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Wastewater Treatment and Bio-Electricity Generation via Microbial Fuel Cell Technology Operating with Starch Proton Exchange Membrane

Livinus A. Obasi, Augustine N. Ajah

***Abstract*—**Biotechnology in recent times has tried to develop a mechanism whereby sustainable electricity can be generated by the activity of microorganisms on waste and renewable biomass (often regarded as "negative value") in a device called microbial fuel cell, MFC. In this paper, we established how the biocatalytic activities of bacteria on organic matter (substrates) produced some electrons with the associated removal of some water pollution parameters; Biochemical oxygen demand (BOD), chemical oxygen demand (COD) to the tune of 77.2% and 88.3% respectively from a petrochemical sanitary wastewater. The electricity generation was possible by conditioning the bacteria to operate anaerobically in one chamber referred to as the anode while the electrons are transferred to the fully aerated counter chamber containing the cathode. Power densities ranging from 12.83 mW/m^2 to 966.66 mW/m^2 were achieved using a dual-chamber starch membrane MFC experimental set-up. The maximum power density obtained in this research shows an improvement in the use of low cost MFC set up to achieve power production. Also, the level of organic matter removal from the sanitary waste water by the operation of this device clearly demonstrates its potential benefit in achieving an improved benign environment. The beauty of the MFCs is their potential utility in areas lacking electrical infrastructures like in most developing countries.

***Keywords*—**Bioelectricity, chemical oxygen demand, microbial fuel cell, sanitary wastewater, wheat starch.

I. Introduction

IT is quite evident that with the advancement of science and technology, the need for energy to carry out various activities in our social environment is on the increase. It is on this note that efforts are being made via research to develop suitable and dependable alternatives that could help to address this challenge so as to secure our global energy future. The present energy scenario in India, Fukushima (Japan), the nuclear disaster of the Gulf of Mexico and other similar situations around the world and the possible depletion of the fossil fuels due to overdependence tends to spell a doom in the world energy sector especially in developing countries, thus driving research to explore the possible and more dependable alternatives. The present trend of active research in biotechnology is trapping renewable energy from "negative value" waste organic resources and converting same to a useful and usable secondary resource, electrical energy. Biotechnology simply refers to the use of living systems or its derivatives to develop or modify technological products or processes for specific use [3]. This is important worldwide because it provides the following: (a) Environmental management through the bioconversion of domestic waste into non-polluting fuels such as methane, ethanol and methanol. (b) Enhancement of soil fertility and stability through the direct application of sludge materials. (c) Treatment of wastewater through microbial systems. (d) Strengthening of public health progresses by elimination of enteric parasite through the anaerobic digestion process. (e) Bioconversion of agro-industrial residues into valuable secondary products. (f) Concentration and leaching of valuable minerals from low-grade ores using microorganisms, and most recently (g) Bio-conversion of organic wastewater into electricity [3].

MFC is a biotechnological device that has successfully produced electricity from the activities of microorganisms on organic wastewater [6], [16], [20]. MFCs have drawn worldwide interest as a method of directly generating electricity from organic matter in waste water, while simultaneously treating the wastewater via BOD and COD removal [17].

MFCs are classified into two with respect to their electron transfer mechanism: the mediatored and the mediatorless MFCs [1]. In the mediatored type, electron transfer to the electrodes is facilitated by exogenous agents referred to as mediators (ones external to the cell). These substances possess the ability to assist the transfer of electrons from the respiratory chain to the anode [7]. Some common mediators commonly used include: thionine, methyl viologen, methyl blue, humic acid, neutral red, [4], [20]. In the mediatorless type, electron transfer is achieved by the bacteria alone which are often described as being sufficiently electrochemically active [17], [23]. Such bacteria may include but not limited to *Escherichia coli*, *Geobacter metallireducens, Shewanella putrefaciens, Clostridium beijerinckii, Clostridium butyricum, Saccharomyces cerevisiae, Desulfotomaculum reducens, Rhodobacter capsulatus, Thiobacillus ferrooxidans* and even *Geovibrio* genus. *Geobacter* species have been found to achieve about 90% recovery of electrons present in a fuel cell via oxidation of organic compounds to produce electricity and carbon dioxide in comparison with *Shewanella putrefaciens* [8], [23]-[24]

