

Biomass derived activated carbon cathode performance for sustainable power generation from Microbial Fuel Cells

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ABSTRACT

The amount of wastewater is generated from Sewage, and treating this wastewater consumes huge amount of energy. Microbial Fuel Cells can be used to treat this wastewater and generate electricity in the process. The paper deals with, an advanced cathode material in the form of an activated carbon derived from biomass sources was evaluated in terms of cathode performance, stability of operation and cost. A fixed external load produced a peak current density and power density of 0.40 mA/m² and 110 ± 6.58 mW/m² respectively. So, polarization curves reveal system stability with varying resistances with a change in COD for the wastewater from 780 ± 20 mg/l to 260 ± 30 mg/l over two weeks of operation, achieving a removal efficiency of around 64%, the BOD content of the wastewater also reduced from 520 ± 20 mg/l to 165 ± 25 mg/l with a dissolved solutes removal efficiency of 51% during time of operation. It was noted that activated carbon derived from biomass sources is a promising alternative to expensive platinum; further it has a low surface pH, lacks any acidic surface functional group.

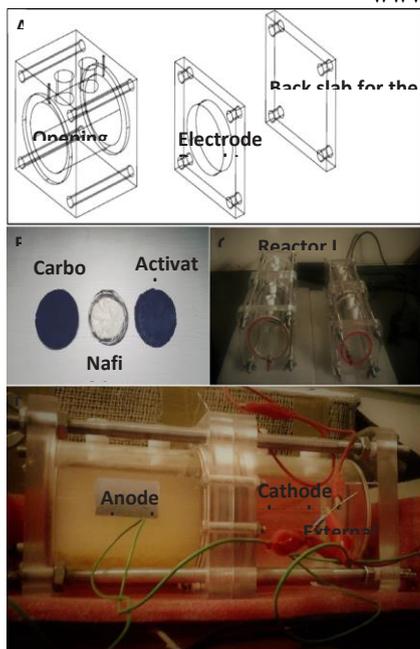
1. Introduction

When we talk about sustainable energy for the future generations, much of the debate shifts to exploring non-combustion based pollution free technologies [1]. An added incentive to these clean forms of energy is if it can be successfully integrated with the water treatment infrastructure. Wastewater generation from both domestic and industrial sources contribute significantly to the inadequate water supply for sanitation and for industries, [2] this contributes to use of expensive chemicals to treat the wastewater before discharging them to an environmentally acceptable level [3,4].

Microbial Fuel Cells or MFCs can effectively treat the wastewater, and at the same time, use the process to generate electrical power [5,6]. This is possible by the bacteria present in the wastewater, which grows on one electrode, consumes the organic matter and releases electrons, thus reducing the organic load from the water, and the electrons released travel through the length of the circuit where the load is connected and the reaction completes at the cathode [7]. In recent years,

while evaluating feasibility of making MFCs a commercial success, a key area of exploration has been the material used for the development of the cathode [8]. Traditionally Platinum (as a catalyst) on carbon cloth is used as the cathode, which is expensive and gets fouled over six months of operation [9]. Thus, finding low cost alternatives to Platinum, which can produce comparable power densities are a key area of exploration. The criteria for a new MFC cathode should include; good catalyst for oxygen reduction, can be derived from carbon-based sources, less susceptible to fouling and can be easily regenerated [10].

In this work, a novel indigenous activated carbon (AC) cathode is prepared with PVDF (Polyvinylidene fluoride) used as a binder on a Stainless Steel Mesh (Type 316L) through a single step phase inversion method [11]. Activated carbon is prepared from sugarcane refuse using a pre-treatment method, and a comparative assessment is made for AC cathode performance derived from other biomass sources [4]. Surface characteristics and functional group analysis for the prepared AC is done using XRD (X-Ray Diffraction) and FTIR (Fourier Transform Infrared Spectroscopy) respectively. Particle size analyser is used to



studies and the anode chamber is filled with wastewater (from sewage sources). Wastewater is collected from the University Sewage Treatment plant inlet. The cathode is platinum on carbon cloth, and a conductive phosphate buffer solution is used in the cathode chamber. Nafion-117 (Dupont, USA) is used as a membrane separating the anode from the cathode [13].

2.2. Advanced cathode material

As an alternative to expensive catalyst (such as Platinum), a comparative analysis is presented, with activated carbon cathode and PVDF as binder, where the cathode itself acts as a catalyst [14] A novel indigenous route was taken for the preparation of AC cathodes. Sugarcane refuse was collected from the local market, as these are freely available from local sugarcane juice suppliers. After collecting the same, the material was put in a dryer for moisture removal at 110 °C for three hours, this was followed by crushing the sugarcane to finer particles, followed by impregnation with 40 wt% Phosphoric acid (BDH Grade, Sigma Aldrich). This was followed by carbonization at 300, 400 and 500 °C at one hour intervals.

