ISSN 2348-313X (Print)
International Journal of Life Sciences Research ISSN 2348-3148 (online)
Vol. 7, Issue 1, pp: (66-73), Month: January - March 2019, Available at: www.researchpublish.com

GENERATION OF ELECTRICITY DURING WASTE WATER TREATMENT USING MICROBIAL FUEL CELLS

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Abstract: **The production of energy without pollution (non-pollutant) is an essential idea to make sure the survival of human mankind. The alternative energy production through microbial conversion of biomass (sewage waste water) is studied in this work to generate electrical energy. The methods that are currently used are at the cost of building and running cells where microbial conversion is taking place. Various developments can be achieved which includes the cell's physical design, the catalyst involved in the cathode chamber, the membrane material and the perfect low cost substrate. Population explosion in the world has lead us to diminishing our energy resources. An approximate estimation is that 13 TW of power is consumed every year around the world where 20 % comes from renewable sources. A new technique where bacteria ferments organic substrates to generate electric energy gives us an efficient alternative energy production. This idea is called as Microbial Fuel Cell (MFC). A microbial fuel cell involves the bacteria being attached to the anode for oxidizing organic material which tends to release CO2 and protons into the anode chamber solution. Here, the electrons move from anode to cathode through electric circuit where electrons involved in reducing oxygen. During this the protons penetrate through a membrane and get to the cathode chamber. Due to the mobility of the electrons, electric current is produced. The main objective of this project is to produce electric current using Microbial Fuel Cells (MFC) from the waste water.**

Keywords: **Bacteria, organic matter, waste water, Microbial fuel cell, electricity.**

1. INTRODUCTION

Fuel cell is an electrochemical cell which converts chemical energy in a fuel to electrical energy. The intermediate steps such as heat and mechanical work are avoided and so these fuel cells are capable of high efficient power production with minimum effect on the environment. (1)

Microorganisms involves in the anaerobic oxidation of the biodegradable substrates present in the waste water and so they act as biocatalysts in a Microbial Fuel Cell (MFC). The electrons that are released move towards the anode. Meanwhile the Protons released near the anode get into the cathode compartment through a semi-permeable membrane.(2) Thus the movement of electrons in an external circuit between anode and cathode leads to the generation of electricity.

PRINCIPLE OF ELECTRON TRANSFER:

The process of biological catalysis in an electro chemical reaction is called as bio-electro catalysis. The biocatalyst used can be an enzyme or whole microorganisms. High energy substances such as glucose is metabolized by the living cell and it gets energy from coupled reactions of oxidation and reduction (Equations). The activation energy is decreased in the cell by the enzymes of the cell in order to help metabolize the substrate. Equation 1.1 represents the reduction reaction and equation 1.2 represents the oxidation reaction.

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$C_{16}H_{12}O_6 + 6H_2O \rightarrow 6\ CO_2 + 24\ H+ + 24\ e-\ E0 = 0.014V$ (1.1)

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

$E0 = 1.23V$ (1.2)

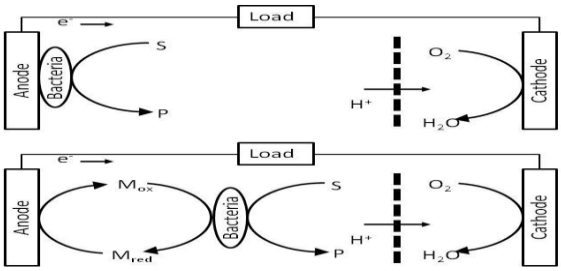

Fig 1: Principle of microbial fuel cells showing the mediated and direct electron transfer

Figure 1 shows the microbial fuel cell principle for mediated and direct electron transfer from the microorganism to the anode. The electrons produced in equation are moved to the anode as a terminal electron acceptor. The electrons then move to the cathode in an external circuit which inturn reacts with oxygen to produce protons that passes via the membrane to form water. (3)

The transfer of electrons is more efficient, which is a key aspect in the microbial Fuel Cells (MFC).Proposed electron pathways from microorganism to anode are either through conduction (direct) or mediated.Redox enzymes facilitate electron transfer in the outer membrane of the microorganisms by means of conduction e.g. cytochromes. The magnification of the isolated strains from waste water is done which is further used for bioremediation of the waste water. Some of the other pathways for direct contact to anode involve using polymeric matrix and conductive nanowires.

