Development of Microbial Desalination Cell with Modified Graphite Paste Electrode for the Generation of Electricity and Salt Removal

Muhammad Waleed Khan[1], Maryam Arain[1], Sheeraz Ahmed Memon[1], Abdul Mubeen[1], Muhammad Tehseen[1].

[1]*Mehran University of Engineering and Technology, Jamshoro, Pakistan*

***Abstract*: MDC are innovative bio electrochemical devices from which the metabolic activity of the bacteria converts biomass into electricity and desalinate saline water. Electricity production through MDC may become a vital source of bioenergy in the upcoming era because MDCs deals with the possibility of salt removal from the saline water, pull out electric current from a renewable biomass and complex organic waste. Sewage water was tested as a food substrate for bacteria in aerobic anode chamber which is connected through external resistance to cathode aerobic chamber filled with distilled water, whereas middle chamber was desalination chamber filled with synthetic saline water separated by ion-exchange membranes i.e. anion & cation membrane. The modified graphite paste electrode was used to obtain the highest power output (810mv) from the MDC. The MDC was run in three cycles in each cycle desalination rate is 79%,78.5% and 80% and increase the COD removal by 68%,65%,70% and the columbic efficiency by 131%. The desalination in MDC improved wastewater characteristics by increasing conductivity by 2.5 times and maintained the anolyte PH, so the resistance was reduced and stabilized the microbial activity. The Biofilm formation was observed on the surface of anode electrode shows that Geobacter is the most predominant with the abundance and meanwhile, electrogenesis related outer-surface octaheme c-type cytochrome is highly expressed in the anode. After 7 days we were observed uniform brown spots on the surface of the electrode at the anode chamber by using stereomicroscope.**

***Keywords*: Biofilm, Bio-energy, Desalination, Microbial desalination cell, Stereomicroscope wastewater.**

I. INTRODUCTION

The world is facing two demanding issues, lack of drinking water and energy crisis, to desalinate the seawater and brackish water to fulfill the demand. According to International Desalination Association, 18,436 desalination industries are operated globally, to covert saline water into fresh water 86.8 million cubic meters per day, whereas, pressure membrane desalination, thermal desalination, reverse osmoses technologies are cost intensive; they consume 3.7 to 655 kwh energy per m3 of water desalinate [1]. Developed countries generate energy from fossil fuels, but their efficiency, security and environmental effects embrace it back from being a preferred energy resource. To fulfill the energy demands, there is a need for clean energy, reliable and sustainable source. Clean and safe potable water is one of the energetic elements for human life on earth, only 3% fresh water present on earth [2]. There are many reactors to convert seawater to potable water. These reactors are energy and cost-effective. There are many procedures to desalinate seawater such as reverse osmosis, thermal desalination, etc [3].

Currently, there is a massive progress in new microbial fuel cells. Microbial desalination cell (MDC) technology is used for salt removal, wastewater treatment, and current production [4]. There are many processes designed to develop with different configuration of microbial desalination cell to generate bioenergy in the form of methane, electricity, and hydrogen [4], [5]. Microbial desalination cells (MDCs) can generate electrons due to anaerobic process or degradation of organic waste, through a bio-electrochemical system, microbial metabolism. In the middle chamber ions move from toward the desalination chamber due to increase in conductivity by bacteria across the MDC bioanode and cathode chamber. MDC has greater efficiency in desalination systems whereas, conventional technologies have low desalination efficiency as well as cost affective. The Addition of microbial to metabolize the organic waste with or without mediator in the variation between fuel cell and MDC Operations [6]. Many electrodes were used to improve the performance of MDC by increasing their biocompatibility, chemical stability and high conductivity [7]. The biofilm attached at the anode electrode surface and the sludge water release proton and electron by bio catalysis reaction [7], [8]. These running scared electrons, electrodes captured the running electron, through external circuit. MDC produces bioelectricity due to the major difference in the anode and cathode section to produce bioenergy in the MDC system [9]. The +ve charged ions circulation to the cathode by a CEM, where the clean water produced by the combination with electrons and oxygen species [11], [12]. There are some important practical applications of MDC, Organic loading, pH, Conductive electrodes with low potential losses. The overall ionic flow in anodic and cathodic chamber of MDC was denoted by the following equations [13] (1, 2)

$$CH_3COO + 2H_2O \rightarrow 2CO_2 + 7H^+ + 8e^- \text{ (Anodic reaction) (1)}$$

$$O_2 + 4e^- + 4H^+ \rightarrow {}_2H_2O \quad \text{..... (Cathodic reaction) (2)}$$