Here phosphoric acid acts as an activating agent and has several

Fig. 1. (A) Plexiglass reactor constructed out of Lexan block, with two openings for the anode and the cathode (B) The anode, membrane and the cathode which constitute the membrane-electrode assembly (C) Two identical reactors used for evaluating MFC performance (D) MFC reactor with wastewater in the anode, and phosphate buffer in the cathode, the terminals of the anode and cathode are connected to an external load (resistor).

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evaluate the average particle size. Microscopic analysis for the surface is done using AFM (Atomic Force Microscopy) and SEM (Scanning Electron Microscopy); SEM imaging is also used to see development of bacteria and nanowires on the anode. A control MFC setup was used with Platinum as catalyst on carbon cloth to see comparative performance of the MFC systems, in terms of power generation, oxygen reduction, operational stability, and water pressure handling capacity.

2. Materials and methods

2.1. MFC reactor

Cube double chambered reactors were used in all the studies. These were made from a lexan block having an inside cylindrical chamber for the anode and cathode liquid respectively [12]. The membrane is sandwiched between the anode and the cathode. As shown in Fig. 1A, the side of the reactor facing the anode holds the anode liquid, and the side facing the cathode will house the cathode liquid. The Membrane Electrode Assembly (MEA) was fabricated by a process which has been discussed previously [6] The anode is plain carbon cloth (E-TEK, USA) without wet proofing (having a surface area of 28.26 cm²) for all the