Mobile Redox shuttles (e.g. phenazine, pyocyanin, humic acids) that are obtained from microorganisms that naturally originate from the substrate are used for Mediated electron transfer.The Mediator which is of the reduced form gets diffused to the anode, it gets oxidized and again diffuses to the microorganism. The most favorable pathway for producing high current from a biofilm would be conductive biofilm polymer matrix (EPS). The redox enzymes aided direct electron transfer is limited as it leaves only one layer of microorganisms being able to transfer electrons to anode when redox enzymes are involved due to the necessity of direct contact.

The inoculation of Microbial Fuel Cell with electro chemically active pure cultures are capable of utilizing the complete oxidation of specific organic substrates that are found in the waste water. When the complete genome sequences and genetic systems for these bacterial strains are available, further detailed analysis of electron transfer mechanism in pure cultures can be made possible and can improve us in understanding the basic workings, physiology and ecology of a microbial Fuel Cell (MFC). Figure 2 shows the block diagram of microbial fuel cell.

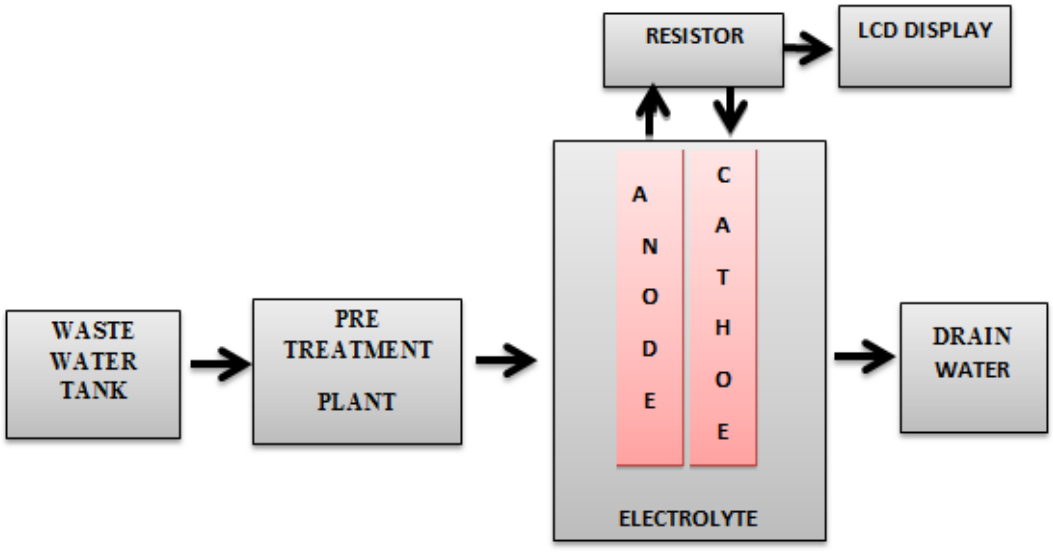

Fig 2: Block Diagram of MFC

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2. MATERIAL AND METHODS

ANODE MATERIALS:

The surface for the biocatalyst to get attached and for the reaction with the substrate is provided by the anode material in a Microbial Fuel Cell (MFC).The material of anode material should be compatible electron transfer between biocatalyst and substrate.

Either biological or non-biological material means can improve the anode. The characterization of electro active microorganisms in a gel on the anode surface is a way to biological enhancement. As only a thin layer of entrapped bacteria is able to act as biocatalysts, entrapping microorganism becomes impractical and the microbial community might not be able to reproduce and grow.

The enrichment of electro active microorganisms through natural selection influenced by the anode material and the system conditions is a more efficient method to enhance the microbial community on the anode. Carbon materials especially carbon paper, carbon cloth and graphite are the most commonly used as anode materials because of their high conductivity, specific surface area, biocompatibility, versatility and low cost. Increasing the specific anode surface area with the help of three dimensional or porous anode materials, relative to the cathode surface area leads to increase in performance of anode and thus increasing the electric generation. Certain three dimensional and porous materials such as Carbon or graphite granules are found to achieve high power densities in up-flow continuous reactor designs presumably due to the large surface area that are available to microorganisms. .However an increased internal resistance was noted.