In this study, greywater was used as the substrate to simulate practical applications. The MDC was designed to desalinate the saline water and power generation as well as to improve the conductivity of electron by modified graphite paste electrode. Buffer solution was used as the catalyst to maintain the pH level of anolyte solution which involves increasing the microbial activity, so the performance of MDC was improved. Ions exchange membranes (AEM, CEM) import from USA these membranes are effective to pass the ions from the desalination chamber to anode and cathode chamber. MDC was operating in three cycles to compare the performance of the reactor and identify the formation of biofilm by using a stereomicroscope.

II. MATERIALS & METHODS

A. Preparation of Graphite Paste Electrode

Graphite powder and Carboxyl methyl cellulose (CMC) were taken from the market. 4g graphite powder mixed with 30 ml binder to prepare the slurry for coating the surface of Copper road. The Composite slurry was left in the bottle and tightly packed to preserve for 24 h to fully agitate. First, graphite paste was applied on the surface of copper rode than put on the oven at 60 ^{0}C for 30 min after 30 min, increase the temp up to 100 ^{0}C so that the vapors can evaporate, the binder can fully bind the graphite paste on the copper surface.

Fig. 1: Graphite Paste Electrode

B. Setup Design

The MDC consist of three chambers, anodic chamber, cathodic chamber, and desalination chamber. The middle chamber is a Desalination chamber separated by an anion exchange membrane (AEM) and cation exchange membrane (CEM) and each chamber have a volume of 1L. Modified graphite paste electrode is used as the anode electrode where as carbon cloth electrode used as the cathode electrode. The anode chamber was feed by synthetic activated sewage water with KPB buffer solution 50%. Inoculum was composed of activated sewage water 50% by volume and potassium phosphate buffer (KPB) 50% by volume with the addition of sodium acetate 3 g L^{-1} is fill in the anode chamber. Sodium acetate was used as fuel for the electroactive bacteria. Distilled water was filled in cathode chamber, saline water was desalinated in middle chamber. The solution conductivity measured using a conductivity meter (HACH). The pH measured by using a pH meter.

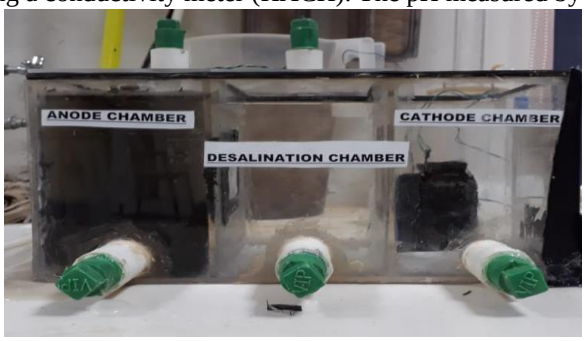

Fig. 2: Microbial desalination cell

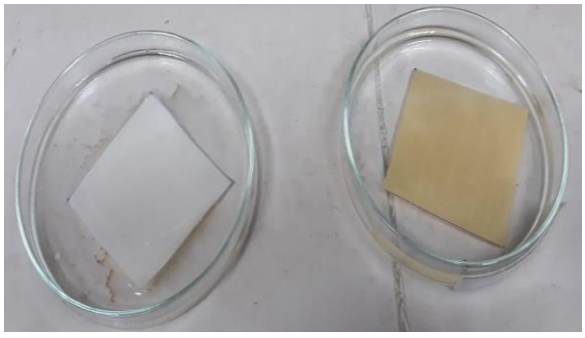

Fig. 3: Anion and cation exchange membrane (AEM, CEM)

C. Biofilm Formation

In the anodic chamber of the MDC, biofilm was formed by bacteria on graphite paste electrode. The biofilm formed at electrode cause increase in respiration of the microbes. Therefore, the biofilm in the anode chamber increase the bioenergy density. Some

major factors can be considered, the age of biofilm and the thickness of biofilm. These factors are able to increase the production of current density. With the biomass increase, the production of current density decreases as the biomass secure the infiltration of the substrate. After 8 days we were observed uniform green spots on the surface of the electrode at the anode chamber by using stereomicroscope (SM).