An MFC is made up of three components: The anode chamber, the cathode chamber and the proton exchange membrane (PEM). Materials used as PEMs in MFCs include fluoropolymer containing cation exchange material such as

Livinus A. Obasi is with the Department of Petroleum Geosciences and Engineering Technology, Federal Polytechnic Ekowe, Bayelsa State, Nigeria (e-mail: manlevi77@yahoo.com).

Nafion TM [2], [4] Polystyrene and divinylbenzene with sulphonic acid group [12] dialysis membranes (2000-14000Da), agar-agar [21]; cassava starch [13]. MFC systems that are capable of functioning without proton exchange membranes have also been developed [14].

MFC has operational and functional advantages over technologies currently used for generating energy from organic matter. Such advantages may include: The direct conversion of substrate to electricity enables high conversion efficiency, MFCs operate efficiently at ambient temperature, it does not require gas treatment because the off-gas of MFCs are enriched in carbon dioxide and normally have no useful energy content. MFC, being a device that can operate with diverse fuels, has potential for widespread applications especially in areas lacking adequate and sustainable electrical infrastructures and hence satisfy our energy requirement [17]. Although MFCs generate lower amount of energy than hydrogen fuel cells, a combination of both electricity production and wastewater treatment would reduce the cost of treating primary effluent wastewater [26]. However, since there has not been a reasonable amount of voltage generated in MFC so far, it therefore becomes imperative to device a way of significantly reducing its production and operating cost [7]. It is in light of this that starch is applied in modified form to replace more expensive substances such as nafion TM to serve as a medium for proton exchange in an MFC.

II. Anodic Fluids (Substrates)

Organic matters undergoing putrefaction (bio-oxidation) in waste water have been considered to be potential sources of electricity. The bacteria present in these media, under anaerobic conditions, produce protons and electrons. MFCs operate in a manner that transfers these electrons via the electrochemical activity of the microorganisms to the electrode (anode). Such biologically oxidizable matters, variously used in MFCs, include but not limited to: Glucose solution, organic manure sludge, marine sediments, anaerobic reactor sludge, swine wastewater, acetate and butyrate, beer brewery wastewater [25], petrochemical effluent, effluent from paper industry and agricultural wastes.

III. Governing Models in MFC Operations

The amount of power generated in MFCs is a function of a combination of various factors. These factors may include, but not limited to; nature of carbon source used, fuel cell configuration (single chamber or multiple chamber), dimensions and volumes, nature and type of electrode, electron acceptors used (mediator present in the cathode chamber), concentration and type of electrolyte used, operating temperature, nature of inoculum (biocatalyst) used in the anode chamber and nature of PEM.

Columbic Efficiencies

This is a measure of electron recovery from the cell operation as transferred to the anode electrode. Mathematically, columbic efficiency is expressed as a percentage of the total charge transferred to the anode per maximum extractable charge upon complete oxidation of the substrate to electricity [10].

The columbic efficiencies are calculated using (1) and (2) [15],

$$E_c = \frac{C_p}{C_n} \times 100\% \tag{1}$$

where C_p = total coulomb calculated by integrating the current over time, C_n = theoretical amount of coulombs that can be produced from the cell.

$$C_n = \frac{Fb_i S_{iv}}{M_i} \tag{2}$$

where F = Faraday's constant (96485 Coulombs/mol-electron), B_i = moles of electrons/mole of substrate, S_i = substrate concentration and M_i = molecular weight of the substrate.

COD Removal Efficiency

The performance of the cell is evaluated by estimating the COD and voltage removal efficiency and power generation. The COD removal efficiency is calculated using (3) [20]:

$$\xi = \frac{C_{so} - C_s}{C_{so}} \times 100\,\% \tag{3}$$

where ξ = COD removal efficiency, C_{so} = initial COD concentration (mg/l), and C_s = COD concentration at time t.

