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By

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Research Article

Generation of Bio-Electricity from Ammonia Fertilizer Plant Liquid Effluent

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ABSTRACT

Microbial fuel cells (MFCs) are typically designed as a two-chamber system with the bacteria in the anode chamber separated from the cathode chamber by a polymeric proton exchange membrane (PEM). Most MFCs use aqueous cathodes where water is exposed to air to provide dissolved oxygen to electrode. To increase energy output and reduce the cost of Microbial Fuel Cells, charcoal electrode (locally prepared) at the composition of 2:1 charcoal/cement ratio was used. Ammonia fertilizer plant liquid effluent was used as the substrate, while the bacteria present in the wastewater were used as the biocatalyst. The cells were operated at room temperature with pH of 6.68. The anode and cathode chambers were kept under anaerobic and aerobic conditions respectively.

The cell 3 set-up with electrode area of $3.63 \times 10^3 \text{m}^2$ was observed to have the highest power density of 134.5455mW/m² and current density of 181.8182mA/m² while cell 4 set-up with electrode area of $3.63 \times 10^3 \text{m}^2$ was observed to have the least power density of 108.9807mW/m² and current density of 126.7218mA/m².

Keywords: Bioelectricity, Ammonia fertilizer plant, liquid effluent.

INTRODUCTION

The need for alternative energy sources to fulfill the environmental friendliness goals in energy production and substitute the depleting fossil fuel reserves has seen active research and a variety of potential alternatives (Debabov, V.G., 2008,. Du, Z., Li, H., Gu, T., 2007).

Microbial fuel cells (MFCs) are amongst the potential alternative solutions to the crises, it take advantage of the oxidation of organic compounds to produce electricity. Their advantages include combining bio-treatment of wastewater and electricity production, their environmental friendliness and ability to be used in remote areas.

However, the wide scale application and realistic scaling up of MFC to significantly substitute current fossil fuel energy generation techniques remain elusive. This is because of the requirement of large area of operation for meaningful power production, low power output due to internal resistances, poor reproducibility of the setups and expensive artificial/defined media for the anode chamber (Logan and Regan, 2006 a, b; Liu and Li, 2007).

Furthermore, the biology of microbial consortia involved is yet to be fully understood (Bullen et al., 2006). Despite the highlighted shortcomings, considerable progress has been made in electrode modifications to increase power output. Such efforts entail incorporation of nano particles and catalysts on the electrodes (Nambiar et al., 2009) and the used of cheap materials as electrode (Lovley DR 2006, Potter, M.C., 1911). While these efforts have yielded notable increases in power, the power remains insufficient to fill in the required credibility gap (leropoulos et al., 2005; Pant et al., 2010). Hence, searching for cheaper substrates and high performing microorganisms can augment the current electrode modification effort. Think about use of waste and alternative microbial sources is ongoing (Asad et al., 2007; Pant et al., 2010) but the searching is not exhaustive. The prospect of simultaneous wastewater bio-treatment and electricity generation is attractive.

MATERIAL AND METHODS

Methodology

All the experimental results were obtained with cells at laboratory room temperature, normally 25°C, during daytime tests. The cells were subjected to overnight cooling, when heating in the laboratory was switched off. It was impractical to try to maintain the temperature of the cells constant owing to equipment constraints and the fact that cells were tested simultaneously. Furthermore, it was appropriate to test the cells under these conditions which would relate more to any potential practical applications of an MFC using waste, i.e. variable temperatures

during day and night. The fuel cell was set up as a battery so that power output could be established without concerns about fuel delivery.

Materials

Microbial fuel cells consist of various materials which include:

S/NO	Materials	Quantity	Make	Specification
1	Plastic bottle	10	Dana plast, Nigeria	5.0L
2	Plastic pipe (PVC)	5	Tigre, Nigeria	1 inch
3	Plastic Flanges	10	Tigre, Nigeria	32 × 1"
4	Agar agar	20g	Hack, UK	Powering
5	Salt	300g	Dangote Salt, Nigeria	
6	Flexible Wire	3 yrds	Sunshine wire, Nigeria	
7	Charcoal	450g	Prepared Locally	610°c
8	Ероху	4		
9	PVC Trunking	10		
10	Cement	250g	Dangote cement, Nigeria	
11	Distilled Water	25L	Condensed water from Air- conditioner	
12	Ammonia fertilizer plant effluent	25L	Notore Chemicals Industry Limited, onne, Rivers State.	