D. Operating Conditions and Calculations of MDC

The MDC was operated in a batch mode at a room temperature of ~ 30 ºC. The anode and cathode electrodes were connected through an external wire using an external resistor of 2kΩ. The voltage and current were recorded by using a multimeter with lag time of 24 hours. The cell voltage and current were recorded using a digital multimeter (UNIT-UT33B), the digital multimeter was connected in parallel to the external wire and the reading was taken after 24 h. Conductivity meter (HACH) was used to measure the conductivity of solution and the testing was carried out on daily basses. The pH was measured with a pH meter. The total dissolved solids (TDS) were measured with a TDS meter (HACH) and all mass measurements were made by using a (Radwag ®) digital weighing balance. The resolution of the pH meter used was 0.01, that of TDS meter was 0.1 g/l and that of the thermometer was 0.1 C0. The minimum reading of conductivity meter was 0.01 µS/cm. The maximum power was calculated from the power law (W).

$$P = IV \quad (1)$$

Current density was measured by

$$j = \frac{I}{A}, \quad \frac{Ij}{V} \quad (2)$$

A is total projected anode and cathode surface area in square meters (m^2) and V is the total reactor anode and cathode chamber volume in cubic meter (m^2).

The Coulombic efficiency (CE) (%) was calculated by:

$$CEcont = \frac{M \int_0^t Idt}{FnVanodic \Delta COD} \quad (3)$$

M = Molecular weight of Oxygen F
= Faraday's constant
n = Number of electrons exchanged per mole of Oxygen, V
= volume of anode chamber
ΔCOD = Change in COD over time t.

Salt concentration was determined by TDS measurements using a TDS meter. The desalination efficiency was calculated by

$$Q_r = (Q_i - Q_o)/ (Q_i) \times 100 \quad (4)$$

Q_r is the salt removal efficiency and Q_i, Q_o is the initial and final concentration of salt. Conductivity of saline water was calculated by conductivity meter (mS/cm-h).

III. RESULTS

A. Electricity Generation in MDC

MDC was run in three times operated with same condition and substrate for result accuracy. During reaction, the ATP to ADP process takes place to generate the voltage. The MDC reactor was monitored for 10 days, under open-circuit condition, to evaluate current generation. The maximum output voltage was recorded in the MDC at 2K Ω was 800 mV, 610mV and 820 mV for each time (Fig: 1). It was probably indicated that voltage slowly decreased due to variation occurs in pH in the anode chamber. The maximum current density value in MDCs was 200 A/m^3, 152.2A/m^3, 205A/m^3 in each time as shown in (Fig: 2).

