Research Square

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Municipal Waste-based Microbial Electrolysis Cell for Sustainable Hydrogen-rich Gas Production

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Abstract

India's rapidly increasing municipal solid waste burden, alongside mounting pressure to adopt cleaner energy pathways, has raised interest in technologies capable of treating waste while simultaneously generating value-added fuels. Among these, microbial electrolysis cells (MECs) remain comparatively underexplored for decentralized conversion of the organic fraction of municipal solid waste (OFMSW) into hydrogen-rich gas. In the present investigation, six OFMSW samples collected from institutional and residential locations were processed through segregation, particle-size reduction, anaerobic fermentation, and hydrolysis using municipal wastewater inoculum prior to electrochemical treatment. APHA-based characterization of the hydrolysates revealed COD (Chemical oxygen demand) values between 5750 and 7200 mg L^{-1}, BOD (biological oxygen demand) to COD ratios of 0.62–0.65, and total volatile solids ranging from 391 to 455 mg L^{-1}, conditions generally regarded as favorable for electroactive microbial activity. A single-chamber MEC reactor assembled with graphite-sheet anodes and stainless-steel cathodes, powered using a 6 V sealed lead-acid source, produced 1.32 and 1.94 L of gas from a 1000 g OFMSW basis for Sample 1 and Sample 2, respectively. Conversion efficiencies reached 60% and 72%, with the higher-performing substrate corresponding to the greatest organic loading (COD = 7200 mg L^{-1}), suggesting that substrate biodegradability exerted a measurable influence on electrohydrogenic performance. Theoretical hydrogen potentials of 1.08 L and 1.68 L were calculated from COD data. The correlation between higher organic loading (COD 7200 mg/L, Sample 2) and improved efficiency (72%) directly validates the core hypothesis of this study. To examine scale-up feasibility, a MATLAB/Simulink model (MEC_Industrial_Model_v3.1) was further developed, predicting hydrogen production approaching 7.0 L over a 12 h cycle together with steady-state current densities of 18–20 A m^{-2}. Taken together, the findings indicate that OFMSW-driven MEC systems could provide a technically viable route toward simultaneous waste stabilization and decentralized green hydrogen generation in rapidly urbanizing regions.

1. INTRODUCTION

Managing municipal solid waste (MSW) and generating sustainable energy have become deeply connected problems, especially in fast-growing economies where infrastructure simply can't keep pace with how much trash people produce. India is a good case in point the country is on track to generate over 165 million tonnes of MSW annually by 2025, yet a significant share of that waste still ends up in uncontrolled landfills or open dumps (CPCB, 2024). This can be observed from Fig. 1. Beyond the obvious land and public health pressures, these practices pump methane into the atmosphere, leach contaminants into groundwater, and leave behind long-term environmental damage. Meanwhile, hydrogen has been gaining traction as a key clean-energy carrier for industries that can't easily run on electricity alone such as fertilizer manufacturing, heavy freight, and steel production (Dawood et al., 2020; IEA, 2024). The catch is that nearly all hydrogen today still comes from fossil fuels via steam methane reforming, which generates substantial CO_2 and undercuts the whole point of decarbonizing (IEA, 2024). These twin pressures have pushed researchers toward technologies that can tackle both problems at once.

Microbial electrolysis cells (MECs) have emerged as one of the more promising options. They work by pairing microbial metabolism with electrochemical hydrogen production under relatively gentle conditions (Kadier et al., 2016; Muddasar et al., 2021). Inside an MEC, electroactive bacteria break down organic material and pass electrons to an anode; a small-applied voltage then drives proton reduction at the cathode, releasing hydrogen gas (Liu et al., 2005). Because the microbes do part of the thermodynamic heavy lifting, MECs need far less external electricity than conventional water electrolysis. The past decade has seen real progress, better electrodes, improved cathode catalysts, refined membranes, and more stable microbial communities have all pushed hydrogen recovery rates higher (Kadier et al., 2016; sharet al., 2024). Researchers have also started feeding MECs with wastewater, fermentation byproducts, agricultural residues, and food-processing waste to make the process more economically viable (Pant et al., 2010; Carlotta-Jones et al., 2020), and there's growing interest in fitting MEC systems into existing urban waste infrastructure as part of broader circular-economy strategies (Katuri et al., 2019).

That said, a major gap remains: moving MECs from clean lab substrates to the messy reality of municipal organic waste is still poorly understood. The organic fraction of MSW (OFMSW) is a chemically chaotic mix carbohydrates, proteins, fats, lignocellulosic material, and partially fermented intermediates, all shifting in composition depending on where you are, what season it is, and what people threw away. That variability hits microbial acclimatization, electron transfer, biofilm stability, and ultimately hydrogen output (Varanasi et al., 2019). Relatively few studies have actually tested MEC performance using real, field-collected OFMSW under practical conditions, particularly in the context of decentralized waste systems in developing countries. Scale-up analyses are similarly scarce the literature is heavy on lab-scale results but light on credible pathways to industrial deployment (Muddasar et al., 2021; Alawadhi et al., 2024).

This study takes aim at those gaps. A lab-scale single-chamber MEC was built and tested using OFMSW collected from both institutional and residential sources. The waste was sorted, pretreated, and characterized before being fed into the system, with a particular focus on linking substrate properties COD, biodegradability, volatile solids to hydrogen generation performance. A MATLAB/Simulink model was also developed in parallel to explore how the process might scale up under larger feed volumes. Rather than relying on synthetic or tightly controlled substrates as most prior work has done, this study deliberately works with minimally modified real-world waste, with the aim of honestly assessing whether MEC-based waste-to-hydrogen conversion is a practical option for decentralized waste management in rapidly urbanizing regions.

2. METHODOLOGY

2.1. Sampling

Municipal solid waste (MSW) was collected from two operationally distinct source streams: the institutional campus of Manav Rachna University, Faridabad, India, and the adjacent residential localities. Campus-derived waste comprised food residues from the student canteen and hostel kitchen operations, vegetable preparation waste, and garden trimmings. Residential waste was obtained from household collection bins, yielding a compositionally heterogeneous matrix representative of domestic MSW. This dual-source strategy was adopted to capture the physicochemical variability inherent to real-world waste streams.

All samples were transported to the laboratory and manually segregated within 2 h of collection to minimize compositional drift and microbial activity. Segregation partitioned the incoming waste into eight fractions: organic matter, paper and cardboard, plastics, glass, textiles, rubber, wood, and inert materials, each quantified gravimetrically as illustrated in Table 1.

Table 1
Waste Segregation Data across Six 1-kg Samples

Sample	Paper (kg)	Organic (kg)	Wood (kg)	Textile (kg)	Plastic (kg)	Glass (kg)	Rubber (kg)	Inert (kg)	Total (kg)
1	0.05	0.62	0.01	0.07	0.01	0.01	0.00	0.23	1
2	0.07	0.50	0.02	0.03	0.01	0.03	0.02	0.32	1
3	0.03	0.56	0.02	0.04	0.01	0.02	0.01	0.31	1
4	0.06	0.58	0.03	0.04	0.02	0.00	0.00	0.27	1
5	0.08	0.57	0.01	0.03	0.03	0.02	0.02	0.24	1
6	0.10	0.59	0.03	0.02	0.03	0.01	0.01	0.21	1
TOTAL	0.39	3.42	0.12	0.23	0.11	0.09	0.06	1.58	6

Only the organic fraction was retained for further processing. Six independent replicate samples (1 kg wet basis each) were processed; the organic fraction constituted 50–62% of total wet mass (mean: 57 ± 4%, n = 6), while inert materials accounted for 21–32%. The recovered organic fraction was air-dried at ambient temperature (28–32°C) for 48 h on perforated trays in a well-ventilated enclosure to reduce moisture content without inducing thermal degradation. Moisture content was determined gravimetrically before and after drying. The dried material was subsequently size-reduced using a laboratory grinding mill to yield a uniform particle size distribution of 2–5 mm, ensuring substrate homogeneity prior to downstream characterization.

