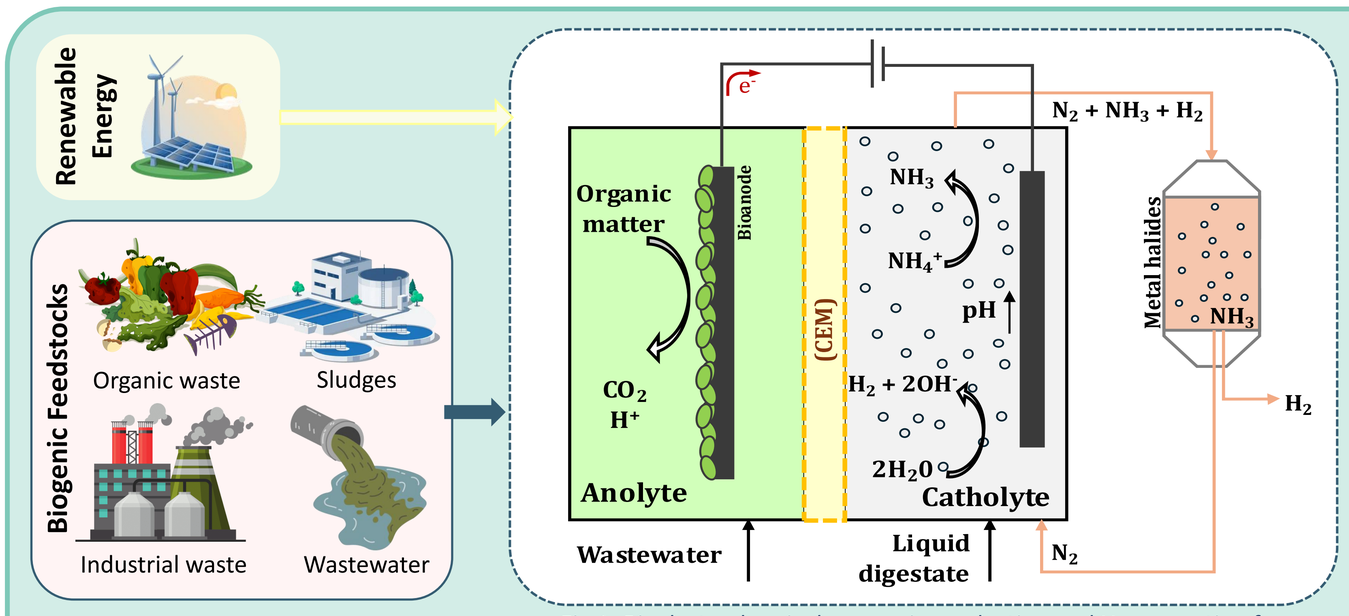


Fig 1: Bioelectrochemical ammonia production and H_2 generation from biogenic feedstocks

- Fuels-C project aims to develop **advanced biofuels** to support the decarbonization of hard-to-electrify transport sectors (maritime and road transport) using **biogenic residues** as feedstocks.
- Our contribution focuses on **bioelectrochemical systems (BES)** for nitrogen recovery and ammonia (NH_3) gas production.

Objectives

1. Evaluate **batch vs. semi-continuous** operation at the anode (synthetic medium).
2. Assess cathode performance using **synthetic medium** and **anaerobic digestate**.
3. Analyse the **impact of operation mode** on NH_4^+ removal, H_2 production, and system stability.

Materials and Methods

Reactor configuration: Two-chamber MEC (anode and cathode) separated by a cation exchange membrane (CEM).

	Bioanode	Cathode
Electrode	Carbon felt (80 cm^2)	Nickel-felt cathode (80 cm^2)
Feed	Synthetic acetate-based medium	Ammonium-rich synthetic medium & Anaerobic digestate
Working volume	1.2 L (batch); 0.5 L (semi-continuous)	0.57 L (batch)
Initial [N-NH_4^+]	-	700 mg L^{-1}
TRH	3-4 d/cycle (batch + acetate pulses); 0.7 d (semi-continuous)	≈ 3-4 d (batch)

Gas recovery: Coupled **stripping column** for H_2 and NH_3 capture.