Salt bridge construction

To construct the salt bridge, 1- inch diameter PVC pipe was cut into 5 pieces with length of 0.08m each, after which PVC socket (flanges) was fixed with epoxy at both ends of the pipe, thereby giving the pipe a new length of 0.103m.

Each of the pipes was sterilized with ethanol to free the internal surface of the pipe from microorganism; the open ends were sealed with masking tape to prevent microorganisms from acting on the internal surface after sterilization.

Proton exchange membrane preparation

In preparation of the proton exchange membrane (PEM), the agar was dissolved in distil water at concentration of 40g/l then salt was added to the agar (7.5g of salt in 40g of agar) and autoclave the agar mixture at about a temperature of 121°C for 15mins. Sealing one end of the PVC pipe and Pour agar/salt mixture into the plastic pipe while it is still warm and before it thickens while allowing the agar/salt to cool and solidify (After 30mins).

Preparation of Electrode

Charcoal was grinded to a fine powder and mixed with cement at the ratio of 2:1 with 130ml of water then the PVC trunk was cut into the desired length (24.2cm) and was lubricated with vegetable oil to allow easy removal of the electrode when it solidifies and finally pour the mixture of the grinded charcoal and cement into the mould (PVC trunking) with flexible wire inserted into it which got solidifies after 48 hours.



Electrode inside the mould



Electrode ready for use

Test the electrode with multimeter – there should be a small amount of resistance between a point on the electrode and the end of the wire opposite the electrode.

At anode, pass the electrode through a hole in the bottle lid and seal with epoxy. Cathode chamber does not necessarily need a lid.

Collection of anolyte

The ammonia fertilizer plant liquid effluent which is the anolyte (substrate) was collected from Notore chemicals industry limited, Onne, Port-Harcourt, Rivers State.

Preparation of the catholyte

The cathode chamber is the oxidant chamber which uses brine as the protons acceptor. The catholyte was prepared by dissolving 300.00g of the salt in 25liters of distilled water and stirred very well to completely dissolve. The prepared catholyte was poured into each of the cathode chambers of the three set-ups.

MFC setup

The anode chamber containing Ammonia fertilizer plant effluent was connected through flexible wires with light emitting diode (LED) to the cathode chamber containing brine. The two chambers were linked with a salt bridge inter-connection. The microbial fuel cell voltage for each set-up was monitored daily using a digital multi-meter. Reading of voltage and current was done within few minutes of stabilization.



Photograph of mfc set up

Running of the microbial fuel cells

To run the microbial fuel cells, the ammonia fertilizer plant liquid effluent is added to the anode chamber then conductive solution (salt water- 300g of salt is dissolved in 25 litres of water) is added to the cathode chamber. The electrode is inserted into the anode and a cathode chamber while an external load (light emitting chambers) is connected then the voltage produced is measured.

After all preparations were done, the Ammonia fertilizer plant effluent was poured into the 5.0L anode chamber. The anode was covered and sealed to prevent oxygen from entering. The anode chamber must be anaerobic.

The cathode chamber (the oxidant) was filled with the catholyte (brine) and was not sealed but partially covered to allow enough oxygen which helps in oxidation.

ANALYTICAL CALCULATIONS

Voltage and current were measured using a digital multimeter and converted to power density $P(mW/m^2)$ according to the equation, P=IV/A, where I (A) is the current, V(v) is the voltage, and $A(m^2)$ the surface area of the projected anode.

Power density was expressed in mW/m² normalized to the projected surface area of the graphite anode (m²). Power density P was analyzed according to Equation (4.1) (Rabaey and Verstraete, 2005).

And current density C, expressed as:

The Monod-type equation was used to model the voltage as a function of substrate concentration (S);

$$V = \frac{V_{\text{max}}S}{K_{\text{s}} + S}$$
 ------ Eqn. (4.3)

Where V_{max} = maximum voltage produced and K_s the saturation constant.