Table 1: Anode Materials

Experiment	Anode
Modified Anode Materials	Carbon cloth[a] Carbonblac
Activated Carbon Cloth[h]	FM30k H[h]
Anode Support Materials	C/HNO_3on titanium mesh[i] C/HNO_3on stainless steel mesh[i] C/HNO_3 on aluminium mesh[i] FM30k[h]

Experiment Anode Modified Anode Materials Carbon cloth a Carbon black b C/HNO_3c C/PANId Activated Carbon Clothh FM30k Hh FM30kh FM70h Anode Support Materials C/HNO3 on titanium meshi C/HNO3onstainlesssteelmeshi C/HNO_3on aluminium meshi FM30kh. The conductivity problem can be solved by using anode made up of carbon fiber brush and also higher power densities were noted for reactors in a laboratory setting using a carbon fiber brush. The usage of similar porous and three dimensional carbon materials, the surface area increases vastly, where the attachment of microorganisms is facilitated. Electrochemically the protons are transferred to cathode crossing the membrane.

CATHODE MATERIALS:

Platinum is the most generally used cathode material because of its high catalytic activity in the Oxygen Reduction Reaction (ORR) in an air-cathode system. Since platinum is more costly it becomes uneconomical in Microbial Fuel Cells (MFC) in the treatment of wastewater.

The catalyst can get deactivated upon the usage of complex substrate when other substances other than protons get pass the membrane which further results in precipitation (eg. carbonate salts) takes place on the cathode side. The process of

electro catalysis of platinum and iron (II) phthalocyanine (FePc) can get inhibited due to the presence of sulphides. Some of the other alternatively used catalyst to enhance the electrochemical activity in the oxygen reduction reaction are phthalocyanine and porphyrin which are selected on the basis of transition metals. (4)Cobalt tetra methoxy phenyl porphyrin (CoTMPP) and (FePc) in half cell show similar reduction current when considered with platinum or carbon. FePc gives high power densities over carbon black in Microbial Fuel Cell (MFC) tests than obtained using platinum cathodes whereas CoTMPP show a slight lower power density as a cathode catalyst than platinum.

Table 2: Cathode Materials

Experiment	Cathode
Modified Anode Materials	Carbon black
Activated Carbon Cloth	Carbon black
Anode Support Materials	Carbon black

Experiment Cathode is shown in table 2.For producing electrons and protons, cathodes rely over anode in a Microbial Fuel Cell gas diffusion and also for transferring them in an external circuit and a protonex change membrane to the cathode. So the activity of the cathode is decreased by anode if it is has bad performance, lower anolyitc conductivity and membrane. The catalyst can get deactivated upon the usage of complex substrate when other substances other than protons get pass the membrane which further results in precipitation (eg.carbonate salts) takes place on the cathode side.The process of electro catalysis of platinum and FePc can get inhibited due to the presence of sulphides.A sustainable and low-cost alternatives to biotic cathode catalysts are microbial biocathodes. Certain substances are poisoning in wastewater, this can be resisted by mixed microbial cathode which is an advantage and also they have the ability to restore themselves.

MEMBRANE MATERIALS:

The cathode and anode reactions are separated by the membrane in an electrochemical system and it selectively allows the protons to transport from anode to cathode while it prevents the transportation of oxygen into anode chamber. While a porous separator also serves as a barrier separating the anode and cathode reaction, any ions can be transported from the anode chamber to the cathode through diffusion processes. Commonly used ion exchange membrane in fuel cell systems is Nafion which is expensive used for the transportation of proton from anode to cathode. It is used as a membrane in Microbial Fuel Cell (MFC) because of its selectivity and good transport properties. Cation species (e.g. Na+, K+, NH4+, Ca2+, Mg2+) that are found in the anolyte in MFCs are also transported selectively by Nafion besides being described as proton exchange membrane for the maintenance of charge balance in the system. Table 3 refers to different membranes and substrates used in this work.

Table 3: Membranes and Substrates

Experiment	Membrane	Substrate
Modified Anode Materials	Rhinohidee	Domestic wastewater with 0.5 % brewery wastewater
Activated Carbon Cloth	Rhinohidee	Domestic wastewater
Anode Support Materials	Rhinohidee	Domestic wastewater
Cathode Studies	Rhinohidee	Domestic wastewater

The preferred ions transfer can occur when using wastewater where the concentrations of protons in the anolyte is 105 times lower than the cations and also leads to precipitation of salt over the cathode which further inhibits the cathode catalyst. The usage of ultrafiltration membranes or separators in a membrane less MFC design are the approaches to minimize the cost and surpass these limitations. Using Anion Exchange Membrane (AEM) shows coulombic efficiencies and higher power densities when compared to inexpensive cation exchange membrane (CEM) or Nafion. A better pH balance in the cathode and anode chamber can be obtained by improved performance of AEM. Similar or higher power densities as CEM in Microbial Fuel Cell tests can be achieved by using microfiltration membranes.