2.2. Physicochemical Characterization of Hydrolysate Feedstock

Three representative hydrolysate samples (S1, S2, and S3) were selected from the six prepared batches via stratified sampling to encompass the observed range of compositional variability across the full batch set. Comprehensive physicochemical characterization of these samples served the dual purpose of confirming feedstock suitability for MEC operation and providing experimentally validated parameters for theoretical hydrogen yield estimation.

Proximate analysis of the raw organic fraction was performed prior to hydrolysis in accordance with ASTM E1756 (moisture content), ASTM E872 (volatile matter), and ASTM E1755 (ash content). Moisture content was determined gravimetrically following oven drying at 105°C to constant mass. Volatile matter was quantified by thermal decomposition at 950°C under a nitrogen atmosphere, and ash content was determined by combustion at 550°C for 1 h in a muffle furnace. Fixed carbon was derived by difference, and gross calorific value (GCV, MJ/kg dry basis) was determined using a bomb calorimeter. Elemental composition (C, H, N, and S) was determined by high-temperature combustion using a CHNS-O elemental analyzer calibrated against a certified reference standard. Oxygen content was calculated by difference as:

$$O\ (wt\%) = 100 - (C + H + N + S + Ash) \quad \text{Eq. 1}$$

The carbon-to-nitrogen (C/N) ratio was derived from the measured elemental fractions; this parameter is a critical determinant of microbial metabolic balance in electroactive biofilm communities, with values in the range of 20–30 generally considered optimal for sustained anodic oxidation activity in bioelectrochemical systems (Li et al., 2018; Mao et al 2017).

2.3. MEC Reactor Fabrication and Configuration

A single-chamber MEC reactor was designed and fabricated in-house using commercially available laboratory materials. The primary reactor vessel consisted of a borosilicate glass jar of nominal working volume 2 L, sealed with a polypropylene screw cap through which electrode assemblies and gas collection tubing were inserted. All electrode penetrations were sealed with a two-component epoxy adhesive (M-Seal) to establish gas-tight boundaries and verified for leakage prior to operation by pressurized nitrogen purge.

Electrode materials were selected following a comparative evaluation of candidates reported in the MEC literature, with selection criteria weighted toward electrochemical performance, biocompatibility, and cost-effectiveness within the constraints of a laboratory-scale fabrication. The evaluated materials and their relative performance characteristics are summarized in Table 2.

Table 2
Comparative Assessment of Electrode Materials for MEC Systems

Electrode Material	Type	Relative Surface Area	H_2 Production Performance	Relative Cost	This study
Carbon cloth	Anode	High	High	Medium	No
Carbon felt	Anode	Very high	Very high	High	No
Graphite sheet	Anode	Medium	Medium	Low	Yes
Graphite granules	Anode	Highest	Highest	Medium	No
Stainless steel sheet	Cathode	Low–medium	Medium	Low	Yes
Nickel foam	Cathode	High	High	Medium–high	No
Platinum mesh	Cathode	High	Very high	Very high	No

On the basis of this assessment, a graphite sheet was chosen as the anode material owing to its stability and effectiveness with the electrode surface and electrically active biofilms. The graphite sheet is also biocompatible, meaning it is safe for the biofilms to grow on and can withstand being used for a long time without being damaged. (Abd-Elrahman et al., 2022; Dubrovin et al., 2024).Although carbon cloth and carbon felt materials could demonstrate better perform, they are too expensive. These materials have a larger surface area and can produce more current and hydrogen, but they are not cost-effective at the current scale (Park et al., 2022; Abadikhah et al., 2023).

The cathode was made from a stainless steel sheet owing to it's strength and ability to withstand the chemicals present in the system. It is also effective at supporting hydrogen production, which is the primary objective of the MEC (Abd-Elrahman et al., 2022). Stainless steel was selected because it is considerably cheaper than alternative materials such as platinum mesh and nickel foam. Electrical connections between the electrodes and the power supply were established via copper wire leads secured with conductive crocodile clips. A 6 V DC regulated bias was applied using an Amptek sealed lead-acid battery. Evolved gas was continuously collected via polyethylene tubing connecting the reactor headspace to a water displacement volumetric measurement apparatus, enabling quantification of cumulative gas production as a function of elapsed operational time. The visualization of the designed reactor can be observed in Fig. 1.

2.4 Substrate Preparation, Fermentation, and MEC Operation

The experimental protocol integrated anaerobic dark fermentation with MEC electrohydrogenesis in a sequential single-vessel operational design. The ground organic feedstock (1000 g, wet basis) was combined with municipal wastewater collected from the Manav Rachna University campus treatment facility in a mass-to-volume ratio of 1:5 (g/mL), yielding a working volume of approximately 6 L distributed across reactor replicates. The municipal wastewater served concurrently as a microbial inoculum, introducing a diverse consortium of indigenous anaerobic microorganisms, and as a diluent, reducing the substrate COD to a range compatible with single-chamber MEC bioelectrochemical operation.

The substrate-inoculum mixture was sealed under anaerobic conditions established by headspace purging with nitrogen gas for 10 min and subsequently incubated at ambient laboratory temperature (25–30°C) for 72 h.

2.5 Analytical Methods

Chemical oxygen demand (COD) was determined using the closed reflux titrimetric method in accordance with APHA Standard Method 5220B. Biochemical oxygen demand (BOD_5) was measured by the 5-day incubation method at 20°C per APHA Standard Method 5210B. Total solids (TS) and volatile solids (VS) were quantified gravimetrically: TS was determined following sample drying at 105°C to constant mass, and VS was subsequently obtained by ignition of the dried residue at 550°C for 1 h in a muffle furnace, with VS expressed as the mass loss on ignition.

It must be explicitly noted that gas-phase hydrogen content was not verified by gas chromatography (GC) in the present study. Reported hydrogen yields are therefore theoretical estimates derived from COD-based stoichiometric calculations and corroborated by comparison with efficiency values reported in the peer-reviewed literature for analogous single-chamber MEC systems operating on fermentative hydrolysate substrates. GC-based confirmation of H_2 purity and composition is identified as a critical requirement for validation in future experimental iterations, and the absence of direct gas-phase analysis represents a defined limitation of the present work.

3. RESULTS AND DISCUSSIONS

3.1. Influence of OFMSW Composition on Substrate Biodegradability and MEC Suitability

The physicochemical nature of organic fraction of municipal solid waste (OFMSW) proved to be an important determining factor for the MEC-based electrohydrogenesis performance due to substrate character influence on microbial accessibility, electron donor availability and the overall electroconversion process efficiency. The segregation analysis showed that the biodegradable organics (B.O.) dominated the samples and constitute between 50 and 62% of samples and the mean value was about 57%. The abundance of biodegradable organics confirms that the sample selected was appropriate for bioelectrochemcial conversion, at the same time it also supports the efficiency of the segregation process to effectively remove the inert and non-biodegradable compounds in the waste before the hydrolysis.

