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Generation of Electricity from Abattoir Waste Water with the Aid of a Relatively Cheap Source of Catholyte

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ABSTRACT: The generation of electricity from high strength abattoir waste water has been demonstrated to be feasible at room temperature using a novel electron acceptor as catholyte in dual-chambered microbial fuel cell systems with agar- salt bridge inter-connection. The utilization of this electron acceptor in the single dual-chambered and double dual-chambered in parallel and series was observed to produce an open circuit voltage of 1560mV, 1400mV and 2860mV respectively. Maximum power density was observed to be 12.26mW/m^2, 20.71mW/m^2 for the single dual-chambered and double dual-chambered in parallel respectively. However, due to very high internal resistance of the double dual-chambered in series (>9999Ω) a very poor polarization data was obtained. Current densities at maximum power for the single dual-chambered and double dual-chambered in parallel were observed to be 16.09mA/m^2 and 35.77mA/m^2 with internal resistances 4000Ω and 600Ω respectively. The application of this novel catholyte for power generation in MFC's systems has the potential of regeneration thus, sustaining its utility for long periods. It was concluded that for large scale applications, MFC's systems utilizing this novel catholyte as electron acceptor, connection in parallel would be preferable, because of the high open circuit voltage, reduced internal resistance and high current density achieved from such connections.
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The quest for alternative sources of energy is pertinent at this period of our history when concerns about global warming are causing topical and sensitive debate worldwide. It is a well known fact that energy can be transformed from one form to the other, for example, mechanical energy can be converted to electrical energy, and so on. One novel process which seems to have confirmed this statement in recent times is the microbial fuel cell technology. This technology has the capability of transforming chemical energy stored up in organic matter to direct current (D.C) in just a single step. In addition to generation of electricity, this technology has the potential of treating wastewater using the micro-organisms inherent in the waste water (Fan et al 2007; Logan and Regan, 2006).

In microbial fuel cell, electrons released during organic or waste water breakdown are transported to the anodes which eventually are oxidized by electron acceptors at the cathode (Logan and Regan, 2006). Although, this technology seems promising, microbial fuel cells are not deficient of their own challenges. Power output from microbial fuel cells has been affected by high internal resistance inherent in these systems. However, in a bid to improve power density in MFC's, the use of electron acceptors apart from oxygen has been extensively explored (Rabaey et al., 2004; Rabaey et al., 2003; You et al., 2006). These authors used ferricyanide and permanganate solution to improve power density via reduction in internal resistance or high open circuit voltage (OCV). The maximum open circuit voltage recorded to date using permanganate solution is 1.532 volts by You et al., (2006).

Though, power generation was enhanced in these studies using chemical catholytes, the problem of continuous replacement and toxicity of these electron acceptor i.e. permanganate and ferricyanide make their application in large scale to be limited. The aim of this research was to establish the feasibility of generating direct electricity current from abattoir waste water which is much in abundance in Nigeria using a novel electron acceptor. To the best of our knowledge the application of this electron acceptor has not been used in any previous study.

MATERIALS AND METHODS

High strength abattoir waste water was collected from abattoir location at Choba community, Rivers State. The total chemical oxygen demand was determined to be 22,000mg/L using standard methods (APHA, 1985) with a pH of 6.68. Experimental set up for a dual chamber microbial fuel cell is as depicted in Fig. 1.

The anode chamber containing about 850ml high strength abattoir waste water was connected via copper wires to the cathode chamber containing 20g/L of calcium hypochlorite powder ($Ca(OCl)_2$) also known as bleaching powder. The two chambers were linked with a salt bridge inter-connection. The single dual-chambered system was closed with a 1000Ω resistor. Similar resistor was used to close the double dual-chambered in parallel and series connection.

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Fig. 1 Experimental set-up for single dual chamber

The microbial fuel cell voltage for the 3-set up that is, single dual-chambered, double dual-chambered in parallel and series was monitored every 3 hours using a digital multimeter, (AVD 890G) (Mohan et al., 2007). Power density, was obtained from polarization test by varying the external resistance over a range of external load using a variable resistor box (J 2362) that ranged between 0 - 9999Ω. Reading of voltage and current was done within few minutes of their stabilization. Polarization was conducted after three single batch cycles have been carried out to obtain the maximum potential difference (Heilmann and Logan, 2006; Liu and Logan, 2004).

