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Assessment of Carrot Juicing Pulp Hydrolysate fed MEC for Bio-Hydrogen production

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Abstract - The thrust for alternative renewable energy carrier with the integration of solid waste management and biofuel production is considering Biohydrogen as one of the most attractive alternatives. The present study aims to assess the suitability of carrot juicing pulp hydrolysate (CJPH) fed membrane less single chambered Microbial Electrolysis Cell (MEC) for the bio-hydrogen production in batch mode under applied voltage of 0.8 V at 30 ± 2 °C. The anode enrichment for bioanode with mixed culture of microorganism was achieved on heat treated graphite rods. The maximum bio-hydrogen production was reported as 0.1 m^3 of $H_2/m^3/d$ at $E_{applied}$ = 0.8 V at HRT of 21 days. The maximum COD removal of 76.6 % was reported. These results demonstrated an energy-efficient approach for biohydrogen production from CJPH coupled with waste mitigation.

Keywords: BioHydrogen, Microbial Electrolysis Cell, Juice Pulp Hydroselate, COD, Bioanode

1. Introduction

The present energy needs are majorily sustained by burning the depleting fossil fuels reserves. Energy crisis along with the environmental pollution e.g green house gases emissions etc are among the major global challenges (Kadier et al., 2020). Hence, the scientific community is penetrating the renewable energy resources to answer the energy scarcity. Bio-fuels derived from waste can be utilized to drive the global energy needs. Hydrogen gas is an promising altemative renewable energy source due to its high energy density, calorific value and only water as clean byproduct. 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 (Hassan et al., 2018). Hydrogen production methods vary from water electrolysis, thermo-chemical methods, biological methods etc (Jabbari et al., 2019). Microbial electro-synthesis systems (MES) are an efficient device for biofuel production (Kumar et al., 2017; Nelabhotla et al., 2020).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 (Lalaurette et al., 2009). MECs are based on electrohydrogenesis process of biodegradable materials (Call & Logan, 2008). They are anaerobic systems, can be either single chambered or double chambered. The double chamber MECs are the earliest, simplest and most studied cells. 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, 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 (Kadier et al., 2020). Biohydrogen production from renewable resources and wastes is gaining attention (Sun et al., 2014).

The present study focuses on the assessment of the carrot juice pulp hydrolysate in single chambered membrane-less MEC for bio-hydrogen production. The bio-hydrogen produced in MEC was quantified by water displacement method.

2. Material and Methods

2.1. Reactor design and construction

Single chambered MEC was constructed with acrylic sheet in a cube shape (a=10 cm) with a working volume of 700 mL. The MEC was equipped with plain graphite rods (approx 10cm^2) as electrodes at an effective distance of 6 cm. The 100 Ω resistor was connected in series with the electrodes by copper wires. The gas collection and sampling port were placed on the top of the reactor (Fig. 1).

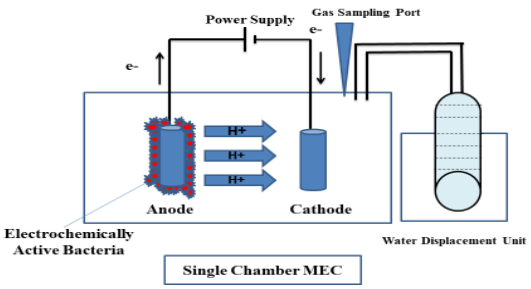

Figure 1. Schematic representation of Experimental setup

2.2. Reactor Inoculation and operation

The MEC was inoculated with mixed culture and achieved by digestate from the Microbial fuel cell fed with spent wash. After acclimatisation CJPH was fed to the MEC and purged with N_2 for 15 min before and after of feeding. The anode electrode was heat treated to avoid methanogens. The bio-film was achieved on anode from MFC kept in MEC mode at 0.5 V for 48 hrs (Lim et al., 2020). MEC was operated at 0.8V and 30 °C for 21 days. The phosphate buffer was used to maintain the pH.

2.3. 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.

Table 1. Comparision of the present study with literature

Feed	E_{ap}	CE (%)	Rc (%)	Q (m3/m3/day)	COD removal %	References
CJPH	0.8	83	54.6	0.1	76.6	Present study
Leachate	1	12-41	66-95	0.04-0.06	65-73	(Hassan et al., 2018)
Acetate	0.8	8-42	65-93.8	0.034-0.237	86.6-97.5	(Yossan et al., 2013)
Acetate	Solar Assisted	NA	NA	1.35 mL/hr	NA	(Wan et al., 2015)
Sludge	0.6	NA	NA	4.6 mg/g VSS	17-53	(Sun et al., 2014)
Acetate	1	22.80 %	101.40 %	0.3	NA	(Rozendal et al., 2007)
Acetate	0.6	21.23	21.31	114.46 mL/m2	NA	(Pasupuleti et al., 2015)
Acetate	0.6	73	87	0.69	NA	(Hu et al., 2009)
Glycerol	0.8	35	4	0.021	100	(Montpart et al., 2014)
Milk	0.8	52	13	0.086	73.5	(Montpart et al., 2014)

3. Results and discussion

3.1. MEC performance and Bio-film formation

After the acclimatization at 0.5 V, MEC fed with CJPH was given 0.8 V in a batch cycle. The maximum current of 15 mA and corresponding current density of 7.5 A/m^2 were achieved. The total volume of gas was recorded as 1760 mL with 60 % of H_2 content (by Gas chromatography). The bio-anode samples were scanned under Scanning Electron Microscope. The bio-film 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 76.6 % was achieved (Fig. 3).