The moisture content of the sample ranged between 80.5 to 85.7% with variable volatile matter (68–82%) but very low ash content (< 10%). High moisture content of the substrate was advantageous to MEC operation as water promotes feedstock solubilization and facilitates efficient proton transfer between the anode and cathode in an aqueous environment (Zhang et al., 2019), unlike thermochemical conversion systems where elevated moisture levels negatively affect performance due to thermal energy losses associated with water evaporation (Subbiah et al., 2025). The proportion of volatile matter increased from Sample 1 to Sample 3 to the maximum value of 82% for Sample 3. Generally, higher percentage of volatile matter corresponds to higher percentage of degradable organic carbon compounds, which include carbohydrates, lipids and proteins, the compounds oxidized by electroactive bacteria. The data is also consistent with the trend in caloric value and carbon content, meaning the samples with higher volatile matter had higher biochemical and electrochemical potential. The C/N ratio of the samples ranged between 21.72 to 24.68 which is considered as the optimal range in most anaerobic processes, since high enough Carbon content could be served to the bacteria for respiration while without excessive nitrogen and ammonia buildup. An optimized C/N ratio is especially important in MEC systems because elevated nitrogen levels in the substrate can alter anodic microbial community composition and promote competing metabolic pathways, thereby reducing electron recovery efficiency (Xu et al., 2025). Sulfur content in the samples were very low, between 0.25 to 0.28% for all samples. Low concentration of sulfur is beneficial for the electrochemical performance of the MEC system because it directly competes with electroactive bacteria for electron donors that is crucial in the electrohydrogenesis and can decrease coulombic efficiency.

The observed discrepancy among different samples highlights the natural heterogeneity of MSW feedstocks and shows one of the most significant operational difficulties in the case of MSW-fed MEC system. Due to the variations of dietary habits, food consumption patterns within a year and efficiency of source-based segregation system, the biodegradability of the waste and thus its electrochemical performance is likely to differ. However, the organic fraction (biodegradable) was high enough to support electroactive bacterial metabolism in all cases which further emphasizes that the utilized pretreatment process converted the heterogeneity of feedstock in a bioavailable substrate. Table 3 shows the physicochemical characterization of OFMSW Organic Fraction.

Table 3
Proximate and Ultimate Analysis of the OFMSW Organic Fraction

Parameter	Sample 1	Sample 2	Sample 3	Mean ± SD
PROXIMATE ANALYSIS				
Moisture Content (%)	82.50	80.50	85.70	82.90 ± 2.63
Volatile Matter (%)	68.00	70.00	82.00	73.33 ± 7.57
Ash Content (%)	9.52	8.97	8.70	9.06 ± 0.42
Calorific Value (kcal/kg)	4607.7	4340.8	4891.1	4613.2 ± 275.4
ULTIMATE ANALYSIS				
Carbon (wt%)	49.60	52.36	57.76	53.24 ± 4.17
Nitrogen (wt%)	2.23	2.41	2.34	2.33 ± 0.09
Hydrogen (wt%)	6.70	7.02	6.16	6.63 ± 0.44
Sulfur (wt%)	0.25	0.28	0.26	0.26 ± 0.02
C/N Ratio	22.24	21.72	24.68	22.88 ± 1.57
All proximate analysis values are reported on a wet basis unless otherwise stated. Ultimate analysis values are reported on a dry ash-free (daf) basis. Mean ± SD calculated across three replicate samples (n = 3).				

3.2 Hydrolysate Characterization and Biodegradability Assessment

Physicochemical characteristics of the hydrolysate fed to anodic chamber were the most important factors influencing the proportion of organic matter directly available to the electroactive microbial consortium (Table 4).

After pre-treatment followed by 72h anaerobic digestion with MW inoculum, COD of the generated hydrolysates varied in a range between 5750 and 7200 mg/L while BOD concentrations varied in between 3750 and 4600 mg/L, which are consistent with the substrate concentrations for mixed microbial consortia at single chamber MECs as indicated in literature (Wu et al., 2013; Yogeswari et al., 2014).

BOD/COD ratios varied in between a relatively narrow range (0.62 and 0.65) throughout the samples. The limited variance in BOD/COD ratios between all samples is remarkable as it shows the pretreatment approach generated hydrolysates with consistent biodegradable characteristic although mixed municipal waste is very complex. BOD/COD ratios of the order of 0.50–0.70 signify high biological accessible organics which can sustain efficiently oxidation and electron transfer. Among the 5 tested samples, sample 2 was characterized by highestCOD concentration (7200 mg/L), highest total volatile solids concentration (455 mg/L), and highest BOD concentration (4600 mg/L), all contributing to high substrate richness and electron donor availability to anodic oxidation. High COD concentrations at the electrode-biofilm interface implies high density of oxidizable compounds, enhancing theoretical electron recovery potential of the system.

Low concentrations of fixed carbon on all the hydrolysates indicate that a large portion of the organic carbon in waste was bio-convertible, not as recalcitrant particulate matter, which was desirable to be applied in MEC as dissolved and semi-dissolved organic matter can be easily assimilated and utilized by electroactive microorganisms. Successful conversion of heterogeneous OFMSW into hydrolysates with reproducible biodegradable characteristic demonstrated that combined pretreatment steps of manual separation, drying, grinding, and anaerobic fermentation had been successfully translated heterogeneous municipal waste to an electrochemical utilizable substrate. The consistent biodegradable characteristics are vital as substrate variability is the one of major limiting factor hindering the scale-up of OFMSW-fed bioelectrochemical system.

Table 4
Physicochemical Characterization of OFMSW Hydrolysate (basis: 150 g input)

Parameter	Sample 1	Sample 2	Sample 3	Optimal Range (Lit.)
Total Solids (g)	8.75	9.75	7.15	—
Total Suspended Solids (mg/L)	583	650	477	400–800
Total Volatile Solids (mg/L)	397	455	391	350–600
Fixed Carbon (mg/L)	131	137	44	< 200
COD (mg/L)	5750	7200	6640	5000–10,000
BOD (mg/L)	3750	4600	4130	2500–6000
BOD/COD Ratio	0.65	0.63	0.62	0.50–0.70

3.3. Electrohydrogenic Performance and Coulombic Efficiency

The MEC experimental performance demonstrated the highly positive correlation between substrate quality and hydrogen production efficiency. Sample 2, having a more readily biodegraded and concentrated substrate in terms of COD than sample 1, showed consistently higher performance in all areas of study with an experimental gas volume of 1.94 L compared to Sample 1's 1.32 L. This equates to roughly 47% more gas being produced even though both experiments were run in the exact same reactor set-up and same operational conditions.

The improved efficiency of Sample 2 was primarily due to increased biodegradability of the substrate and higher COD content. The higher COD concentration correlates with a higher concentration of electron-donating organics that are oxidized at the anode surface by electroactive microorganisms. In electroexhydrogenesis the organic substrate is oxidized by electroactive microorganisms and then the electrons are transmitted out of the cells, through a conductive medium to the anode where proton-electron fluxes are produced that lead to proton and electron flow across the cathode for hydrogen generation. Therefore, higher concentrations of biodegradable carbon will yield higher current generation and hydrogen production efficiency.

Efficiencies for each condition reached 60% in Sample 1 and 72% in Sample 2; coulombic efficiencies were estimated to be 58% and 69% respectively. The efficiencies observed in this experiment are in the higher range of performance generally reported in single chamber MECs utilizing mixed inocula with complex, waste derived substrates. High percentages of electrons recovered indicated that significant portions of the electrons derived from the substrate were successfully applied to the production of cathodic hydrogen. However, coulombic efficiency alone does not confirm hydrogen purity or cathodic hydrogen recovery. CE quantifies electron flow from substrate oxidation through the external circuit, but does not distinguish whether those electrons ultimately produced H_2 or were consumed by competing cathodic reactions. Cathodic hydrogen recovery (r_cat), which measures the fraction of cathode-directed electrons that result in recoverable hydrogen gas, would need to be independently determined to fully characterise system performance.