Power density was expressed in mW/m^2 normalized to the projected surface area of the graphite anode (m^2) respectively. Power density (P) was analyzed according to the Equation (1) (Rabaey and Verstraete, 2005)

$$P = \frac{Current(mA) \times Volts(V)}{Surface area\ of\ \ projected anode} \quad (1)$$

Table 1: Design criteria of single dual-chambered microbial fuel cell

Volume of cathode and anode chamber	1000ml
Volume of abattoir waste water	850ml
Nature of anode and cathode	Graphite rod
Length of projected graphite rod	4.4cm
Total area of projected graphite rod at anode	$0.01156m^2$
Operating temperature	27 ± 3 °C
Operating pH	2.83(Cathode) and 6.68 (Anode)
Membrane	Agar -Salt bridge
COD	22,000mg/l
Agar casing	3/4 inch diameter PVC about 8cm long

RESULTS AND DISCUSSIONS

The generation of electricity from the high strength abattoir waste water was observed to be feasible for the three set-ups. After three single batch cycles, maximum potential difference of 320mV, 650mV and 32mV were observed for the single dual-chambered, double dual-chambered in parallel and series respectively each connected to 1000Ω resistor. A single batch cycle spanned for a period of 96hrs and after three single batch reactor cycles, polarization was carried out in order to establish the maximum power density and internal resistances of the three set-ups (Fig 2 and 4).

Maximum open circuit voltages observed prior to polarization were 1560mV, 1400mV and 2890mV for the single dual-chambered, and the double dual-chambered in parallel and series respectively. Maximum surface power density observed for these set-ups were $12.26mW/m^2$, $20.71mW/m^2$ for the single dual-chambered, double dual-chambered in parallel with current densities at maximum power being $16.09mA/m^2$, $35.71mA/m^2$ respectively (Fig 3 and 5). Due to very high internal resistance of the double dual-chambered in series (›9999Ω) the maximum power density was outside the range of the variable resistor box. However, at 9999Ω the surface power density was $0.36mW/m^2$ with a very poorly polarized current and voltage data (data not shown).

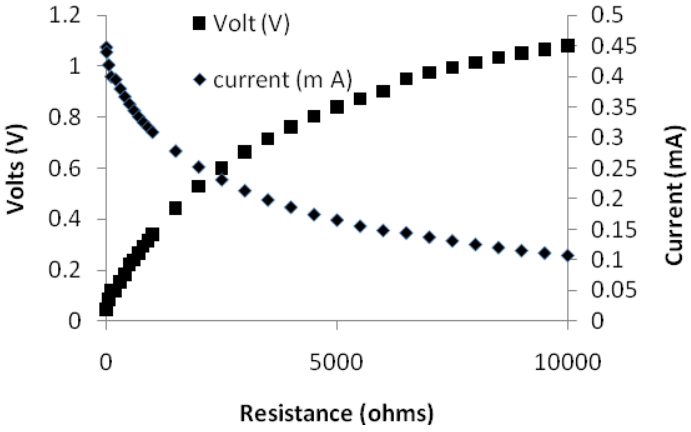

Fig. 2. Polarization plot for single dual-chambered MFC

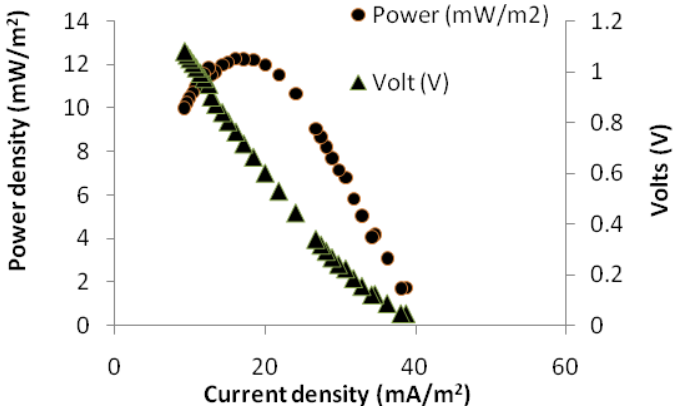

Fig. 3. Power density and voltage against current density for single dual-chambered MFC

The maximum power transferred by the microbial fuel cell usually occurs when the external load (resistance) just equals the internal resistance i.e. (R_L = R_{int}). Thus, the internal resistances at maximum power were determined to be 4000Ω, 600Ω and ›9999Ω, for the single dual-chamber, double dual-chambered in parallel and series respectively (Fig 6). The maximum surface power density observed for the single-dual-chambered system is consistent with results obtained in previous studies (Kim et al 2004; Ghangrekar and Shinde 2006). Though, similar work using agar-salt bridge with oxygen as electron acceptor was observed to produce an internal resistance of 19,920Ω for a single dual-chambered system (Min et al, 2005) the reduced internal resistance observed here for this set-up suggests that the use bleaching powder as electron acceptor may possess the potential in lowering the internal resistance between electrolyte in the anode and cathode chambers.