Number of reactors: two identical BES units.

Reactors were operated at 30ºC, with applied voltage of 1.1V, with internal liquid recirculation at 100 rpm and gas stripping at 50 rpm.

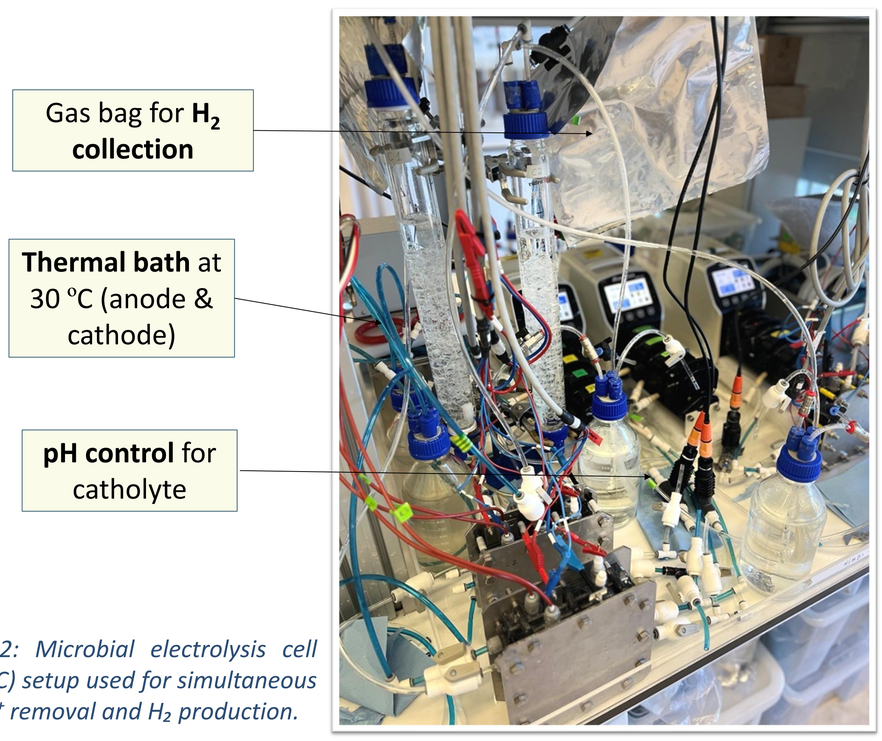


Fig 2: Microbial electrolysis cell (MEC) setup used for simultaneous NH_4^+ removal and H_2 production.

Abbreviations: MEC: microbial electrolysis cell; BES: bioelectrochemical system; COD: chemical oxygen demand; CE: coulombic efficiency; AD: anaerobic digestate; N-NH_4^+: ammonium nitrogen; NH_3: ammonia.

Results

Cathode performance: NH_4^+ recovery and H_2 production

Batch operation enhances NH_4^+ removal and H_2 production

- NH_4^+ removal efficiency remained stable (58-62%) across all conditions.
- Highest removal rate in AD batch (9.5 gN m^{-2} d^{-1})
- Highest H_2 production obtained in synthetic batch (59.9 L m^{-2} d^{-1}).
- Cathodic CE remained constant (80-85%).
- Energy consumption: 28-38 kWh kg^{-1} H_2, remaining below conventional electrolysis values