The solutions to the pH gradient that has been noted in many studies are given by an in-depth membranes characterization. High mechanical strength, durability and low-costs are the most important characteristics of the materials that are used as separators. Battery separators, carbon paper and various other materials are the materials that are investigated as separators in MFC tests. In separators, the conduction of protons takes place through the diffusion processes involving pH and balancing charge from anode to cathode. Any substances can get transferred to cathode since the separators are not being selective and so it was observed that higher diffusion of oxygen into the anode chamber was taking place.

So high power densities were observed in membrane less reactors while comparing to the reactors that use proton exchange membrane. However lower coulombic efficiencies (CE) were achieved since the substrate was undergoing aerobic digestion. Low coulombic efficiencies can be solved by using membrane-less MFCs which is also cost efficient. Coulombic efficiencies can be increased by introducing a material layer (carbon fibers or J-cloth) at the front of the separator which is further achieved by reducing the diffusion of oxygen into the anode chamber by assuming through formation of an aerobic biofilm or material's lower oxygen permeability. Aerobic degradation still takes place in this configuration besides achieving higher coulombic efficiencies.

PROPERTIES OF MEMBRANE:

The selection of a membrane separator should be based on the characteristics that are required by the system used.In microbial fuel cell system these requirements include with the following properties.

Low oxygen diffusion coefficient; Minimal ionic resistance; the substrate should be hydrophilic and readily wettable; Proton or ion conducting depending on the cathode catalyst; Effective in preventing crossover/migration between the two electrodes; Resistant to fouling; Degradation by microorganisms and blocking of_substances in the membrane pores; Sufficient chemical stability; Durable with sufficient physical strength to allow easy handling;Inexpensive; Biocompatible;

REACTOR DESIGN AND OPERATION:

The limitations of the materials (i.e. anode, cathode and membrane) and substrate in the reactor design of MFC should be overcome to get increased power production and also the coulombic efficiencies. Some of the problems faced by the MFCs are: Capital costs of the materials used; Low coulombic efficiencies; Low power densities.

High ohmic losses are resulted in the system because of the poor conductivity of wastewater (1-2 Mscm-1 for domestic wastewater) which leads to increased internal resistance in the reactor and so the production of energy is less. The low catalytic activity or inhibition of cathode catalyst and deactivation due to the other substances in wastewater causes ohmic losses on the electrode which are the other ohmic losses that causes reduction in power generation. In electro genesis, the main electron donor is anaerobic respiration. The degradation of the substrates by certain processes such as fermentation during which the electrons produced get transported to the terminal electron acceptors instead of anode causes low coulombic efficiencies in wastewater. The problem of cost must be solved by the research studies which involves increasing the efficiency and the material activity with the reduction in cost of membrane, cathode and anode. Meanwhile coulombic efficiencies and low power densities can be solved by the operational parameters and the design. The internal resistance can be slightly reduced (79 Ω to 71 Ω) and also power density can be doubled (720 Mw m-2 to 1210 Mw m-2) by decreasing the electrode distance from 4 to 2 cm. But unexpectedly when the electrode distance is further reduced, internal resistance, coulombic efficiency and power density tends to decrease which may be on cause of diffusion of oxygen into anode chamber. The power production can be improved by making a flow via the porous surface of the anode as the substrate gets diffused into the anode as well as protons gets diffused into cathode.

The pH balance, quality of the effluent and the coulombic efficiencies can be improved by the sequential flow from anode to cathode. To achieve high power densities at high coulombic efficiencies, the reactor operation and design should be matched to the application. The factors that influence the wastewater treatment, coulombic efficiencies and power generation should be found and known in order to enhance and optimize them Thus to seek better understanding of the physiology and ecology of MFCs and electrochemical engineering limitations such as materials and physical design. Cathodic and anodic electron transfer mechanisms have to be understood in depth, including detailed behavior of the interfacial electron transfer rates, biocatalytic rate constants, cell resistance, COD and nutrient removal mechanisms and the knowledge about which steps are rate-limiting.