It must be noted however that the deviation between theoretical and experimental hydrogen yields suggest several electrochemical and biological mechanisms of loss. Electrical resistance was arguably the most dominant cause of low efficiency. In single chamber MECs losses in

electrical energy can occur due to electrolyte resistance and resistance across the electrode/electrolyte interface and activation overpotentials, reducing efficiency of electron transfer. The electrode-spacing in this reactor was approximately 3 cm, which likely contributed to higher electrical resistances as it increases the path length of proton transport through the solution.

Besides electrochemical resistance it is probable that biological pathways compete in the process, hence limiting the efficiency of electron transfer; specifically in membrane free, single chamber MECs methane producing archaea can consume produced hydrogen for methane synthesis rather than the release of H2. This is often more dominant at substrates of higher complexity that contain high concentrations of readily fermentable carbon. The heterogenous nature of the substrates may also lead to loss in electron efficiency as not all organics can be consumed at high rate within the operational period.

The lack of a GC in this analysis of MEC efficiency represents a significant limitation to the interpretation of the data. Using water displacement measures total gas production but doesn't account for differences between H2 and CO2 or CH4 so hydrogen yields and coulombic efficiencies are estimations. Consequently, the reported CE values should be treated as upper-bound approximations the actual proportion of electrons contributing specifically to hydrogen evolution, as distinct from methane or other cathodic products, remains unresolved without compositional gas analysis.

However, even with these shortcomings the efficiencies determined compare to what has previously been reported using food wastes and municipal wastewater derived substrates, confirming that OFMSW hydrolysate can indeed be used to drive electrohydrogenesis in a low-cost and simple reactor design.

3.4. Kinetic Behavior of Hydrogen Evolution

As would be expected for substrate limited microbial electrochemical systems the hydrogen production profiles displayed the standard saturation-type kinetics, as illustrated in Fig. 3. In both samples hydrogen evolution peaked and increased quickly in the first few hours of operation, then decreased further with operation as both substrate became depleted and mass-transfer limitations begin to be realized. The final produced amount of hydrogen at 10h was about 1.92 L for Sample 2 while that for Sample 1 reached nearly 1.27 L at the same condition. The increased evolution rate of Sample 2 confirms our hypothesis that the improved substrate biodegradability had increased the microbial electron transfer activity throughout the operation period. The initial fast raise of hydrogen production could be attributed to the high amount of available substrate and active exoelectrogenic metabolism at the biofilm-anode interface where readily biodegradable organic matters are being oxidized rapidly, therefore a higher rate of electron flow to the cathode can be achieved. As operation proceeds, the amount of soluble organic matters decrease, and the mass-transfer of organic matters frombulk medium to the biofilm or from biofilm bulk to anode surface, as well as metabolic intermediates produced in biofilm, gradually inhibited the electron transfer rate leading to saturation curves.

Figure 4 shows the process efficiency curves for both samples over time. Sample 1 reached approximately 58% efficiency and Sample 2 approached 68% by 10 hours, with both still slowly increasing suggesting that longer operational periods could recover additional hydrogen from the remaining substrate, though with diminishing marginal return. The similar efficiency versus time profiles showed rapid increase followed by slowly saturation plateau. Within first 4-6h of the operation more than 80% of overall efficiency raise reached, that meant the majority of easily biodegradable fractions of substrates have been consumed at the early stage of the operation.

3.5. Industrial-Scale Projection through Dynamic Simulink Modelling

In order to assess the scalability of the fabricated MEC system, a transient MATLAB/Simulink model was built utilizing experimentally determined substrate and performance parameters. This model incorporated anodic microbial kinetics, cathodic hydrogen evolution, ion transport, and subsequent gas separation.

For a 10 kg equivalent OFMSW input scenario, predicted hydrogen production was approximately 5.8-7.0 L in a 12-h operational window, depending on the quality of the waste substrate. Table 5 shows Simulink model parameters corresponding to a 10 kg input scale, using initial substrate concentrations and microbial kinetic parameters calibrated to match the experimental hydrolysate characterization data from this study In all simulation cases, saturation-type kinetic behavior was observed in the model, similar to experimentally obtained data, implying that the substrate depletion and electron transfer remain controlling factors at a larger scale. A comparative analysis of this work and previous research work can be observed in Table 6.

Figure 5 presents the hydrogen production versus time curves from the 10 kg industrial-scale Simulink simulation. Three scenarios are shown, corresponding to different sample quality profiles: Sample 1 (80% efficiency assignment), Sample 2 (71% efficiency assignment), and Sample 3 (85% efficiency assignment). All curves show the characteristic saturation profiles expected from Monod-kinetics-based substrate utilization. Sample 3 in the simulation reaches approximately 7.0 L of hydrogen by 12 hours; Sample 1 plateaus at approximately 5.9 L; and Sample 2 reaches approximately 6.3 L. The rapid initial rise reflects the period of maximum substrate availability and biofilm metabolic activity, while the flattening after approximately 8–10 hours reflects progressive substrate depletion and mass-transfer limitation. At 10 kg scale, total hydrogen production is roughly 4–5 times the bench-scale results, broadly consistent with the linear scaling of feed mass.

Figure 6 shows the efficiency versus time curves for the three simulation scenarios. Sample 3 achieves the highest final efficiency (~ 85%), followed by Sample 1 (~ 80%) and Sample 2 (~ 71%). The ordering differs somewhat from the bench experiment because the simulation applies efficiency parameters calibrated to represent different substrate quality scenarios, whereas the bench experiment reflects the actual measured performance of specific hydrolysate batches. The initial rapid rise and subsequent flattening of efficiency reflects the kinetic profile of biofilm-mediated electron transfer. The simulation indicates that steady-state coulombic efficiency (plateau value) is largely determined by substrate biodegradability and electrode kinetics rather than reactor operational time beyond the first 6 hours, an important insight for optimising batch operational cycle length in industrial applications.

Simulated current density and cathodic potential at steady-state approached approximately 18–20 A m2 and 0.25 V, respectively. Both of these values fall within reported ranges for single-chamber MEC systems with complex organic substrates and non-noble metal cathodes. Again, this implies steady-state condition is not directly affected by size, though it also suggests that biofilm growth and conductivity play a significant role in the initial transient startup before reaching steady state.

It should be emphasized that the industrial simulation is not to be interpreted as a validated engineering-scale prediction; it is a speculative extrapolation utilizing a series of experimentally obtained kinetic parameters and simplified assumptions. Important large-scale parameters such as hydrodynamic behavior, biofilm heterogeneity, electrode aging, gas crossover, and fouling behavior were not validated experimentally in this work.

Nonetheless, the simulation provides a helpful understanding of the interplay between substrate quality, electrochemical kinetics, and hydrogen generation at a reactor scale. Moreover, it highlights crucial engineering concerns associated with scale-up, such as maintaining a favorable surface-area to volume ratio, and overcoming increased ohmic resistance as reactor size increases.

The predicted rates suggest that OFMSW fed MEC systems can be promising for a decentralized waste to hydrogen application, especially in areas that generate large volumes of organic Municipal Solid Waste and have a concurrent demand for energy. However, gas purification, characterization, a pilot-scale study and techno-economic analysis, at a minimum, are required before large scale deployment can be contemplated.