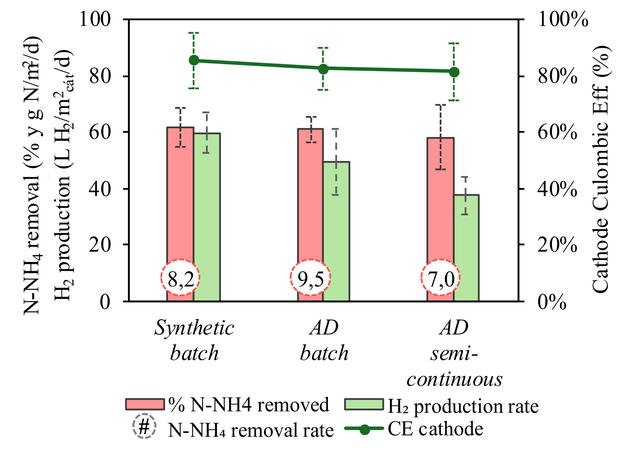
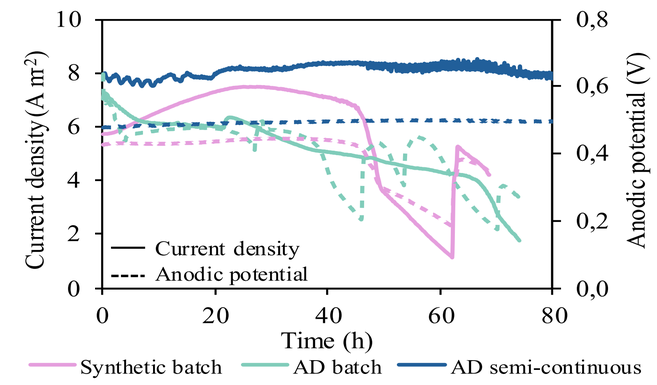


Fig 3: NH_4^+ removal efficiency and rate, H_2 production, and cathodic coulombic efficiency under different operation modes.

Cell stability: operation mode comparison



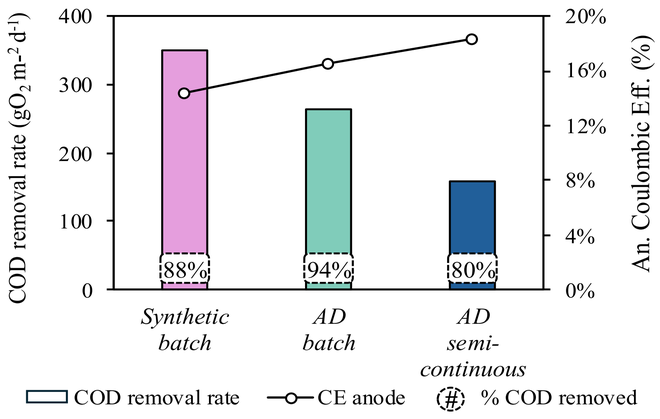


Fig 4: Top: Current density and anodic potential over time under batch and semi-continuous operation. Bottom: COD removal rate and efficiency, and anodic coulombic efficiency under different operation modes.

Semi-continuous mode improves current stability

- Batch shows fluctuations due to substrate depletion.
- Current drops coincide with increases in E_{an}.
- Semi-continuous feeding reduces fluctuations and improves stability over time.

Higher COD removal in batch, higher CE in semi-continuous mode

- High COD removal efficiency achieved in all conditions (75-95%).
- COD removal rates were higher under batch operation.
- Anodic coulombic efficiency (CE) increased under semi-continuous operation (14 → 18%).

Conditions: synthetic (batch, both chambers); AD batch (synthetic anode, digestate cathode); AD semi-continuous (synthetic anode in semi-continuous, digestate cathode).

Conclusions

The MEC demonstrated robust performance for ammonium removal as well as hydrogen production under different anode operating modes (batch and semi-continuous) and for different catholyte media tested (synthetic and real wastewater).

- ✓ **Stable NH_4^+ removal and H_2 production** achieved with both synthetic and real wastewater (digestate).
- ✓ **Batch operation** enhanced performance (higher removal rates and H_2 production) but was **limited over time** due to instability and substrate depletion.
- ✓ **Semi-continuous operation improved stability** by reducing current fluctuations.
- ✓ Operation mode determines a trade-off between performance (batch) and stability (continuous).
- ✓ **High COD removal** (75-95%) in all configurations confirmed effective anodic activity.
- ✓ Energy demand for H_2 production (28-38 kWh kg^{-1} H_2) remained below conventional electrolysis.

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