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Agro-Industry Waste Fed Microbial Electrolysis Cell for Biohydrogen Production

Ghosh Uttam Kumar[1*], **Gautam Rahul**[2]

[1]Associate Professor, Polymer and Process Engineering, IIT Roorkee, India
[2] Ph.D Scholar, Polymer and Process Engineering, IIT Roorkee, India

*corresponding author:
e-mail: **uttam.ghosh@pe.iitr.ac.in**

Abstract-.

The microbial electrolysis cell is gaining advantage over the other biological hydrogen production techniques as it requires less energy for hydrogen generation as compared to the water electrolysis process. The present study aims to assess the aptness of Agro-Industry Waste (AIW) fed membrane-less single chambered Microbial Electrolysis Cell (SC-MEC) for the biohydrogen production in batch mode under applied voltage of 1 V at 30 ± 2 °C (Fig.1). The performance of the reactor was assessed through volume of hydrogen per gram of COD removed, columbic efficiency, cathodic hydrogen recovery and COD removal efficiency. The highest COD removal of 71% was reported with columbic efficiency of around 45%. These results demonstrated an energy-efficient approach for biohydrogen production from AIW coupled with waste mitigation

Keywords: Electro-hydrogenesis, Microbial Electrolysis Cell, Electrode Modification, Over-potential Reduction, Hydrogen Evolution Reaction

1. Introduction

The energy crisis along with environmental pollution e.g. greenhouse gas emissions etc. are among the major global challenges [1–3]. Fossil fuels are the major fuels sustaining the current energy needs. The world's focus towards sustainability to counter fuel scarcity and souring prices, thus thrust for alternative renewable energy carrier is getting intensified[4,5]. The biological H_2 production methods are based on waste to energy route which gives this technology an edge. They are cheaper and environment friendly [6]. Hydrogen production methods vary from water electrolysis, thermo-chemical methods, biological methods etc. [7]. Microbial electro-synthesis systems (MES) are an efficient device for biofuel production [8,9].The biological routes of hydrogen production are promising as they deliver hydrogen from waste as well as manages the waste and pollution. Hence, the scientific community is penetrating renewable energy resources to answer the energy scarcity through the waste energy route. This has led to an integration of solid waste management and biofuel production. Among the potential biofuels studied, Bio-hydrogen is considered as one of the most attractive alternatives owing to the properties of the hydrogen as fuel [10–14]. The combustion of hydrogen produces only heat and water without any greenhouse emissions which makes it a potential fuel. The evolution of Microbial Electrolysis Cell (MEC) in recent times has gained momentum for H_2 production from inexpensive organic materials such as waste food materials, thermal and chemical hydrolysate, sludge, industrial effluents, landfill leachate etc. [15]. MECs are based on electro-hydrogenesis process of biodegradable materials [14]. They are anaerobic systems, can be either single chambered or double chambered. The exo-electrogenic bacteria at anode oxidize organic matter and transfer electrons extracellularly to cathode via external circuit, while proton travel through proton exchange membrane or directly to cathode. The catalyst if present, at cathode catalyzes the formation of H_2 from electrons and protons. Theoretically, MECs require only external voltage of around 0.11 V to drive the H_2 production from acetate [1,16].

The current study focuses on the utilization of Agro-Industry Waste (AIW) in batch mode of membrane less single chambered Microbial Electrolysis Cell (SC-MEC) for the biohydrogen production at an applied voltage of 1 V at 30 ± 2 °C (Fig.1).

2. Experiments

2.1. Reactor design and construction

Single chambered MEC was constructed with acrylic sheet in a cube shape with side = 12 cm with a working volume of 700 mL. The carbon cloth electrodes of surface area (approx. 10 cm^2) were kept at an effective distance of 6 cm to reduce the overpotential in MEC. A 100 Ω resistor was connected in series with the electrodes by copper wires.