The value of current and voltage thereafter increased until maximum value of was recorded between 16th to 19th days across the five set- ups . The low amount of current and voltage recorded resulted from high internal

resistance in the cell. This high internal resistance could be handled by connecting a load on it in order to improve the current and power density of the cell (Rabaey et al; 2004; Rabaey et al; 2003).

The voltage and current drop was observed after the 20th day which is attributed to continued degradation of the substrate by the bacteria. The current and voltage generation however dropped gradually after some time and later increased sharply in the cell. This was as a result of the eventual growth and multiplication of the microorganisms with corresponding increased oxidative activity.

This non-linear relationship between current and voltage produced was due to unsteady rate of microbial activity which is often one of the reasons why the operation of MFCs does not obey Ohm's law (Ohm's law draw a direct relationship between current and voltage at current electrical resistance in physical systems.). Also this power source (microorganism oxidative activity) is not constant due to the effect of an amount of internal resistance in the system.

Conversely, as can be seen in Figure (4.6 to 4.10), the power density, which is a measure of the amounts of voltage and current produced per unit surface area of the projected anode, increased as the current and voltage increased up to a maximum value of 134.5455 mW/m² at 0.74 volts and 0.66mA. The maximum current density obtained was 181.8182 mA/m².

PRECAUTIONARY MEASURES

Certain precautionary measures were necessarily observed in achieving the desired results in the construction and operation of the dual-chambered microbial fuel cell. They include:

1. Leakage Test: The MFCs operate with liquid environments in the anode and cathode. Hence there is the possibility of leakage and eventual loss of electrolytic fluids, and this could mar the successful operation. Therefore the parts should be properly fitted together during coupling. A quantity of clean water equivalent to the reactor capacity was then poured into the empty chambers and the system allowed standing for about six hours to ascertain the absence of leakage before the electrolytes are charged in.

2. Anode Chamber: The anode chamber environment must be completely anaerobic. Hence absolute care should be taken not to allow oxygen into the chamber either through openings (ports) or during inoculation. The bacteria should be grown in a sealed container, and when the bacterial solution is added to the MFC, it must be done quickly to limit oxygen exposure.

3. Cathode Chamber: The cathode chamber should be fully aerated. Oxygen in this chamber functions as the final electron acceptor. The cathode chamber therefore needs to be filled with a solution like brine and aerated to provide oxygen (an ultimate "electron sink" or end point of the redox reaction) to the cathode. This is however one of the major challenges in MFC operations.

Cathodic equation: $6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O$

4. Maintenance of Stable pH: pH refers to the concentration of hydrogen ion (H⁺) in a solution. An acidic environment or medium is reach in hydrogen ion concentration while a basic medium is depleted of hydrogen ions.

The operation of an MFC is usually accompanied with the production of hydrogen ion at the anode. This implies that with the progress of time, the medium gets more acidic if there is no measure to check the pH. This could threaten the growth and metabolism of the existing bacteria. Most of the microorganisms prefer pH that approximates that of distilled water, a neutral solution (7.0). Hence in order to maintain a stable neutral P^{H} in the anode chamber, a well-buffered solution was used to extract the substrate and charged into the anode chamber.

RESULT AND DISCUSSION

Results from this study established that Ammonia Fertilizer Plant Effluent could be an efficient and cheaper technology to offset the expensive wastewater treatment technology employed by many industries and that cheaper and easily sourced materials could be used to replace the expensive ones in the MFC. The following results were obtained in the various attempts to maximize the power output from five different set-ups of the MFC with a salt bridge. Cell one produced power density of 120.3306mW/m² and current density of 146.0055 mA/m², while Cell two produced power density of 113.0579mW/m² and current density of 148.7603mA/m², Cell three produced power density of 134.5455mW/m² and current density of 181.8182mA/m², Cell four produced power density of 126.7218mA/m² and Cell five produced power density of 146.0055mA/m². Hence, it could be said that ammonia fertilizer plant liquid effluent is a good substrate for the MFC.

Several fuel cells may be joined together in series to give a greater voltage; the current produced will remain the same.