Power Generation

The power generated is also modeled as a function of substrate concentration using an empirical Monod-type equation as

$$P = P_{\max} \frac{S}{K_s + S} \tag{4}$$

where P_{max} = maximum power, S = substrate concentration and K_s = half-saturation constant [15]. Similarly, the voltage generated was modeled as a function of the type of PEM material as a measure of its proton conductivity (k) and time of operation (t) (Figs. 2, 3) as an empirical Arrhenius-type equation as:

$$V = V_o e^{-kt} \tag{5}$$

where V = voltage generated at time t, V_o = initial voltage at t = 0, k = proton conductivity of the PEM, t = time [13].

Microbial Growth Rate

In sewage or waste water treatment using MFC, the Monod equation is applied to draw a relationship between specific microbial growth rate and the substrate concentration as

$$\mu = \mu_{max} \frac{S}{K_s + S} \quad (6)$$

where μ = specific microbial growth rate, μ_{max} = maximum specific growth rate, K_s= half-velocity constant, and S= concentration of substrate for bacteria growth.

IV. Materials and Methods

A. Starch-Membrane MFCs

The starch-membrane MFC (SM-MFC) fuel used in this study was a dual chamber type with the chambers (reactors) made of polyvinyl chloride (PVC) cylinders having internal diameters of 15 cm and a depth of 15 cm with a total volume of 1697.14 cm^3 each (Fig. 1). This formed the cathode and anode chambers. The two chambers were separated by a short piece of cylindrical pipe measuring 10 cm whose internal volume was loaded with a soft mass of wheat starch whose physical properties were modified with carrageenan to increase the gel strength, serve as a cross-linking agent and hence impart a sustainable strength and viscosity on the starch while its molecules provide a medium for proton exchange between the two reactors. Solid graphite rods were used for both anode and cathode. The apparent surface area of each electrode was 11.39 cm^2. A urea reach sanitary wastewater (pH 8.3) from a petrochemical industry was supplied to the anode chamber. The presence of ions such as chloride (Cl^-), potassium ion (K^+), sodium (Na^+), creatinine, faecal coliforms (enteric bacteria) and other dissolved ions could set up a number of ionic equilibria in the system, hence the substrate was buffered with phosphate (K_2HPO_4+ KH_2PO_4) solution to stabilize the operating pH. The cathode chamber was filled with 0. 5M potassium ferry cyanide solution to serve as electron sink. An environmental inoculum (a mixed anaerobic consortium from mangrove swamp predominantly *Geobacter metallireducens*) as determined from the laboratory via culture, isolation and identification at incubation temperature of 30 °C, was used to 'seed' the anode fluid in order to induce accelerated bacterial action [5]. The two chambers were connected with a copper wire.

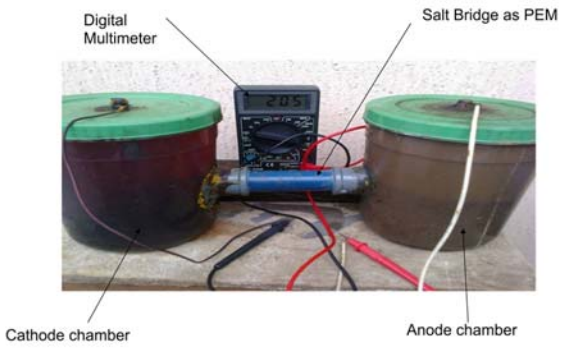

Fig. 1 Experimental Set-up of a dual chambered MFC (pilot scale)

PEM

PEMs in MFCs are simply conductive materials which are able to inhibit the transfer of other materials such as oxygen gas, fuel (substrates) or the electron acceptor while conducting protons to the cathode at high efficiency [18]. For the MFC in our study, 120 g of wheat floor was measured using the digital balance. This was mixed with about 60 cm^3 of distilled water to form a suspension. About 10 cm^3 of 0.5 M NaCl was added to improve the proton conductivity of the starch [21]. The mixture was stirred vigorously. A pre-heated suspension of 10 g carrageenan powder was then added and the entire mixture heated for about 20 minutes with a gradual increase in temperature from 20 to 60 °C. The paste formed was quickly charged into the short PVC pipe, allowed to cool and fitted between the two chambers. This forms the PEM for the cell.