2.2. Reactor Inoculation and operation

The electrode enrichment for bioanode was achieved with a pure culture of *Shewanella putrefaciens* on heat treated carbon cloth and then switched to fully anaerobic SC-MEC. The MEC was inoculated with pure culture digestate from the Microbial fuel cell fed AIW. After acclimatization AIW was fed to the MEC and purged with N_2 for 15 min before and after of feeding. The bio-film was achieved on anode from MFC kept in MEC mode at 1 V for 72 h [2]. The phosphate buffer was used to maintain the pH.

2.3. Reactor performance parameters

The performance of the reactor was assessed through volume of hydrogen per gram of COD removed, columbic efficiency, cathodic hydrogen recovery and COD removal efficiency. The highest COD removal of 71% was reported with columbic efficiency of around 45%. These results demonstrated an energy-efficient approach for biohydrogen production from AIW coupled with waste mitigation. This lab scale study of 500 mL of SC-MEC resulted in the promising approach of hydrogen production and can be escalate to subsequent pilot scale studies. The FE-SEM image of bioanode had shown a biofilm cover over the carbon cloth (Fig.2).

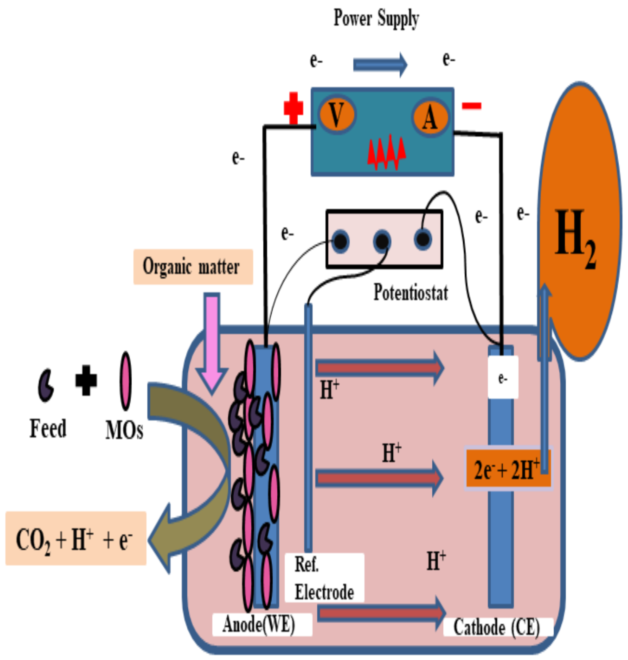

Figure 1. Schematic representation of MEC

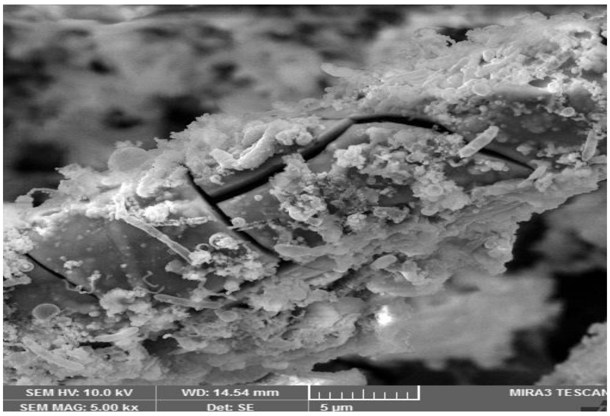

Figure 2. SEM image of bio-anode

2.4. Gas measurement, storage and analysis

The produced bio-hydrogen was measured by the well-established water displacement method. The gas was stored in a graduated measuring cylinder. After the batch cycle, produced gas was analysed by the Gas Chromatography by using a gas tight syringe and argon as the carrier gas in TCD mode.