Table 5
Summary of Simulink Simulation Results vs Lab-Scale Experimental Data

Metric	**Lab-Scale (This Study)**	**Industrial Simulation (10 kg)**
Sample size / input	1 kg OFMSW	10 kg OFMSW
H2 Production (Sample 1 equiv.)	1.32 L	5.8–5.9 L (plateau ~ 12 h)
H2 Production (Sample 2/3 equiv.)	1.94 L	6.3–7.0 L (plateau ~ 12 h)
Efficiency (Sample 1)	60% (80% assigned)	Reaches ~ 80% asymptote
Efficiency (Sample 2)	72% (71–85% assigned)	Reaches 71–85% asymptote
H2 Production Rate (industrial)	—	4.85 L/min
Current Density (modelled)	—	~ 18–20 A/m2 (steady state)
Cathodic Potential (modelled)	—	Stabilises to ~-0.25 V
COD Removal (%)	~ 60–72%	Coulombic efficiency > = 80%

Study	Substrate	Feedstock	H_2 Yield (reported)	Applied Voltage (V)	Efficiency (CE)	Cathode H_2 recovery	Key Limitations	References
Two-chamber concentric tubular MEC	Acetate (synthetic)	S	0.20 m^3 H_2/m^3/day	0.85	60%	45%	Hydrogen production decreased at higher catholyte pH and temperatures above optimum; possible hydrogen diffusion to anode reduced recovery and yield	Kyazze et al. (2010)
MEC (UV-irradiated, 30 cycles)	Acetate (synthetic)	S	3.70 mol H_2/mol acetate	0.2–0.9	~ 78%	Not reported	Methanogenesis reduces yield over extended runs; requires methanogen inhibition strategy	Hou et al., 2014
Flat-plate MEC with central anode chamber and dual cathode chambers	Sludge	R	0.37 m^3 H_2/m^3/day	~ 1.1	61 ± 6%	93 ± 15%	Methanogenesis reduced electron recovery at longer HRT; reactor performance strongly depended on HRT and maintaining alkaline anode conditions (~ pH 8.1)	Ki et al., 2017
Dual-chamber MEC	Lignocellulosic biomass	S	2.46 mmol H_2/L/day	0.8	Not reported	Not reported	Hydrogen production strongly depended on anolyte pH and temperature; low pH favored hydrolysis but inhibited exoelectrogenic activity, while high temperature improved hydrolysis but reduced hydrogen production	Wang et al. (2017)
MEC (MWEC, high-current)	Domestic wastewater COD	R	121 m^3 H_2/m^3/day (400 mA/cm^2)	2.2	Not reported	Not reported	High voltage demand at industrial current densities; 5.93 kWh/m^3 H_2 energy cost	Dong et al., 2024
MEC Dark fermentation effluent	Organic waste (cheese whey)	R	75.5–78.8 NL H_2/kg TOC	Not externally applied (galvanic bio-electrochemical configuration)	Not reported	Not reported	Hydrogen production depended on metabolic acid formation and electrochemical coupling efficiency; performance limited by integration of fermentation and	De Gioannis et al., 2023

Notes: MFC= Microbial fuel cell; MEC = Microbial electrolysis cell; R = Real waste stream; S = Synthetic/laboratory substrate. Coulombic efficiency (CE). All voltages are applied external voltages vs. open-circuit potential unless stated otherwise.

Study	Substrate	Feedstock	H_2 Yield (reported)	Applied Voltage (V)	Efficiency (CE)	Cathode H_2 recovery	Key Limitations	References
							electrochemical stages	
THIS STUDY Single-chamber MEC	**OFMSW (institutional + residential, field-collected)**	**R**	**1.32–1.94 L gas/run (10 h batch operation for 10kg)**	**6**	**58% (Sample 1) 69% (Sample 2)**	**Not measured**	**Single-chamber; no membrane; gas composition uncharacterised; CE = upper-bound estimate**	**This study**

Notes: MFC= Microbial fuel cell; MEC = Microbial electrolysis cell; R = Real waste stream; S = Synthetic/laboratory substrate. Coulombic efficiency (CE). All voltages are applied external voltages vs. open-circuit potential unless stated otherwise.

CONCLUSIONS

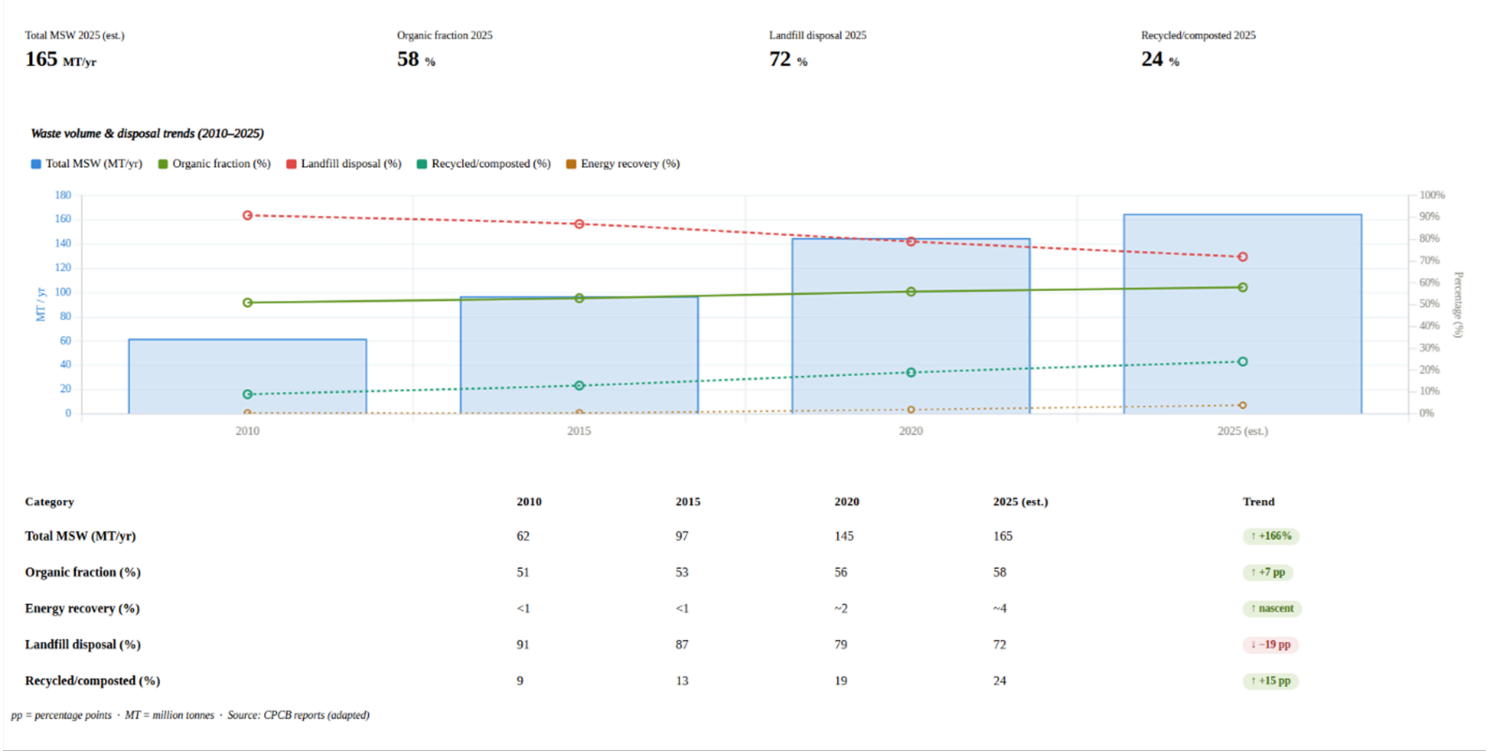
This work explores the potential of organic fraction of municipal solid waste (OFMSW) as a substrate for gas production from a Microbial Electrolysis Cell (MEC) in view of developing it into a sustainable method for biohydrogen generation. Both experimental and simulation results offer a basic proof-of-concept demonstration of a laboratory scale conversion from OFMSW-derived hydrolysate to bioelectrochemical processing, while also revealing significant technical barriers in moving toward practical application. Both pretreatments that were assessed gave comparable BOD/COD values (0.62–0.65) and COD (5750–7200 mg/L), desirable traits for readily degradable substrates in an MEC system. The 72h mixed culture fermentations that were run resulted in gas production of 1.32 and 1.94 L (based on 1000g OFMSW feed), with calculated process efficiencies of 60% and 72%, and improved performance with increasing COD values. Estimated Coulombic efficiencies (based on power usage and CODs, ~ 58% and 69% for two highest energy runs) are high, suggesting a significant proportion of substrate-derived electrons are being utilized for gas production. Based on the model simulation for a 10 kg input, a continuous operating 12 hr output of 5.8-7.0 L of gas was calculated with hydrogen production rates of 4.85 L/min at 18–20 A/m, and stabilized cathodic potentials of ~ 0.25 V with simulated Coulombic efficiencies nearing 80%. Since the gas composition was not characterized by Gas Chromatography and there was no control over the input voltage, limited to 6 V, this work can only be considered an initial demonstration of gas generation rather than a definitive proof of biohydrogen generation capabilities. Further investigation should focus on maintaining the system at closer to 0.8 V, decreasing electrode spacing, better cathode materials, gas composition verification, and pilot scale runs to confirm the technical and commercial viability of MECs operated on OFMSW.