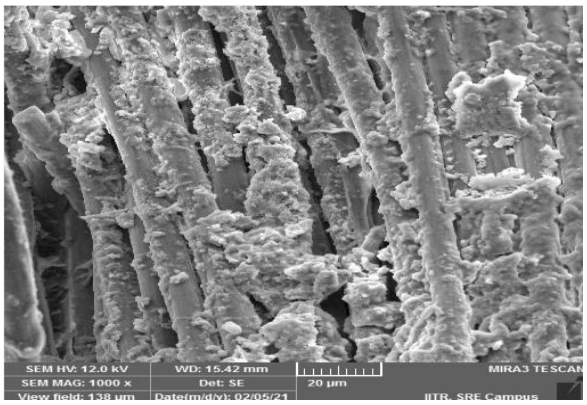

Figure 2. SEM image of Bio-anode

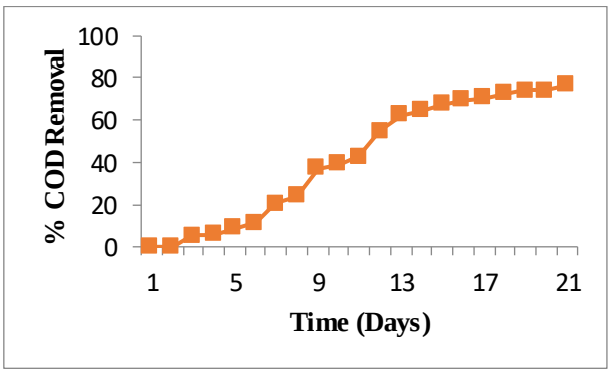

Figure 3. Variation of COD Vs Time

3.3. H_2 production rate –

The production rate for hydrogen was investigated to evaluate the performance of the MEC. A total of 1560 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 (Logan et al., 2008; Pasupuleti et al., 2015).

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

$$Vh = (Hs + Vt)Gf \qquad \text{Eq -1}$$

Where –

V_h - volume of Hydrogen in total gas
H_s – headspace volume in mL
V_t – total volume of gas in mL
G_f – fraction of Hydrogen in gas measured by GC

The expected gas production (V_{expt}) from the complex substrate is given by Eq. 2

$$Vexpt = Ct * \frac{Vm}{2F} \qquad \text{Eq} - 2$$

Where
C_t – charge over the given time in Coulomb
V_m – volume of one mole of gas in mL
F – Faraday Constant

The Cathodic hydrogen recovery (R_c) is the measure of the conversion of electrons to hydrogen (Eq. 3). It is the ratio of V_h to V_{expt}. The R_c is used to calculate the coulombic efficiency (CE) in Eq. 4.

$$Rc = \frac{Vh}{Vexpt} \qquad \text{Eq - 3}$$

$$CE = \frac{\eta ce}{\eta th} \qquad \text{Eq - 4}$$

Based on the results obtained from gas chromatograph, the amount of hydrogen in 1560 mL of gas produced and 200 mL of headspace, was estimated as 1056 mL. The corresponding values for Cathothic hydrogen recovery 54.6% and Coulombic Efficiency of 83% were estimated. The hydrogen production rate (Q) on the basis of substrate volume was normalized to 0.1 m^3 of Hydrogen / m^3 /day. The results obtained were in accordance and comparable to other studies on wastewater,leachate, wasted activated sludge etc. as shown in Table. 1.

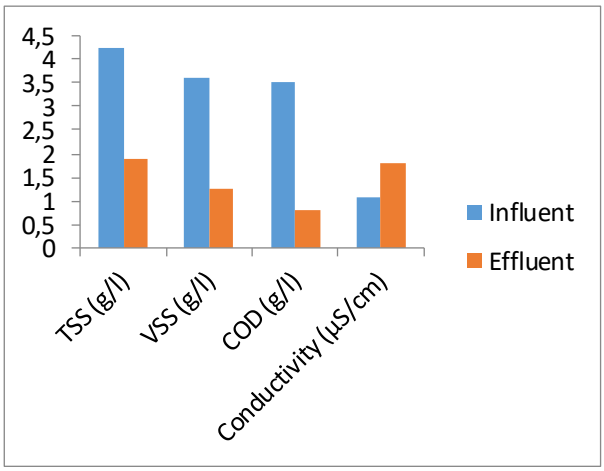

Figure 4. Pre and post treatment comparison of physicochemical parameters in MEC

4. Conclusion –

Results of this study on single chambered membrane-less MEC, demonstrated the feasibility to use carrot juice pulp hydrosylate (CJPH) for electrohydrogenesis. The Cathodic hydrogen recovery of 54.6 % and coloumbic efficiency of 83 % establish the potency of MEC to convert the waste into Bio-hydrogen. Higher COD removal can be achieved by increasing the duration of batch cycle. The rate of bio-hydrogen production of 0.1 m^3 of Hydrogen/m^3/day could be improved by selecting the pure culture of exoelectrogens over mixed culture.
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