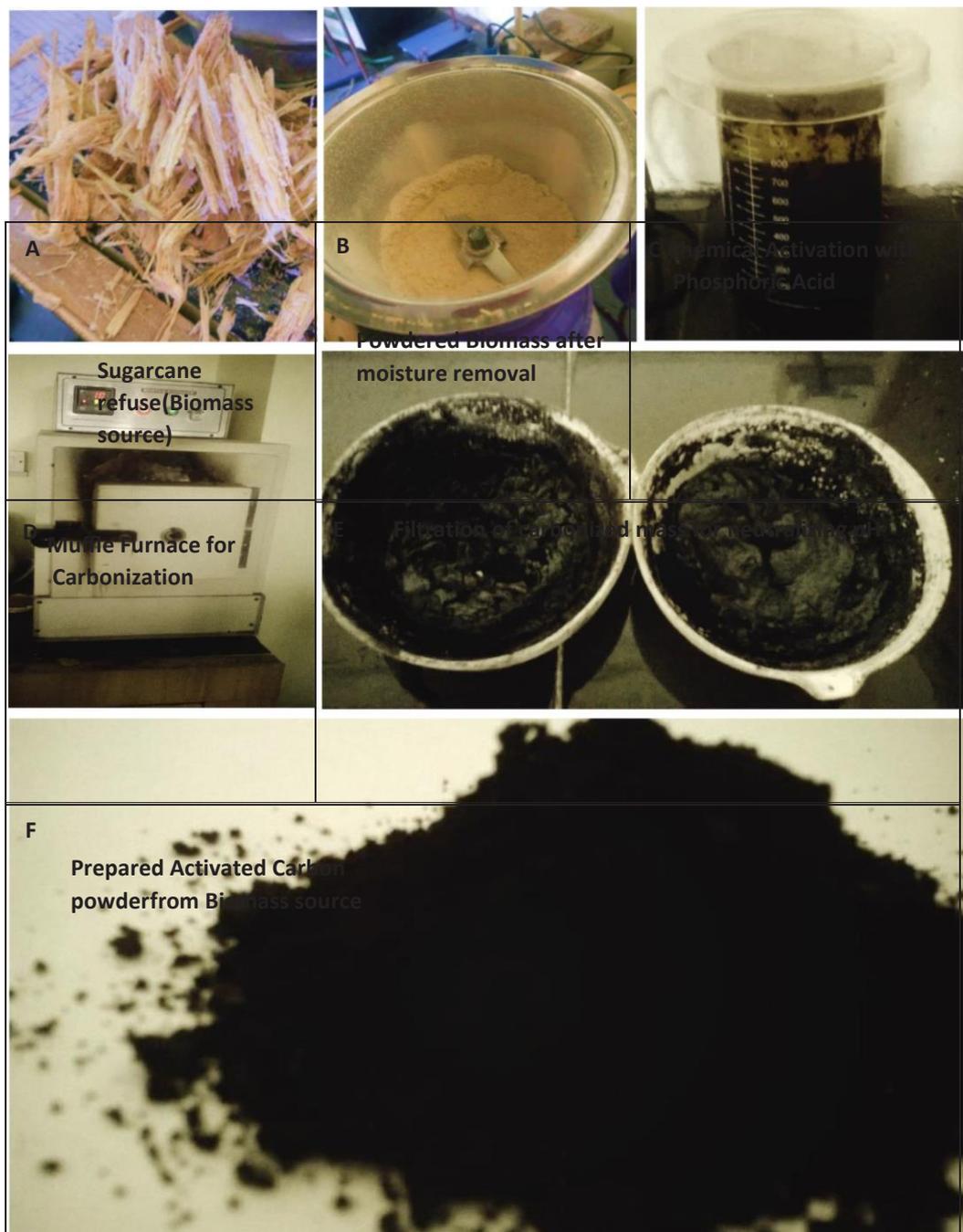


Fig. 2. (A) Sugarcane refuse collected from market (B) Powdered biomass after grinding (C) Activation with phosphoric acid for increasing pore size (D) Following carbonization, the same was washed with hot water over filter papers for neutralization reaction, this was followed by heating of the filter paper to remove the AC powder from it (E) Prepared Activated carbon which is used for making the MFC cathode.

advantages such as allowing a single step process in comparison to the traditional two-stage process of carbonization and activation [15]. Further, this is achieved at room temperature and most of the acid is easily recovered in the washing of the products, and the yield is high as the burn off at higher temperature is avoided [16]. After Carbonization, the material was allowed to cool, this was followed by thorough washing of the carbon in hot water (around 90 °C) on filter paper (Whatman, Type 101) to adjust the pH to 7 (basic range), and then finally dried. The same is shown in Fig. 2 with all the processes where the end product is activated carbon.

The Binder was prepared using a modified method from one previous study of similar nature [11]. PVDF (534,000 Da; GPC Powder, Sigma Aldrich) was prepared (10% by wt.) by mixing it in N, N-

dimethyl acetamide (DMAc, 99.8%, Sigma-Aldrich) with vigorous stirring at room temperature for ten hours using magnetic stirrers (at room temp 25 ± 1 °C) until the polymer completely dissolves in it. Activated carbon and PVDF mixture was spread directly onto a stainless steel mesh (AISI 316L alloy, 40 × 40 wires/inch, 0.37 open area, Sigma Aldrich) using a spatula, the cathode was then immersed in deionized water (for 15 min) to induce single step phase inversion process [17], and then air dried before use.

2.3. Power generation

For MFCs, the voltage drop recorded across arms of the resistor is used to calculate current (using Ohm's law) [18] as shown in the

