# Enhanced hydrogen production rates in Microbial Electrolysis Cell using Biocatalyst

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**Abstract** Energy consumption around the world has increased significantly and depleting reserves pose a major concern. Green energy sources are the need of the hour to counter fuel scarcity and soaring prices. Hydrogen production through a microbial electrolysis cell (MEC) is an effective and green technology. It is a bio-electrochemical system where microbial oxidation of organic feed at the anode and reduction of protons to Hydrogen at the cathode takes place. To derive hydrogen evolution reaction (HER) over the cathode, an externally applied voltage of 0.2V is required which is very nominal in comparison to the voltage required for water electrolysis.
In the present study, the reactor digestate-derived biochar biocatalyst was evaluated for its impact on the process parameter enhancements. The bio-catalyzed single-chambered MEC (BC-SC-MEC) in a batch mode at an applied voltage of 0.8 V resulted in higher COD removal efficiency and hydrogen production rates at 30 ± 2 °C (Fig.1). The COD removal of 78%, with Coulombic efficiency of 60% and cathodic hydrogen recovery of 52 % was reported in BC-SC-MEC, while SC-MEC resulted into COD removal of 72%, coulombic efficiency of 55% and cathodic hydrogen recovery of 48% were reported. These results support the claim of boosted hydrogen production in the bio-catalyzed MEC for enhanced energy recovery.

**Keywords: Electro-hydrogenesis, Microbial Electrolysis Cell, Biochar, Bio-catalyst, Hydrogen Evolution Reaction**

## 1. Introduction

There is an intensified thrust for renewable energy for the increased energy demand and soaring fuel prices. Hydrogen as a fuel is promising, and biological routes are auspicious. The major biological routes are based on photosynthesis, fermentation, and electrochemical, out of which electrochemical routes include Microbial Electrolysis Cells (MEC) as recent promising development based on electrohydrogenesis.

The advancement in the bio-electrochemical systems has opened the doors of bio-electrochemical routes of hydrogen production. The hydrogen production through the organic waste in the bio-electrochemical systems is an attempt for clean energy and simultaneous waste utilization. Hydrogen often cited as the fuel of the future, gives water on combustion. There has been a paradigm shift in the acceptance of the hydrogen vehicle in the last decade.

The present study has evaluated the impact of the biochar-derived bio-catalyst in microbial electrolysis. The catalyst was prepared from the reactor digestate and activated using the chemical methods. The two sets of the MECs, i.e. single chamber MEC without bio-catalyst (SC-MEC) and bio-catalyst single chamber MEC (BC-SC-MEC) fed with the sugarcane bagasse were studied for the hydrogen evolution reaction at 0.8 V and 30 ± 2 °C. The performance parameters evaluated in this study are COD removal efficiency, coulombic efficiency, cathodic hydrogen recovery, along with the mL of hydrogen produced per gram of COD removed.

## 2. Methodology

### 2.1. Reactor design and construction

Single-chambered MECs were constructed using a 1000 mL 3-neck round bottom flask with a working volume of 700 mL. The anode and the cathode were of carbon cloth (surface area approx. 10cm$^2$), and were kept at an effective distance of 5 cm. The 100 Ω resistors were connected in series with the electrodes by titanium wires.

### 2.2. Reactor Inoculation and Operation

Both the MECs were first inoculated with the digestate from the previously running MEC on *Shewanella putrefaciens* for the last 2 years. The electrodes were treated with acetone and then heat-treated before putting into the SC-MEC. After acclimatization, shredded sugarcane bagasse was fed to the SC-MEC and BC-SC-MEC and purged with $N_2$ for 15 min before and after the feeding. 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, moles of hydrogen, columbic efficiency, cathodic hydrogen recovery and COD removal efficiency.

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

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

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

$$Vexpt = \ Ct * \frac{Vm}{2F} \qquad \textbf{Eq – 2}$$

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

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

$$CE = \frac{\eta ce}{\eta th} \qquad \textbf{Eq – 4}$$

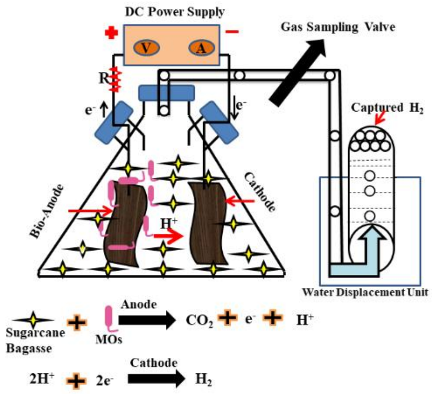


**Figure 1. Schematic diagram of the set-up**

## 3. Results and Discussion

### 3.1. MEC performance and Bio-film formation

After the acclimatization, bagasse fed MEC was supplied with 0.8 V of power supply. The maximum current of 18 mA and corresponding current density of 6.2 A/ $m^2$ were achieved in BC-SC-MEC. The total volume of gas was recorded as 1080 mL and 1250 mL in SC-MEC and BC-SC-MEC respectively with 64% and 65.4% of $H_2$ content. The bio-anode samples were scanned under Scanning Electron Microscope.

### 3.2. COD removal and $H_2$ production rate

The COD removal efficiency were reported as 72% and 78% in SC-MEC and BC-SC-MEC, which suggests that biochar derived catalyst results into higher COD removal, thus higher production rates. The initial phase resulted in lower COD removal due to initial lag phase of the microbes, but with the passage of time COD removal efficiency of the MEC increased continuously.

The production rate for hydrogen was investigated to evaluate the performance of the MEC. A total of 1080 mL and 1250 mL of gas collected in SC-MEC and BC-SC-MEC respectively at the end of the batch cycle with 64% and 65.4% of $H_2$ content. 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

The results for both the MECs are given in Table. 1 and compared in Fig.2

| *Parameters* | *Applied Voltage* | *COD removal (%)* | *CE (%)* | *Rc (%)* | *Q ($m^3/m^3/day$)* | *mL $H_2$/gm COD removed* |
|---|---|---|---|---|---|---|
| ***SC-MEC*** | 0.8 | 72 | 60 | 52 | 0.2 | 54 |
| ***BC-SC-MEC*** | 0.8 | 78 | 55 | 48 | 0.24 | 56.8 |

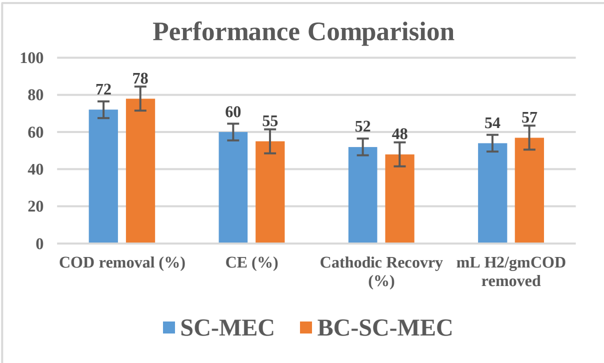


**Figure 2. Performance Comparision**

## 4. Conclusion

The current study on the biochar-based bio-catalysed MEC has resulted in higher COD removal and hydrogen production rates. The nano-structures present in the biochar are possibly responsible for the enhanced biofilm over the anode thus resulting in efficient extracellular electron transfer. The biochar as a catalyst also augments the hydrogen evolution reaction. The modifications of electrodes and reducing the space between the electrodes could result in higher cathodic hydrogen recovery and coulombic efficiency in BC-SC-MEC in comparison to SC-MEC.

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