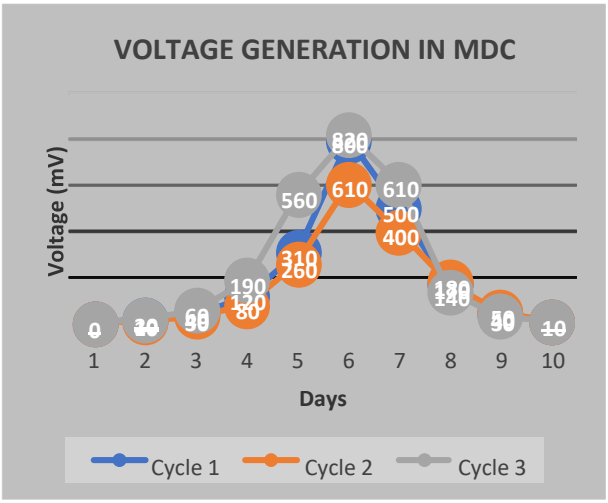

FIG. 1: VOLTAGE GENERATION IN MDC

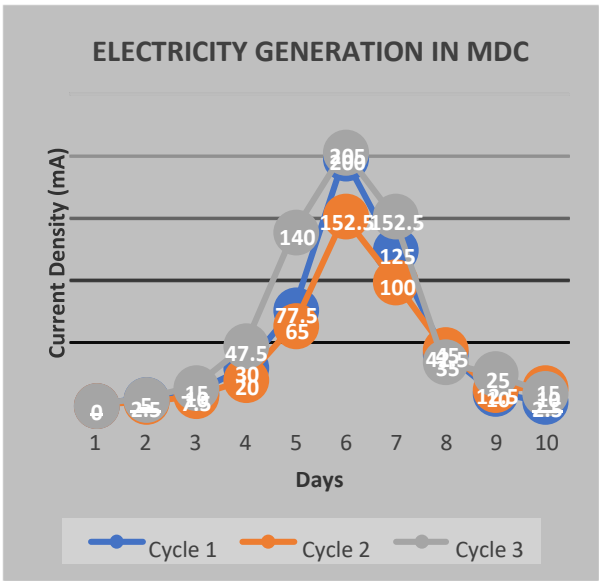

FIG. 2: CURRENT DENSITY IN MDC

B. Salt Removal in MDC

In this study, salt concentration in each cycle had the initial TDS 35 g/l of saline water. The maximum salt removal rate 80% was achieved. The highest desalination efficiency was recorded 79%, 78.5% and 80 % NaCl L^{-1} in each batch cycle as shown in (Fig: 3, 4, 5). As the graph shows the Desalination rate was increased gradually after 4 days reaction in MDC reactor and then after 7 days desalination rate was partially decreased over the cycle. The maximum desalination rate was achieved due to the presence of oxygen in cathodic chamber which enhanced OH^- ions release and resulted in the maximum transfer of +ve ions from the middle chamber to the cathode chamber of MDC. In this work, the anolyte pH was 7.21 ± 0.083 in MDC reactor.