The open circuit voltage (OCV) for the single dual-chambered system was very high (1560mV) as shown in Fig. 1 which could have translated to higher power density (Logan, 2007). However, the low power density observed here may be related to the high organic strength waste water used in this set-up and possibly poor utilization of the graphite anodes

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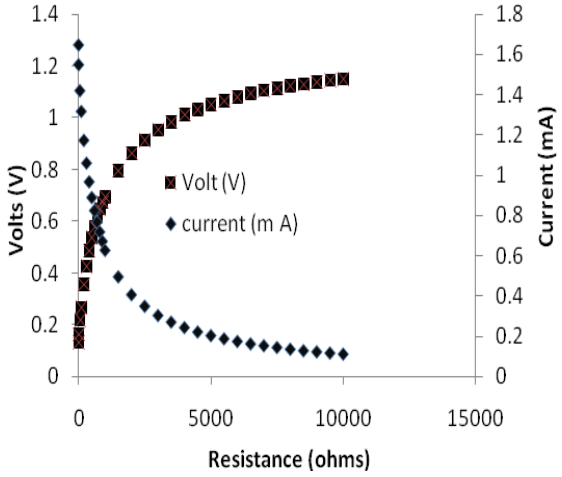

Fig. 4. Polarization plot for double dual-chambered MFC

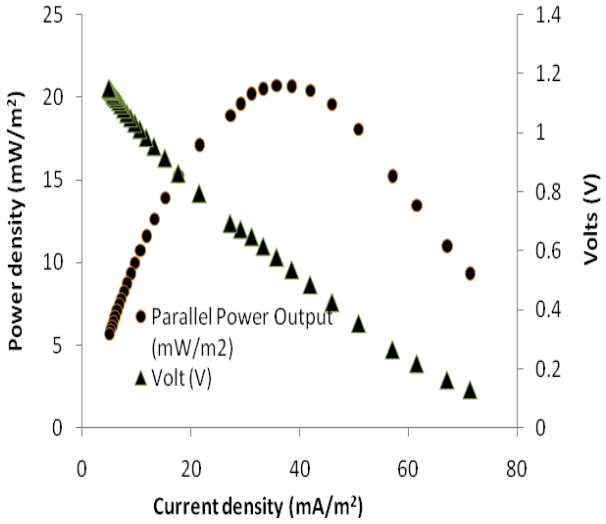

Fig. 5. Power density and voltage against current density for double dual-chambered MFC in parallel

For the double dual-chambered system in parallel, the open circuit voltage was slightly lower than the single dual-chambered system (1400mV) with a higher current density at maximum power (37.77Mw/m^2). This is consistent with parallel connection, in which voltage averages while, the total currents add up i.e., the current density at maximum power for the double dual chambered in parallel is almost twice that of the current density at maximum power for the single dual-chambered system. Also, the observed low internal resistance (600Ω) is again consistent with parallel connections i.e., the total resistance of the double dual-chambered in parallel is close the sum of the reciprocal of the resistances of two single dual-chambered system.

The double dual-chambered system connected in series showed a high open circuit voltage of 2860mV but a low power and current density was observed due to the very large internal resistance of the set-up (>9999Ω). It thus seemed that, the sum of resistances for series connection for this set-up was additive. In essence, for large scale application, where high current density is needed using calcium hypochlorite (bleaching powder), connection in parallel may provide a suitable means for maximizing power.

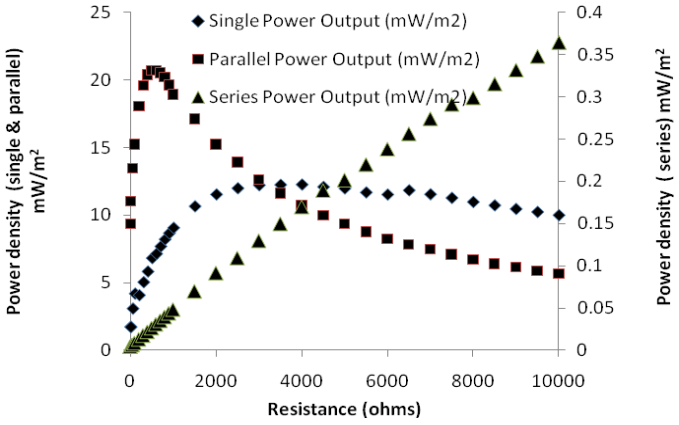

Fig. 6. Power density for 3 set-ups against varying resistances

Mechanism of Power Generation Using Bleaching powder: The process of power generation in MFC is usually linked to electron release at the anode which is terminally accepted at the cathode chamber by suitable electron acceptor. For MFC with oxygen as terminal acceptor, the maximum theoretical voltage is 1120mV volts, resulting from the difference in potential between the cathode and anode chamber represented by the Equation (2). The breakdown of carbohydrate is usually linked to the NADH/NAD$^+$ couple with a half cell potential (E^{01} = 320mV) (Rabaey and Verstraete, 2005) while the oxygen at the cathode has the half cell potential (E^{01} = 0.80 volts). The E_{cell} for this system usually have a maximum theoretical voltage of 1200mV.

$$E^{1}_{cell} = E^{01}_{cathode} - E^{01}_{anode} \qquad (2)$$

However, the half cell potential for the cathode using bleaching powder as the electron acceptor can only be appreciated by understanding the chemistry of bleaching powder in water.