Fig. 4: Photograph showing voltage taken on the 14th day from cell 1

Reactor Configuration			Substrate	Ammonia fertilizer Plant Effluent				
	Single	Dual		Catholyte	Salt Water	Salt Water(Brine)		
Chamber		$\sqrt{}$		Electrode	Cathode	Anode		
Parameters	Start	End		Туре	Charcoal	Charcoal		
рН	8.26	6.68		Open Circuit				
Temperature	26°C			Close circuit	$\sqrt{\sqrt{1}}$			
Conductivity	320µs	3350µs		Startup Date	13/06/2013	3		
% Urea	298.5ppm	0.53ppm		Electrode Si	ze 3.63×10	$D^{-3}m^2$		
% NH₃	1375ppm	220ppm			•			
BOD	712mg/L	263mg/L						
COD	955mg/L	61.6mg/L						

Table 4.1 Result Data Table

Table 4.2 Voltage and Current Production in MFC Cell One

Date	Days	Voltage (V)	Current (mA)
13/06/2013	1	0.36	0.04
14/06/2013	2	0.44	0.08
15/06/2013	3	0.54	0.12
16/06/2013	1	0.56	0.10
10/00/2013	4	0.30	0.10
17/06/2013	5	0.43	0.15
18/06/2013	6	0.52	0.16
19/06/2013	7	0.41	0.14
20/06/2013	8	0.53	0.16
21/06/2013	9	0.55	0.18
22/06/2013	10	0.38	0.21
23/06/2013	11	0.59	0.20
24/06/2013	12	0.70	0.22

25/06/2013	13	0.88	0.36
26/06/2013	14	0.89	0.4
27/06/2013	15	0.91	0.48
28/06/2013	16	0.81	0.45
29/06/2013	17	0.61	0.53
30/06/2013	18	0.44	0.39
01/07/2013	19	0.55	0.20
02/07/2013	20	0.78	0.18
03/07/2013	21	0.71	0.19
04/07/2013	22	0.62	0.32
05/07/2013	23	0.55	0.4
06/07/2013	24	0.61	0.3
07/07/2013	25	0.57	0.22
08/07/2013	26	0.52	0.24
09/07/2013	27	0.47	0.24
10/07/2013	28	0.38	0.23
11/07/2013	29	0.31	0.19
12/07/2013	30	0.25	0.19

Table 4.3 Voltage and Current Production in MFC Cell Two

Date	Days	Voltage (V)	Current (mA)
13/06/2013	1	0.41	0.22
14/06/2013	2	0.45	0.18
15/06/2013	3	0.48	0.19
16/06/2013	4	0.46	0.23
17/06/2013	5	0.49	0.20
18/06/2013	6	0.51	0.24
19/06/2013	7	0.53	0.25
20/06/2013	8	0.55	0.26
21/06/2013	9	0.54	0.35
22/06/2013	10	0.60	0.32
23/06/2013	11	0.61	0.36
24/06/2013	12	0.59	0.36
25/06/2013	13	0.55	0.38
26/06/2013	14	0.68	0.39
27/06/2013	15	0.77	0.40
28/06/2013	16	0.81	0.37
29/06/2013	17	0.89	0.41

30/06/2013	18	0.82	0.43
01/07/2013	19	0.80	0.42
02/07/2013	20	0.83	0.46
03/07/2013	21	0.76	0.54
04/07/2013	22	0.69	0.51
05/07/2013	23	0.61	0.53
06/07/2013	24	0.55	0.59
07/07/2013	25	0.48	0.56
08/07/2013	26	0.50	0.51
09/07/2013	27	0.45	0.52
10/07/2013	28	0.41	0.44
11/07/2013	29	0.37	0.35
12/07/2013	30	0.32	0.30