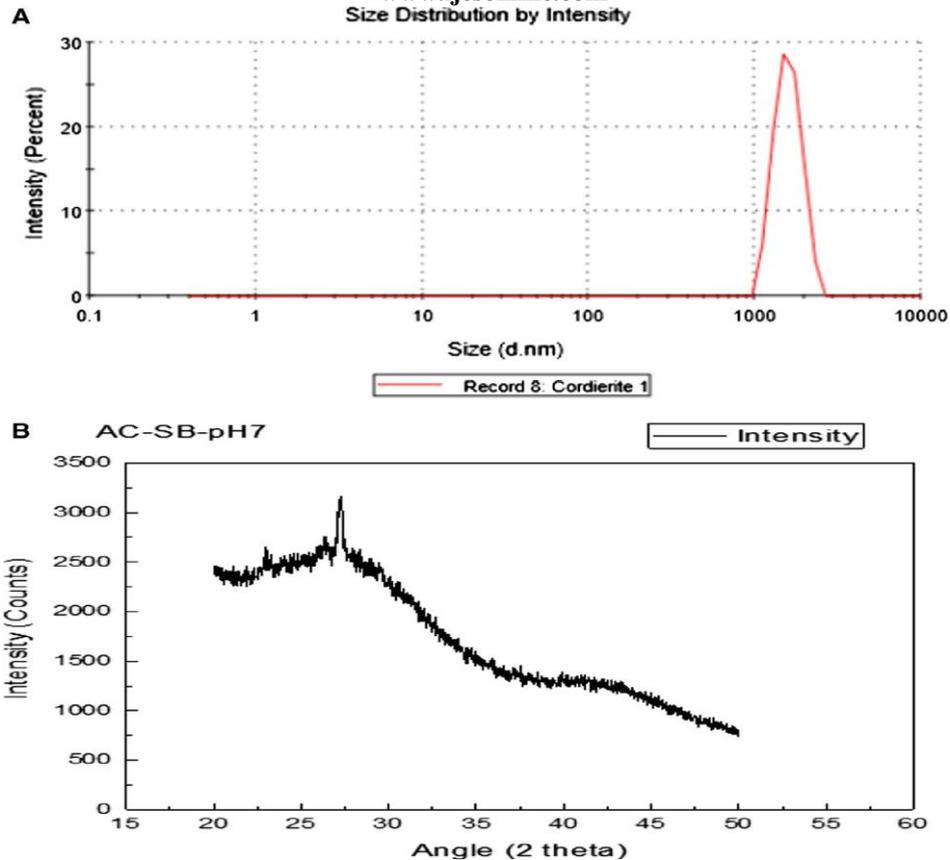


Fig. 3. (A) Particle Size Analyser data for average particle size of AC prepared from sugarcane bagasse, particle size was 1593 nm or 1.59 μm . (B) XRD for same AC sample at pH 7, peak intensity recorded at 27.27° at 2920, this provides surface morphology similar to that of graphite.

equation given below.

$$V = IR \quad (1)$$

where V is the voltage in volts, R is the applied external resistance in ohms, and I is the calculated current, further power can be calculated using:

$$P = VI \quad (2)$$

where P is the power generation in Watts, V is the voltage drop and I is the current calculated for the corresponding resistance. The Current density and Power Density by normalizing the current and power values to the anode surface area [19], and can be calculated from equation 3 and 4 as given below.

$$I_{\text{Density}} = \frac{V_{MFC}}{R \times A_{\text{anode}}} \quad (3)$$

$$P_{\text{Density}} = \frac{V_{MFC}}{R \times A_{\text{anode}}} \quad (4)$$

where A_{anode} is the anode surface area, where the biofilm growth of the microbes take place, responsible for electron transfer. I_{Density} is the current density in mA/m^2 and P_{Density} is the power density in mW/m^2 . The power density generated by the system was further evaluated through polarization method, where variable resistances are used to see

the voltage output from the system, resistance used are from 4700 Ω through 1000, 500, 250, 100 and 40 Ω at thirty minutes interval. Polarization curves were recorded after first and second week of operation.

2.4. Characterizations

Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) analysis were conducted for each of the wastewater samples both before and after period of operation to see the effectiveness of wastewater treatment [10]. As a measure of dissolved solutes removal, TDS (Total Dissolved Solutes) removal efficiency was also calculated. Coulombic efficiency was calculated based on changes in COD concentration by using a 1000 Ω resistor for thirty minutes [11]. For the indigenously prepared AC electrodes, surface morphology was evaluated using XRD; FTIR was used to see the functional group present in it, along with particle size analyser to evaluate average particle size. AFM was used to study surfaces of electrodes, and SEM was used to see bacteria development on the anode [20].

2.5. Water pressure test

A single chamber of the reactor with having the cathode at one end

and a piston to push water at the other was used to determine maximum water pressure (in cm of static head) that can be withstand by the cathode, this test is a key to understand commercial scaling up of such systems [11]. A gasket was used layered with duct tape to seal the edges during the pressure test. Further this was reviewed with the existing literature [4,17,19] for water pressure holding capacity for other MFC cathodes.

3. Conclusion

Present work with AC cathodes generated an OCV of around 580 ± 30 mV between cycles, and achieved peak current density of 0.40 mA/m² and power density of 110 ± 6.58 mW/m² with COD removal efficiency of around 64% and BOD removal from an initial 520 ± 20 mg/l to 165 ± 25 mg/l, with a dissolved solutes removal of around 51%, the same performance for the AC cathode was consistent when sewage sludge was inoculated as a substrate in the wastewater and produced similar efficiency in terms of power generation and wastewater treatment. The same has been contrasted and compared with platinum catalyst based MFC system, and system performance is found to be comparable.

However, as platinum is not suitable for oxygen reduction at the cathode, PtO layer fouls the cathode and ends its catalytic activity, for AC cathodes, on fouling from biofilms and salt precipitation, these can be regenerated to around 85% of original activity using weak hydrochloric acid wash. The use of PVDF as binder has the potential to be used in scaled up systems owing to high water pressure resistance capacity of about a meter of water column.

The use of Carbon black as a supplement for AC cathodes is cost effective and has superior catalytic performance compared with other sources of activated carbon for the same; further the absence of

Table 1
FTIR analysis for Activated Carbon.

Sr. No	Vibrational Energy (cm ⁻¹)	Functional Groups
1	3454.11	N-H group
2	1631.97	1,3-Butadiene
3	1116.86	3-Iodo-1-propyne
4	619.64	Hexafluoroethane

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The authors declare no Conflict of Interest.

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