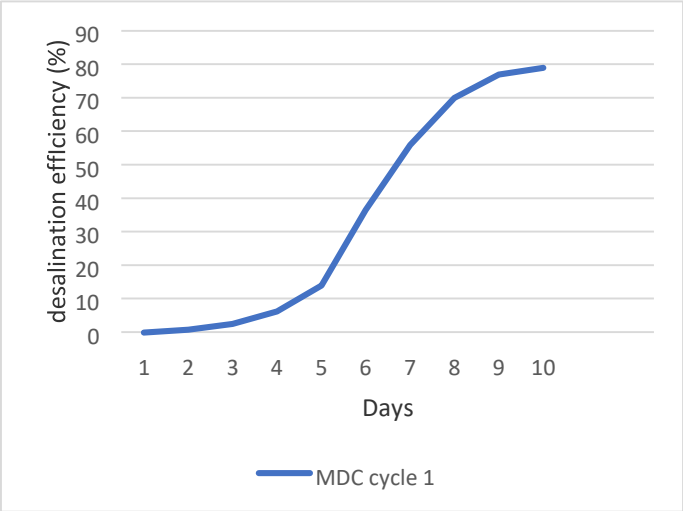

FIG. 3: *Desalination efficiency in MDC*

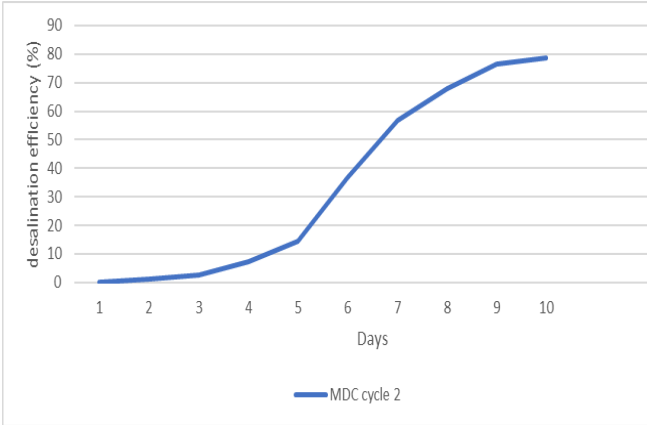

FIG. 4: *Desalination efficiency in MDC*

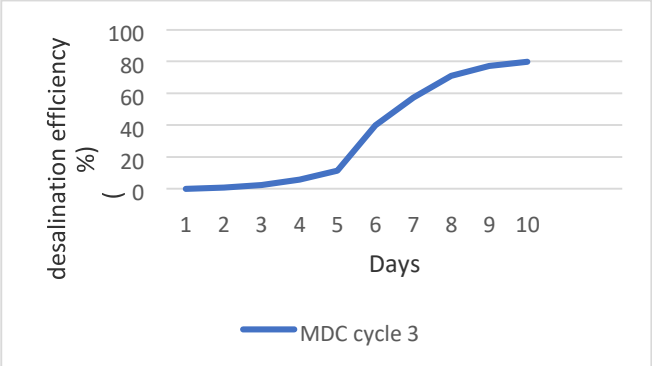

FIG. 5: *Desalination efficiency in MDC*

C. Evaluation of COD Removal and Columbic Efficiency

One of the main functions of MDC using actual sewage water is organic matter removal. Thus, the important parameter of MDC performance to evaluate the amount of COD removed in the anode chamber. The anode chamber of MDC, COD is remove by using graphite paste electrode was measured after each batch cycle. This study MDC reactor gives a better performance for COD (more than 70%). However, batch cycle time and power generation also affected the coulombic efficiency and COD. Initial COD of wastewater in the anode chamber of MDC in each cycle were 800 mg L^{-1}, 900 mgL^{-1} and 850 mgL^{-1}. MDC achieved the maximum rate of COD removal is 70 ± 7% at the all batch cycle table 1, showing that the mixture of wastewater and oxygen as the electron acceptor had the maximum benefit in COD removal. In MDC, amount of COD (68%, 65%, 70%) was removed in all cycles (fig: 6). These results suggested that biodegradation rate may increase due to the type of electron accepters in forward reactions.

Table: 1 Determine the COD efficiency.

MDC cycles	COD initial	COD final	COD removal efficiency
MDC cycle 1	800	250	68%
MDC cycle 2	900	310	65%
MDC cycle 3	850	250	70%

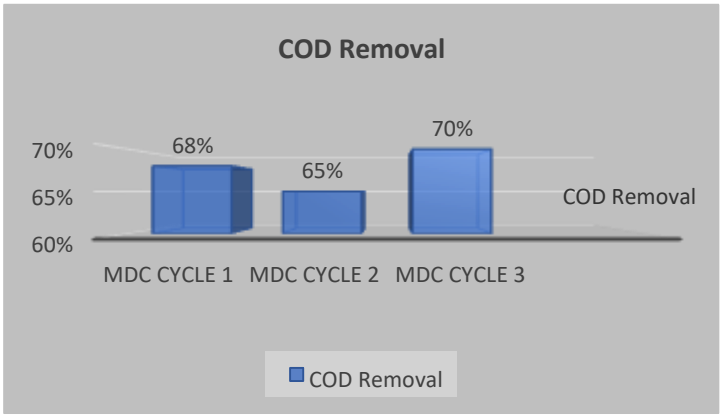

FIG. 6: *COD Removal Rate*

D. Identification of Biofilm

The layers of biofilm were identified, surface morphology was detected by using stereomicroscope. Stereomicroscope exhibited the structure and colures of microbes at different magnifications. in the results brown bacteria colonies were shown on the surface of electrode in plate 4 at 1mm 2mm, 500µm. Subsequently, the most predominant Geobacter with the abundance of 81.4%, and meanwhile, electrogenesis related outer-surface octaheme c-type cytochrome is highly expressed in the anode.

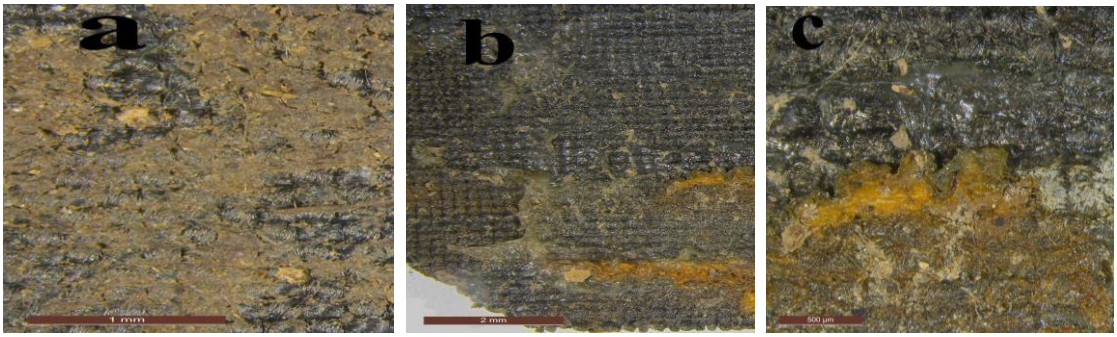

Fig. 4: Multiple images of the large samples were merged with stereomicroscope. Scale bars = 1mm, 2mm, 500µm.