V. Inoculation and Operation

The anode chamber of the starch membrane MFC in our study was first inoculated with about 2.0 ml solution of anaerobic sludge sourced from mangrove forest sub-surface. This solution is replete with a consortium of bacteria aimed at enriching and activating the microorganisms in the anode chamber for a more effective electron recovery, the system was operated for 20 days after which effluent samples from the anode chamber were removed and analyzed for various pollution parameters. The pH of the medium was stabilized via initial treatment of the waste with phosphate buffer solution and kept between 7.2 and 7.4. The cathode chamber was kept fully aerated throughout the experiment. The experiments were carried out at room temperature (27±3 °C).

Cell Reactions

At the Anode: (Oxidation)

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$
$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$$
$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$

At the Cathode: (Reduction)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$K_3Fe(CN)_6 \rightarrow 3K^+ + Fe(CN)_6^{3-} \text{ (Ferry cyanide ion)}$$

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-} \text{ (Ferro cyanide ion)}$$

VI. Analyses

At the 20th day of the SM-MFC batch operated dual chamber MFC, the effluent samples were analyzed for the presence and levels of certain pollution parameters using standard laboratory methods: COD, BOD, total suspended solid (TSS), total dissolved solid (TDS), Total solid (TS) and volatile suspended solid (VSS) using standard methods. The potential and current were measured daily using a digital multimeter (DT-830) and further converted to power using the relations: P=IV, where P=power (mW), I=current (mA) and

V=voltage (V). Power and current densities were also analyzed according to (7) and (8) [22]:

$$P = \frac{Current(mA) \times Volts(v)}{Surface\,area\,of\ \ projected\,anode(m^2)} \quad (7)$$

and current density C, expressed as:

$$C = \frac{Current\ \ produced(mA)}{Surface\,area\,of\ \ projected\,anode(m^2)} \quad (8)$$

VII. Results and Discussion

TABLE I
POLLUTION PARAMETERS TESTED

Parameter	Effluent sample	
	Initial (mg/l)	*Final (mg/l)*
COD	580	62
BOD	430	98
pH	6.90	6.92
Dissolved Oxygen (DO)	70.3	42.7
Alkalinity	19.75	14.6
TDS	600	81.9
TSS	1880	790
VSS	34.6	28.1
Ammonia Nitrogen	25.6	19.8

TABLE II
EXPERIMENTAL RESULTS FOR SM-MFC WITH CARRAGEENAN-MODIFIED STARCH PEM

Time (days)	Current (mA)	Voltage (volts)	Current Density (mA/m^2)	Power Density (mW/m^2)
1	0.81	1.33	711.78	966.66
2	0.66	1.30	579.96	753.95
3	0.50	0.93	439.37	408.61
4	0.40	0.92	351.49	323.37
5	0.23	0.75	202.11	151.58
6	0.25	0.77	219.68	125.22
7	0.07	0.79	61.51	48.59
8	0.07	0.77	61.51	47.36
9	0.05	0.75	43.94	32.95
10	0.04	0.71	35.15	24.96
11	0.06	0.76	52.73	40.07
12	0.05	0.75	43.94	32.95
13	0.04	0.74	35.15	26.01
14	0.03	0.71	26.36	18.72
15	0.05	0.75	43.94	32.95
16	0.04	0.75	35.15	26.36
17	0.04	0.73	35.15	25.66
18	0.03	0.74	26.36	19.5
19	0.03	0.75	26.36	19.77
20	0.02	0.73	17.57	12.83