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WASTE WATER TREATMENT:

For the understanding of the reactions between biofilm and anolyte, the COD, conductivity and the Ph of the substrate were estimated for the control reactor, MFCs and the dummy reactors. The pH gives a measure of the protons in the reactor and conductivity indicates all ions in thereactor and how their number changes while microorganisms digest substrate to produce protons and electrons.

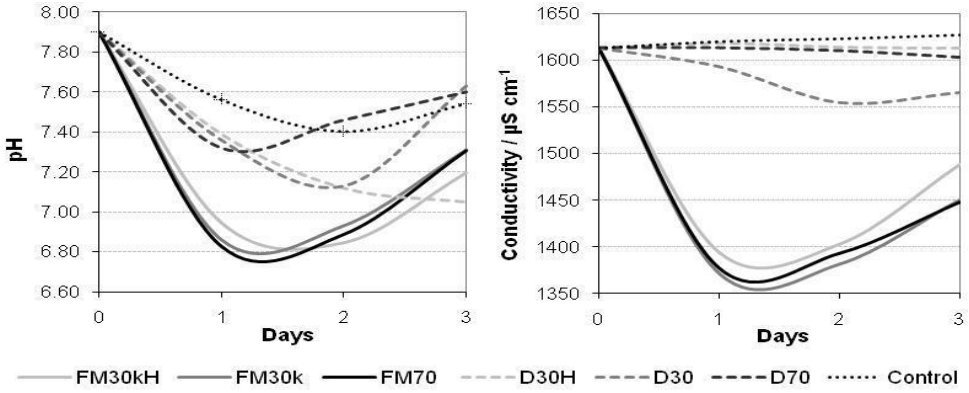

Fig 3: Variation in Conductivity and pH of MFCs, Dummy Reactors and the Control Reactor

The pH decreased during a batch once power production commenced and protons were produced in the anode chamber to be transferred to the cathode. For the MFC reactors using CAC materials as the anode the pH decreased sharply from pH7.9 to pH6.8point while the pH in the dummy reactors decreased less sharply from pH 7.9 toPh7.3. The control reactor showed the most stable pH with a slight decrease from pH 7.9 to pH 7.4. For all reactors the pH increased slowly again once peak power was reached. The conductivity followed the same profile as the pH and decreased from1613µScm-1 to around1370µScm-1 for the MFC reactors over the first day. The conductivity then slowly recovered at the end of the batch, whereas the conductivity of the control reactor and the dummy reactors remained comparatively constant.

The pH influence on the system seems to depend on the system used. As domestic waste water is used as feed substrate slight difference in pH of one pH unit during the power production were not thought to be a major influence on the power production and efficiency of the system as the wide spread peak power performances between pH 9 and pH 6 were observed in literature. The minimum observed for pH and conductivity was possibly linked to most of the substrate being degraded by the second day which lead to less protons being produced and thus an increase in pH and conductivity as also current production started to decline. (Fig.3)

An explanation for the different characterization of pH (more protons in the electrolyte) and conductivity (less ions allover in the electrolyte) was that the minor number or protons present in all reactors did not represent the actual ion movement in the different reactors. As Rozendal et al described the proton concentration at neutral pH (around 7) is with 10-4 Mm very low whereas other action concentrations are up to 105 times higher. As the reactors used a microporous membrane as separator in this study any ion would be able to move from the anolyte to the cathode reacting with oxygen to produce salts (e.g. calcium carbonate) on the cathode surface which could affect the cathode performance. Different ions contribute differently to the conductivity of water.

3. RESULT

This work presents the output of the generated electricity. The result for the particular value of the input/output is illustrated here for the reference demonstration and the step by step output of the generated voltage with respect to time is displayed . The result can be obtained in two sections namely simulation experimental setup and hardware experimental setup. The simulation result shows the output in LCD display and the hardware setup runs the gear motor by utilizing the generated voltage. Simulation (Fig. 4)

The program below uses the Liquid Crystal library. This library contains all of the functions needed to write to the LCD. The loop reads the analog value from the analog input, and because the reference voltage is 5 V, it multiples that value by 5, then divided by 1024 to calculate the actual voltage value. Once the voltage has been calculated, the value is written to the LCD. The voltage obtained in the LCD is 3.81V.