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Figures



Category	2010	2015	2020	2025 (est.)	Trend
Total MSW (MT/yr)	62	97	145	165	↑ +166%
Organic fraction (%)	51	53	56	58	↑ +7 pp
Energy recovery (%)	<1	<1	~2	~4	↑ nascent
Landfill disposal (%)	91	87	79	72	↓ −19 pp
Recycled/composted (%)	9	13	19	24	↑ +15 pp

pp = percentage points · MT = million tonnes · Source: CPCB reports (adapted)

Figure 1

Trends in MSW generation and management in India, 2010–2025 (estimated). Data adapted from CPCB annual reports.

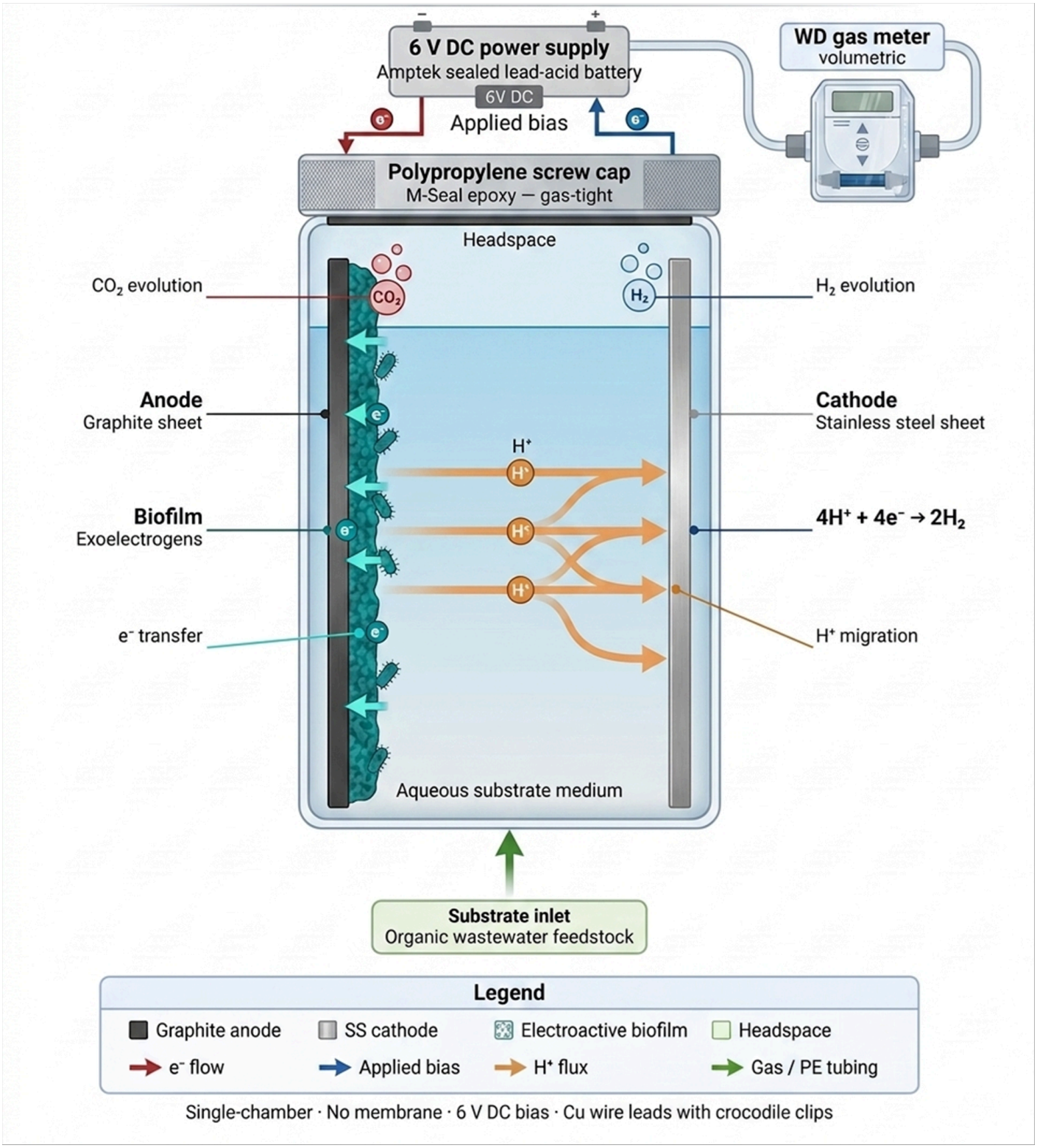


Figure 2

Designed Single chamber microbial electrolysis cell-cross section schematics

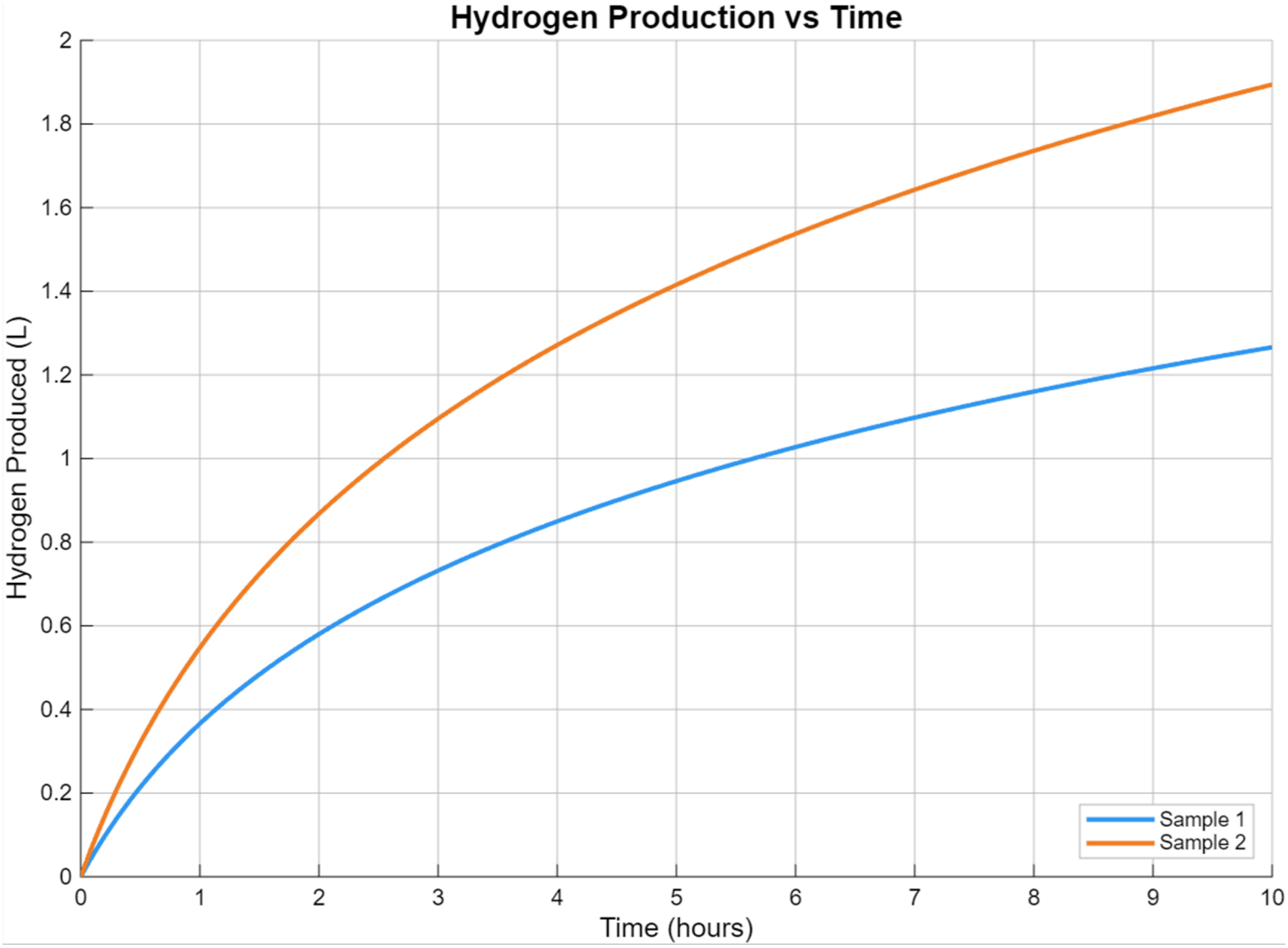


Figure 3

Hydrogen production (L) as a function of time (h) for Sample 1 and Sample 2. Data plotted using MATLAB R2025b.

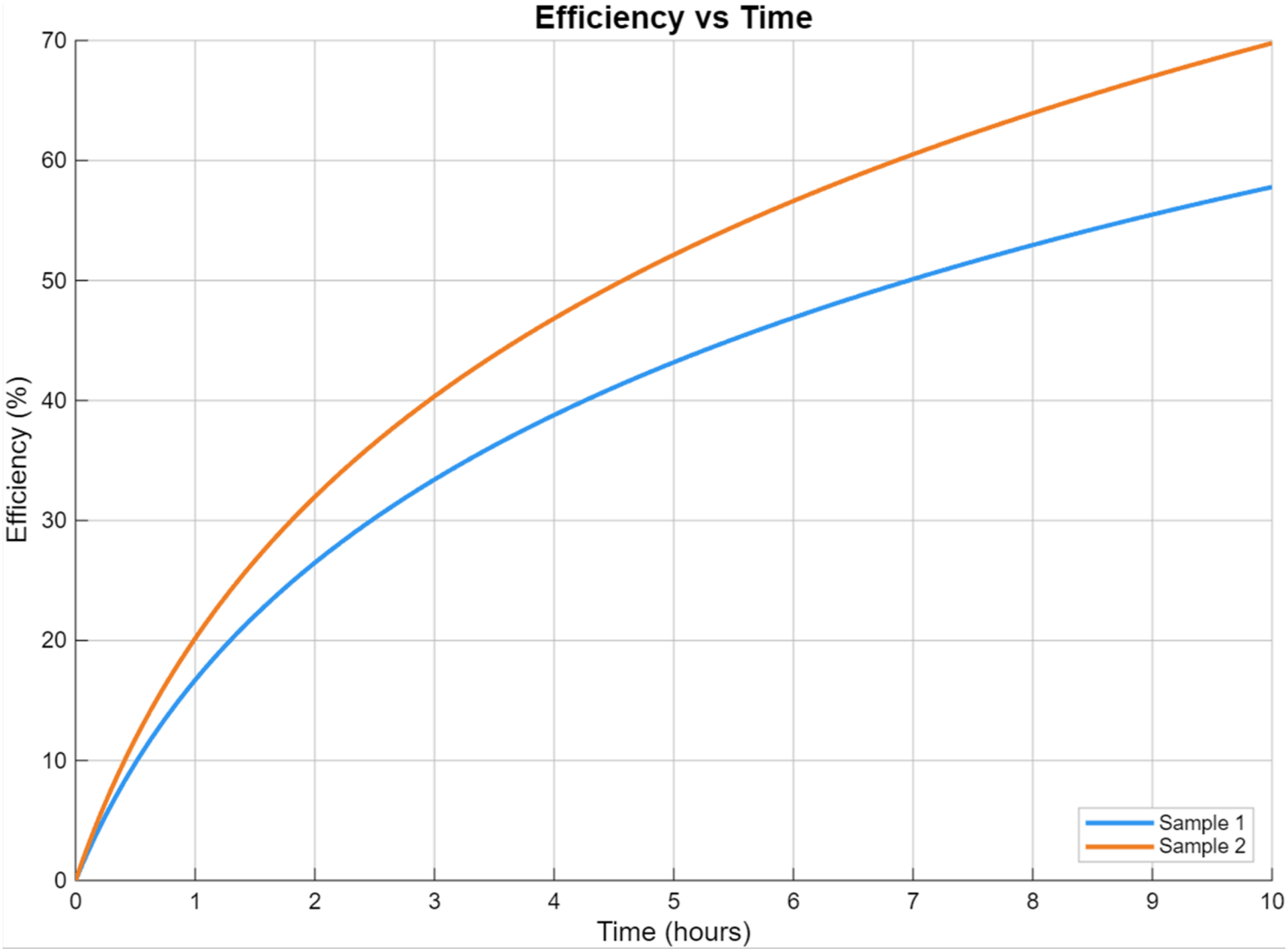


Figure 4

Faradaic efficiency (%) as a function of time (h) for Sample 1 and Sample 2. Data plotted using MATLAB R2025b.