IV. CONCLUSIONS

The present study demonstrates the performance of MDC by using graphite paste electrode. The obtained results show that the graphite paste based material having biocompatibility, chemical stability and high conductivity. The Conductivity of wastewater increased due to desalination and anolyte pH was stabilized, resulting in maximum output of current density, removal of COD by 68%, 65%,70% and Coulombic efficiency by 131% within each batch cycle. Graphite based material exhibited the bio-fouling on the surface at anode chamber of MDC. The integration of desalination, energy production and wastewater treatment in MDC established application possibilities of the technology in desalination and wastewater treatment industries.

V. RECOMMENDATIONS

In the future, MDC efficiency can be improved by electrode material for maximum electron transfer, so it will be helpful to maximize the desalination efficiency.

.

REFERENCES

[1]. United Nations.Water in a Changing Worlds The United Nations World Water Development Report 3, http://www. unesco. org/water/wwap/wwdr/wwdr3/,2009.

[2]. Atieh Ebrahimia,b, Ghasem D. Najafpourc,⁎, Daryoush Yousefi Kebriaa. Performance of microbial desalination cell for salt removal and energy generation using different catholyte solutions. Desalination 432 (2018) 1–9

[3]. A Carmalin Sophiaa, V.M. Bhalambaala, Eder C. Limab, M. Thirunavoukkarasua. Microbial desalination cell technology: Contribution to sustainable waste water treatment process, current status and future applications Journal of Environmental Chemical Engineering 4 (2016) 3468–3478

[4]. Abdullah Al-Mamun, Waqar Ahmad, Mahad Said Baawain, Mohammad Khadem, Bipro Ranjan Dhar (2014) Microbial desalination cell technology: A review and a case study.

[5]. Atieh Ebrahimia,b, Daryoush Yousefi Kebriab, Ghasem D. Najafpour (2018) Co-treatment of septage and municipal wastewater in a quadripartite microbial desalination cell.

[6]. Carlo Santoroa,1, Fernando Benito Abada,1, Alexey Serova, Mounika Kodalia, Kerry J. Howeb, Francesca Soavic, Plamen Atanassova, Supercapacitive microbial desalination cells: New class of power generating devices for reduction of salinity content, Applied Energy 208 (2017) 25–36

[7]. Minghua Zhoua, Meiling Chia, Jianmei Luob, Huanhuan Hea, Tao Jin a, An overview of electrde materials in microbial fuel cells. Food Research International 73 (2015) 213–225

[8]. Haiping Luo a, Pei Xu b, Timberley M. Roane c, Peter E. Jenkins d, Zhiyong Ren a,⇑, Microbial desalination cells for improved performance in wastewater treatment, electricity production, and desalination, Journal of Power Sources 196 (2011) 4427–4435

[9]. Xiao-Qiu Lin a, Zhi-Ling Li a, *, Bin Liang b, Jun Nan a, Ai-Jie Wan Identification of biofilm formation and exoelectrogenic population structure and function with graphene/polyanliline modified anode in microbial fuel cell (2019) 358e364

[10]. Simultaneous Electricity Generation and Sea Water Desalination by a Modified microbial fuel Cell, S. Rishi kumar and M. Praveen (NCSET – 2016).

[11]. Sabina Kalleary a, Fayidh Mohammed Abbas a,c, Archana Ganesan a,Sivarajan Meenatchisundaram b, Babuskin Srinivasan a,Azhagu Saravana Babu Packirisamy a, Radha krishnan Kesavan a, Sukumar Muthusamy a,*(2014) Biodegradation and bioelectricity generation by Microbial Cell.

[12]. Xiao-Qiu Lin a, Zhi-Ling Li a, *, Bin Liang b, Jun Nan a, Ai-Jie Wan Identification of biofilm formation and exoelectrogenic population structure and

[13]. Zhang, Y., Mo, G., Li, X., Zhang, W., Zhang, J., Ye, J., Huang, X., Yu, C.: A graphene modified anode to improve the performance of microbial fuel cells. J. Power Sources 196(13), 5402 (2011).