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Fig 4: Simulation Experimental Setup

Hardware Result Analysis:

The hardware setup explained the voltage obtained in the LCD display can be used to run the motor. The motor used in this work DC gear motor. The voltage developed by the microbial fuel cells is also stored in a 6V battery. The hardware setup is shown in Figure 4.

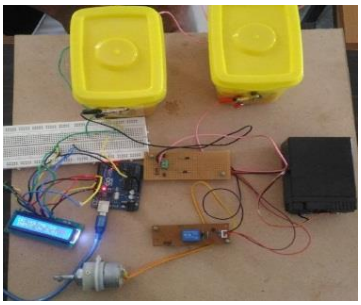

Fig 5: Hardware Experimental Setup

Table 4: Observation

S.no	Time in minutes	Voltage in volt
1	0	0.0
2	5	0.32
3	15	1.8
4	20	2.4
5	30	3.81

S.no, Time in minutes, Voltage in volt

The Figure 6 shows the charging of the generated voltage. The discharging of the stored voltage is processed by connecting load. The load given here is LED. Three LEDs are connected in series with the generated output. The time taken for discharge of the 3.81 volt is five minute. .Figure 6 shows the discharge graph of stored voltage.

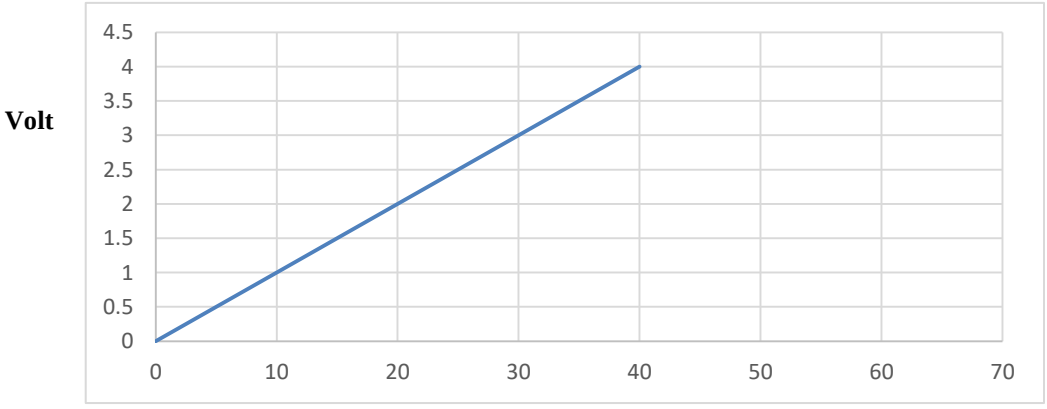

Fig 6: Charging graph

4. CONCLUSION

Microbial fuel cells have been operated in fed batch and continuous mode using different anode, cathode and membrane materials and changing the reactor architecture while using wastewater as substrate. The most active and stable materials were a range of activated carbon cloth and activated carbon black (powdered carbon black activated with nitric acid) supported on carbon cloth. The high surface area, conductivity, porosity, and adsorption capabilities of the activated materials presumably gave the microorganisms a large surface to adhere to and facilitated extensive contact between microorganisms (biocatalyst), substrate and current collector.

Activated carbon as anode material achieved comparatively high coulombic efficiencies and good power and wastewater treatment efficiencies. Activated carbon cloth showed great potential as anode material during polarization, but a decline in power performance under constant external load was observed over time. In contrast coulombic efficiencies increased considerably from 23% CE to 42% CE over time while COD redction remained constant.

The community analysis of activated and modified anode materials revealed the significant influence of the external load on the anodic biofilm. These results supported the hypothesis that the microbial community could be selected based on external load and surface chemistry of the anode material if power generation is the most important process in the system.

Brewery wastewater as part of the substrate (0.5%) seemingly inhibited power generation and masked the influence of the anode materials on the reactor performance. It was associated with very low coulombic efficiencies resumably due to preferential degradation of the high carbohydrate content by fermentation. Power densities produced were limited largely by high ohmic losses (internal resistance) which were mainly due to the low conductivity of the substrate (wastewater). Reducing the electrode spacing to 2 mm decreased the internal resistance to 12 Ω (for low distance activated carbon cloth) or lower (1-7 Ω for the mesh anodes). An expected increase in power performance was offset by oxygen diffusion into the anode chamber which decreased the anode potential by 100 mV.

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