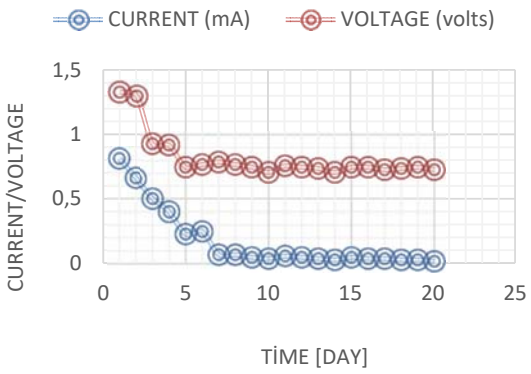

Fig. 2 Graph of current and voltage against time

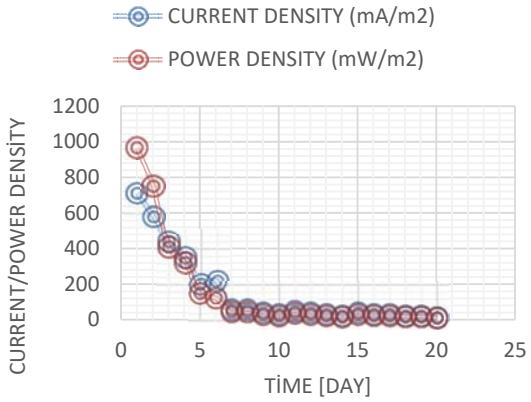

Fig. 3 Graph of power density and current density against time

After inoculation, the operation of the SM-MFC recorded a value of current to the tune of 0.81 mA and a corresponding power density of 966.66 mW/m^2 on the first day after start-up. This demonstrates that *Geobacter metallireducens* quickly developed active microbial biofilms on graphite anode to produce current nearly as effectively as with *Geobacter sulfurreducens* on graphite anodes [8]. These values however saw a downward trend up to the 6th day of operation. Between the 7th and 8th day, the current produced became relatively stable at 0.07 mA. From the 9th day, the magnitude of current produced decreased gradually with time thus recording a mimimum value of 0.02 mA on the 20th day. The reduction in the strength of physical bonding between the starch molecules and the carrageenan molecules could have resulted in the leakage of oxygen into the anode chamber which could have reacted with any untransfered proton in the anode chamber to form water. Such reaction could further decrease the concentration (mg/l) of the organic medium in the anode chamber. Besides, proton reduction by any untransfered electrons could cause a build-up of hydrogen gas around the anode thus leading to some level of impedance to the flow of electrons and therefore reduced current flow. Also due to bacteria activity methanogens growth could occur giving rise to formation of methane (an anaerobic metabolic byproduct) in the anode chamber which over time might have reduced the

thickness of the biofilm and bacterial growth with could have negative effect on the amount of current produced [7]. The mode of operation of the cell being strictly anaerobic does not necessarily guarantee progressive autoxidation of the organisms' cellular mass thereby stopping any possible replication or formation of new cells to further oxidize the substrate as would occur in an aerobic condition according to the equation:

$$Organic\ matter + O_2 + NH_3 \longrightarrow New\ cells + CO_2 + H_2O$$

After 20 days of operation of SM-MFC, the average COD and BOD removal efficiencies were 88.3% and 77.2% respectively. This value of COD removal efficiency in the operation of SM-MFC agrees with the value reported in literature, in the range of 80 to 90% [9], [11], [19]. This therefore demonstrated that the use of SM-MFC as an effective waste treatment and electricity generation processes.

VIII. Conclusion

The current reliance of fossil fuels is unsustainable due to pollution and finite supplies. This is why there is need for an alternative source of energy. The effort to properly address this current challenge requires a multidisciplinary approach. As such, it is imperative that effort should be made to maximize this attractive possibility of producing electricity from waste and renewable biomass. The SM-MFC under our study has shown that it can be adopted not only as a source of electricity but also an effective waste treatment process at minimum operational cost. In this study, a maximum power density of 966.66 mW/m^2 was realized with a corresponding BOD, COD removal efficiencies of 77.2% and 88.3% respectively from wastewater. Therefore, MFCs a biotechnological device provides a platform for this conversion. This has recently gained world research interest as an alternative source of electrical energy and hence, is highly recommended for investment, especially in developing economies.

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