3. Results and Discussion

3.1. MEC performance and Bio-film formation

After the acclimatization at 0.5 V, MEC fed with AIW was given 1 V in a batch cycle. The maximum current of 15 mA and corresponding current density of 5.5 A/ m^2 were achieved. The total volume of gas was recorded as 1890 mL with 64 % of H_2 content (by Gas chromatography). The bio-anode samples were scanned under Scanning Electron Microscope. The biofilm formation on the electrode surface can be seen in the image (Fig. 2).

3.2. COD removal and Substrate degradation

The organic matter of substrate reportedly degraded by microorganisms and reflected in terms of the COD removal, Total Suspended Solid (TSS), Volatile Suspended Solids (VSS) reductions (Fig.4) and eventual Hydrogen production. The initial phase resulted in lower COD removal but with the passage of time COD removal efficiency of the MEC increased continuously and at the end of the 21st day cycle, COD removal of 70.8 % was achieved.

3.3. H_2 production rate

The production rate for hydrogen was investigated to evaluate the performance of the MEC. A total of 1890 mL of gas was collected at the end of the batch cycle. The hydrogen production rate continuously increased as indicated by the COD removal percentage. The coulombic efficiency (CE) and the cathodic gas recovery (Rc) are two parameters to evaluate the MEC performance along with the production rate [13,17].

Total amount of Hydrogen (Vh) in total gas is calculated based on Eq. 1.

$$Vh = (Hs + Vt)Gf \qquad \textbf{(1)}$$

Where –
Vh - volume of Hydrogen in total gas
Hs – headspace volume in mL
Vt – total volume of gas in mL
Gf – fraction of Hydrogen in gas measured by GC

The expected gas production (Vexpt) from the complex substrate is given by Eq. 2

$$Vexpt = Ct * \frac{Vm}{2F} \qquad \textbf{(2)}$$

where,
Ct – charge over the given time in Coulomb
Vm – volume of one mole of gas in mL
F – Faraday Constant

The Cathodic hydrogen recovery (Rc) is the measure of the conversion of electrons to hydrogen (Eq. 3). It is the ratio of V_h to Vexpt. The Rc is used to calculate the coulombic efficiency (CE) in Eq. 4. It is the ratio of current measured over a time to the theoretical current based on COD.

$$\mathrm{Rc} = \frac{\mathrm{Vh}}{\mathrm{Vexpt}} \qquad \textbf{(3)}$$

$$\mathrm{CE} = \frac{\eta\mathrm{ce}}{\eta\mathrm{th}} \qquad \textbf{(4)}$$

Based on the results obtained from gas chromatograph, the amount of hydrogen in 1890 mL of gas produced and 200 mL of headspace, was estimated as 1690 mL. The results obtained were in accordance and comparable to other studies on waste as shown in Table. 1.

Feed	**E_{ap}**	**CE (%)**	**Rc (%)**	**Q ($m^3/m^3/day$)**	**COD removal %**	**References**
Agro Industry Waste	1	45	54.6	0.2	71	**Present study**
Leachate	1	12-41	66-95	0.04-0.06	65-73	**[6]**
Acetate	0.8	8-42	65-93.8	0.034-0.237	86.6-97.5	**[18]**
Sludge	0.6	NA	NA	4.6 mg/g VSS	17-53	**[16]**
Acetate	1	22.80 %	101.40%	0.3	NA	**[20]**
Glycerol	0.8	35	4	0.021	100	**[22]**
Milk	0.8	52	13	0.086	73.5	**[22]**

4. Conclusion

The present study on the SC-MEC fed with agro industry waste resulted into 71 % of COD removal and 45% of coulombic efficiency. The results of this study has been compared with the other similar studies and has shown in table 1. The hydrogen production rate and current density of 0.2 m^3/m^3/day and 5.5 A/m^2 could be further increased by efficient extracellular electron transfer achieved through electrode modifications. This study indicated that AIW resulted into comparable or even higher coulombic efficiencies and COD removal in comparison to the most studied feed acetate. Also, enhanced rate of hydrogen production was achieved.

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