Chemistry of Bleaching Powder in Water: The following reactions have been proposed for the processes that occurs when $Ca(OCl)_2$ is used as an electron acceptor;

$$Ca(OCl)_2 + H_2O \rightarrow Ca(OH)_2 + 2HOCl \qquad (i)$$

The release of protons and electrons at the anode are accepted by the hypochlorite as follows;

$$2HOCl + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O \qquad (ii)$$

The sum of the reaction process (i & ii) adds up to

$$Ca(OCl)_2 + 2H^+ + 2e^- \rightarrow Cl_2 + Ca(OH)_2 \qquad (iii)$$

However, the product chlorine gas in readily soluble in water and in a closed system dissolves in water to yield HOCl as follows;

$$Cl_2 + H_2O \rightarrow HOCl + HCl \qquad (iv)$$

The sum of process iii and iv adds up to

$$Ca(OCl)_2 + H_2O + 2H^+ + 2e^- \rightarrow HOCl + HCl + Ca(OH)_2 \qquad (v)$$

Again, HOCl is made available for another process of electron and proton acceptance made possible by the bacteria degradation at the anode chamber which releases electrons that is transported via copper wires to the cathode and protons that are transported through the salt bridge into the cathode chamber.

$$HOCl + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O \qquad (vi)$$

The sum of process (v) and (vi) adds up to

$$Ca(OCl)_2 + HOCl + 4H^+ + 4e^- \rightarrow Cl_2 + H_2O + HCl + Ca(OH)_2 \qquad (vii)$$

Again the chlorine generated at step (vii) re-dissolves in water which, in closed system yields;

$$Cl_2 + H_2O \rightarrow HOCl + HCl \qquad (viii)$$

Addition of step (vii) and (viii) yield a summed process as follows;

$$Ca(OCl)_2 + 4H^+ + 4e^- \rightarrow 2HCl + Ca(OH)_2 \qquad (ix)$$

Finally the end products react to form salt and water as follows;

$$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O \qquad (x)$$

From the reaction processes described above it was observed that the direct electron and proton acceptor was HOCl as depicted in steps (ii) and (vi). Hypochlorite acid is a very strong oxidant which was indirectly generated by $Ca(OCl)_2$ when dissolved in

water with a half cell potential (E^{01}) of 1690mV (Mathews, 2002). In essence the theoretical maximum potential difference obtainable from this set-up would be

E^0cell = (1690 - (-320) (mV) = 2010mV

This very high theoretical open circuit voltage may position bleaching powder as a potential catholyte for maximizing power in MFC systems. However, in using bleaching powder as the chemical electrolyte, the advantages and disadvantages should be considered. Some advantages of bleaching powder are (a) The use of bleaching powder solution as chemical catholyte has the potential to generate very high open circuit voltage compared to other chemical catholytes, for example, permanganate and ferricyanide. (b) The regeneration of hypochlorite in the process during utilization of bleaching powder may make it more sustainable than other chemical catholytes. (c) Cations such as K^+, Na^+, Ca^+ and NH_4^+ that are normally transported alongside protons (Rozendal and Halmeter, 2006) Stamee et al (1997); Stenina et al, 2004) which, ultimately make the cathode chamber basic could be effectively managed by the acid/base system in the cathode chamber i.e. the HCl/$Ca(OH)_2$ thus enhancing an efficient transfer of protons into the cathode. (d) Bleaching powder is relatively cheap compared with other chemical catholytes presently in use. Some disadvantages are (a) The use of bleaching powder as chemical catholyte results in the visible production of chlorine bubbles at the cathode chamber, thus, the cathode chamber must be operated in a closed system to avoid contamination of surrounding air with chlorine gas. (b) The use of nafion membrane may not be feasible because the likelihood of chlorine gas to diffuse through the membrane into the anode chamber, similar to the diffusion of oxygen across the membrane in MFC's systems that lead to low columbic efficiency (Logan et al, 2006).

Conclusion: The use of abattoir wastewater as substrate for Microbial fuel cell has the potential to generate electricity during its degradation using bleaching powder as the electron acceptor. Power optimization was observed to be realized when circuits were connected in parallel instead of being single or connected in series due to the high resistance in these later set-up. Parallel connection seems to optimize power by reducing the internal resistance when bleaching powder was the electron acceptor. Thus, the process of power generation and simultaneous treatment of abattoir wastewater in large scale systems can become practicable with proper design and reactor configuration.

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