Table 4.4 Voltage and Current Production in MFC Cell Three

Date	Days	Voltage (V)	Current (mA)
13/06/2013	1	0.38	0.36
14/06/2013	2	0.36	0.31
15/06/2013	3	0.39	0.29
16/06/2013	4	0.45	0.30
17/06/2013	5	0.42	0.33
18/06/2013	6	0.40	0.40
19/06/2013	7	0.48	0.42
20/06/2013	8	0.53	0.46
21/06/2013	9	0.56	0.49
22/06/2013	10	0.60	0.54
23/06/2013	11	0.61	0.58
24/06/2013	12	0.66	0.62
25/06/2013	13	0.74	0.66
26/06/2013	14	0.80	0.50
27/06/2013	15	0.83	0.46
28/06/2013	16	0.82	0.44
29/06/2013	17	0.85	0.40
30/06/2013	18	0.81	0.37
01/07/2013	19	0.79	0.37
02/07/2013	20	0.75	0.41
03/07/2013	21	0.70	0.43
04/07/2013	22	0.66	0.40

05/07/2013	23	0.61	0.38
06/07/2013	24	0.55	0.31
07/07/2013	25	0.58	0.35
08/07/2013	26	0.51	0.37
09/07/2013	27	0.47	0.34
10/07/2013	28	0.41	0.32
11/07/2013	29	0.37	0.30
12/07/2013	30	0.33	0.30

Table 4.5 Voltage and Current Production in MFC Cell Four

Date	Davs	Voltage (V)	Current (mA)
13/06/2013	1	0.35	0.14
	-		
14/06/2013	2	0.39	0.15
15/06/2013	3	0.43	0.10
16/06/2013	4	0.40	0.13
17/06/2013	5	0.39	0.13
18/06/2013	6	0.39	0.17
19/06/2013	7	0.41	0.20
20/06/2013	8	0.43	0.19
21/06/2013	9	0.44	0.20
22/06/2013	10	0.43	0.22
23/06/2013	11	0.45	0.25
24/06/2013	12	0.42	0.26
25/06/2013	13	0.50	0.35
26/06/2013	14	0.44	0.37
27/06/2013	15	0.59	0.37
28/06/2013	16	0.64	0.40
	10		
29/06/2013	17	0.71	0.39
30/06/2013	18	0.80	0.41
01/07/2013	19	0.86	0.46
02/07/2013	20	0.81	0.35
03/07/2013	21	0.75	0.35
04/07/2013	22	0.67	0.32
05/07/2013	23	0.61	0.25
00/07/2010	20	0.01	0.20
06/07/2013	24	0.54	0.28
07/07/2013	25	0.49	0.29
08/07/2013	26	0.44	0.27
09/07/2013	27	0.48	0.25

10/07/2013	28	0.48	0.22
11/07/2013	29	0.41	0.23
12/07/2013	30	0.40	0.21

Table 4.6 Voltage and Current Production in MFC Cell Five

Date	Days	Voltage (V)	Current (mA)
13/06/2013	1	0.37	0.30
14/06/2013	2	0.38	0.30
15/06/2013	3	0.35	0.27
16/06/2013	4	0.35	0.32
17/06/2013	5	0.40	0.36
18/06/2013	6	0.45	0.41
19/06/2013	7	0.43	0.40
20/06/2013	8	0.46	0.40
21/06/2013	9	0.48	0.38
22/06/2013	10	0.54	0.45
23/06/2013	11	0.56	0.42
24/06/2013	12	0.55	0.44
25/06/2012	12	0.52	0.50
26/06/2013	14	0.58	0.52
27/06/2013	15	0.62	0.51
		0.02	
28/06/2013	16	0.66	0.51
29/06/2013	17	0.71	0.54
30/06/2013	18	0.77	0.58
01/07/2013	19	0.85	0.53
02/07/2013	20	0.83	0.50
03/07/2013	21	0.79	0.38
04/07/2013	22	0.81	0.39
05/07/2013	22	0.74	0.39
03/07/2013	23	0.74	0.42
06/07/2013	24	0.69	0.41
07/07/2013	25	0.67	0.43
08/07/2013	26	0.61	0.44
09/07/2013	27	0.58	0.39
10/07/2013	28	0.53	0.37
11/07/2013	29	0.49	0.33
12/07/2013	30	0.44	0.32