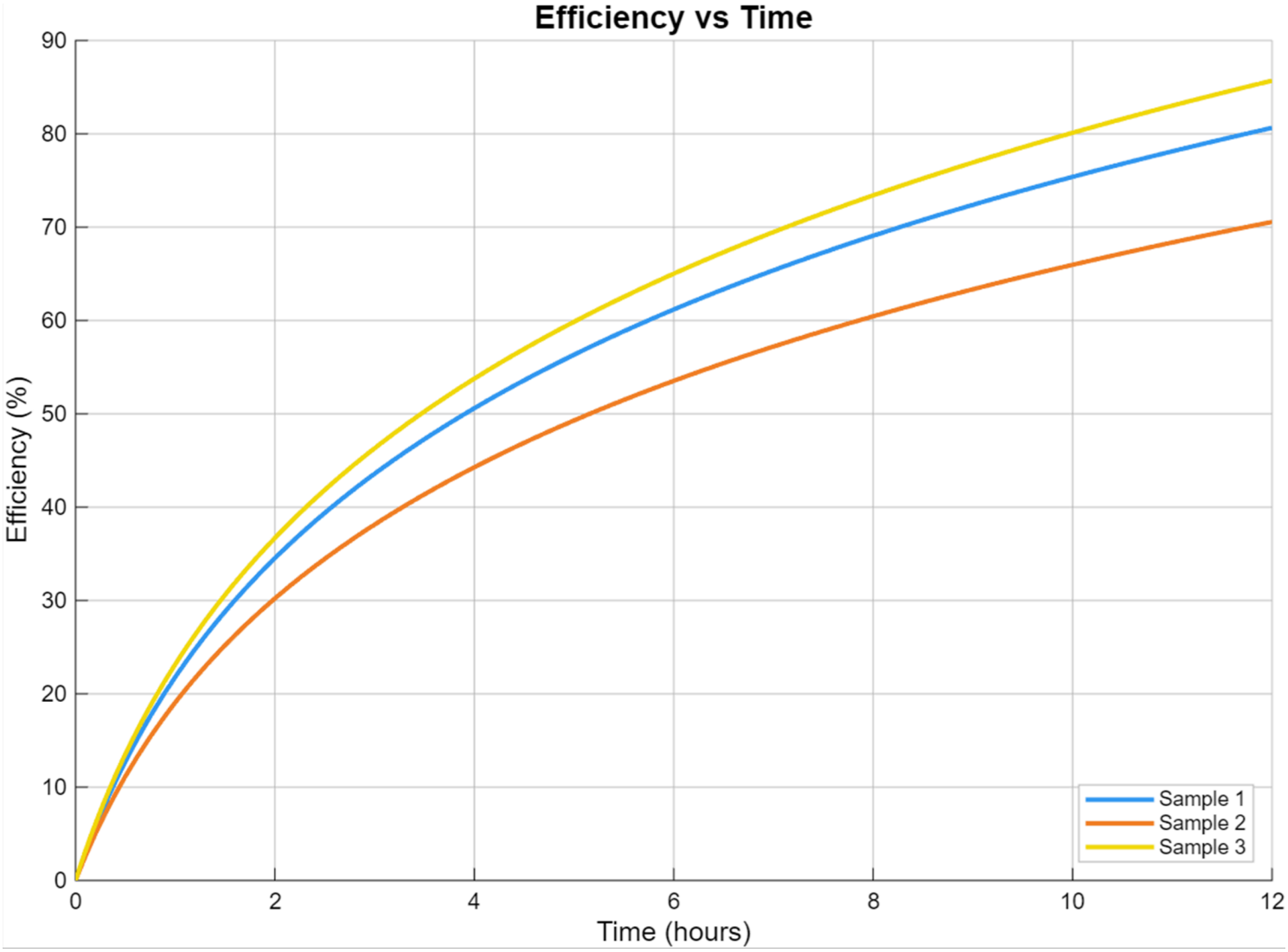


Figure 5

Faradaic efficiency (%) versus time (h) from a 10 kg industrial-scale Simulink simulation for three substrate quality scenarios, with final plateaus of ~85%, ~80%, and ~71% for Sample 3, Sample 1, and Sample 2, respectively. Plots were generated using MATLAB R2025b.

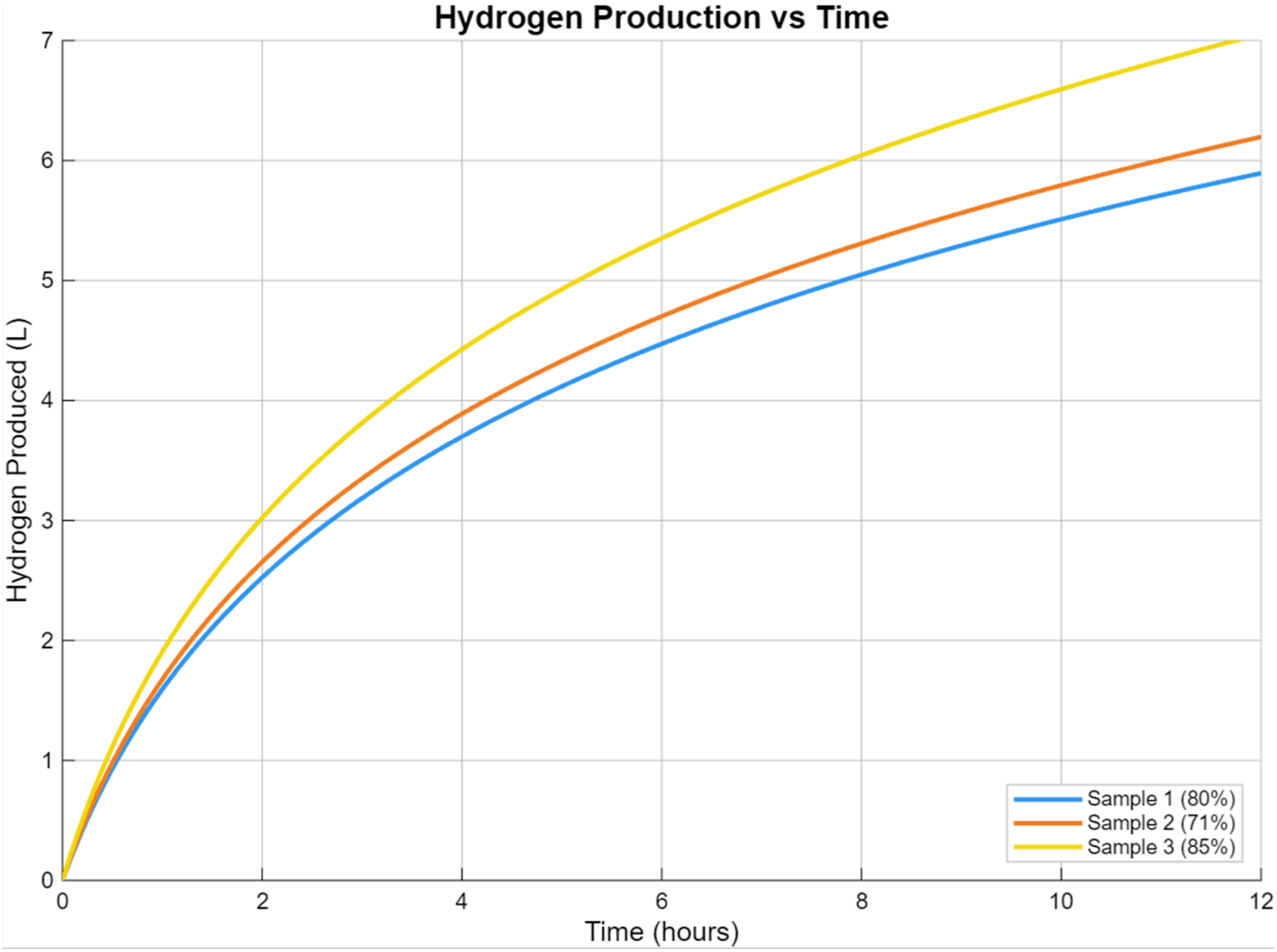


Figure 6

Hydrogen production (L) versus time (h) from a 10 kg industrial-scale Simulink simulation for Sample 1 (80%), Sample 2 (71%), and Sample 3 (85%), exhibiting Monod-kinetics saturation behavior. Plots were generated using MATLAB R2025b.