	Cell One		Cell Two		Cell Three Cell Four			Cell Five		
Days	Power density (mW/m2)	Current Density (mA/m2)								
1	3.97	11.01	24.84	60.60	37.68	99.17	13.49	38.56	30.57	82.6446
2	9.69	22.03	22.31	49.58	30.74	85.39	16.11	41.32	31.40	82.6446
3	17.85	33.05	25.12	52.34	31.15	79.88	11.84	27.54	26.03	74.3802
4	15.42	27.54	29.14	63.36	37.19	82.64	14.32	35.81	30.85	88.1543
5	17.76	41.32	26.99	55.09	38.18	90.90	13.96	35.81	39.66	99.1736
6	22.92	44.07	33.71	66.11	44.07	110.19	18.26	46.83	50.82	112.948
7	15.81	38.56	36.50	68.87	55.53	115.70	22.58	55.09	47.38	110.193
8	23.36	44.07	39.39	71.62	67.16	126.72	22.50	52.34	50.68	110.193
9	27.27	49.58	52.06	96.41	75.59	134.98	24.24	55.09	50.24	104.683
10	21.98	57.85	52.89	88.15	89.25	148.76	26.06	60.60	66.94	123.967
11	32.50	55.09	60.49	99.17	97.46	159.78	30.99	68.87	64.79	115.703
12	42.42	60.60	58.51	99.17	112.72	170.79	30.08	71.62	66.66	121.212
13	87.27	99.17	57.57	104.44	134.54	181.81	48.20	96.41	71.62	137.741
14	98.07	110.19	73.05	107.43	110.19	137.74	56.06	101.92	83.08	143.251
15	120.33	132.23	84.84	110.19	105.17	126.72	60.13	101.92	87.10	140.496
16	100.41	123.96	82.56	101.92	99.39	121.212	70.52	110.19	92.72	140.496
17	89.06	146.00	100.55	112.94	93.66	110.19	76.28	107.43	105.62	148.76
18	47.27	107.43	97.13	118.45	82.56	101.92	90.35	112.94	123.03	159.78
19	30.30	55.09	92.56	115.70	89.22	112.94	108.91	126.72	124.10	146.006
20	38.68	49.58	105.19	126.72	84.71	112.94	78.09	96.41	114.32	137.741
21	37.16	52.34	113.05	148.76	82.92	118.45	72.31	96.41	82.69	104.683
22	54.65	88.15	96.94	140.49	72.72	110.19	59.06	88.15	87.02	107.438
23	60.60	110.19	89.06	146.00	63.85	104.68	42.01	68.87	85.61	115.703
24	50.41	82.64	89.39	162.53	46.96	85.39	41.65	77.13	77.93	112.948
25	34.54	60.606	74.05	154.27	55.92	96.41	39.14	79.88	79.36	118.457
26	34.38	66.11	70.25	140.49	51.98	101.92	32.72	74.38	73.93	121.212
27	31.07	66.11	64.46	143.25	44.02	93.66	33.05	68.87	62.31	107.438
28	24.07	63.36	49.70	121.21	36.14	88.15	27.87	60.60	54.02	101.928
29	16.22	52.34	35.67	96.41	30.57	82.64	25.97	63.36	44.54	90.9091
30	13.08	52.34	26.45	82.64	27.27	82.64	23.14	57.85	38.78	88.1543

Table 4.7 power density and current density table

Table 4.8 experimental analysis of substrate for four weeks

S/no	Parameters	Week One	Week Two	Week Three	Week Four
1	pН	8.26	7.96	7.35	6.68
2	Conductivity	320µs	988µs	2763µs	3350µs
3	% Urea	298.5ppm	184ppm	102ppm	0.53ppm
4	$\% NH_3$	1375ppm	947ppm	458ppm	220ppm
5	BOD	712mg/L	598mg/L	326mg/L	263mg/L
6	COD	955mg/L	749mg/L	231mg/L	61.6mg/L
7	Temperature	26°C			

Graghs of the Results Gotten



Fig. 4.1 Graph of Voltage and Current production in MFC for Cell One



Fig. 4.2 Graph of Voltage and Current production in MFC for Cell Two



Fig. 4.3 Graph of Voltage and Current production in MFC for Cell Three



Fig. 4.4 Graph of Voltage and Current production in MFC for Cell Four







Fig.4.7 Graph of Power and Current Density in an MFC for Cell Two







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