Pharmaceutical Wastewater Treatment Associated with Renewable Energy Generation in Microbial Fuel Cell Based on Mobilized Electroactive Biofilm on Zeolite Bearer

Dr. Zainab Ziad Ismail
Assistant Professor
Department of Environmental Engineering
College of Engineering- University of Baghdad
E.mail:zismail9@gmail.com

Ali Awaid Habeeb
Researcher
Department of Environmental Engineering
College of Engineering- University of Baghdad
E.mail:envalihabeeb@gmail.com

ABSTRACT

In this study, a novel application of lab-scale dual chambered air-cathode microbial fuel cell (MFC) has been developed for simultaneous bio-treatment of real pharmaceutical wastewater and renewable electricity generation. The microbial fuel cell (MFC) was provided with zeolite-packed anodic compartment and a cation exchange membrane (CEM) to separate the anode and cathode. The performance of the proposed MFC was evaluated in terms of COD removal and power generation based on the activity of the bacterial consortium in the biofilm mobilized on zeolite bearer. The MFC was fueled with real pharmaceutical wastewater having an initial COD concentration equal to 800 mg/L and inoculated with anaerobic aged sludge. Results demonstrated that the COD removal efficiency, power density and current density were 66%, 2.4 mW/m^2 and 10 mA/m^2, respectively.

Key words: microbial fuel cell, pharmaceutical wastewater, zeolite bearer, energy production.

معالجة المطروحات السائلة للصناعة الدوائية مقترنة بتوليد الطاقة الكهربائية المستدامة بأستخدام خلية الوقود الاحيائية المجهزة بحبيبات الزيولايت كحامل بايولوجي في حجرة الانود

د. زينب زياد اسماعيل
استاذ مساعد
قسم الهندسة البيئية- كلية الهندسة-جامعة بغداد
E.mail:zismail9@gmail.com

علي عويد حبيب
باحث
قسمالهندسةالبيئية- كليةالهندسة-جامعةبغداد
E.mail:envalihabeeb@gmail.com

الخلاصة

في هذه الدراسة, تم تطوير منظومة مختبرية مبتكرة لخلية الوقود الاحيائية ثنائية الحجرات لمعالجة المطروحات السائلة للصناعة الدوائية بطريقة بايولوجية وانتاج الطاقة الكهربائية المتجددة في أن واحد. جهزت حجرة الانود لخلية الوقود الاحيائية بحبيبات الزيولايت وغشاء ايوني يسمح بمرور البروتونات من حجرة الانود الى حجرة الكاثود. تم تقييم اداء خلية الوقود الاحيائية على اساس كفاءة ازالة المحتوى الكيمياوي للاوكسجين وانتاج الطاقة الكهربائية نتيجة نشاط الكتلة البايولوجية(حمأة لا هوائية) التي تم تنميتها باستخدام حبيبات الزيولايت كحامل بايولوجي. تم ضخ مياه المخلفات السائلة الحقيقية للصناعة الدوائية

ذات محتوى كيمياوي للاوكسجين بمقدار 800 مليغرام/لتر. أظهرت النتائج المختبرية بأن مستوى ازالة محتوى الاوكسجين الكيمياوي و كثافة القدرة وكثافة التيار كانت 66%,2.4 ملي واط/م^2 و10 ملي امبير/م^2 على التوالي.

الكلمات الرئيسية:خلية الوقود الاحيائية، مطروحات السائلة للصناعة الدوائية، حبيبات الزيولايت، توليد الكهرباء

1.INTRODUCTION

The insufficient availability of oil and natural gas could be augmented by other fuels such as coal and oil shale. However, if obtainable energy from these sources using conventional technologies, it will release additional carbon dioxide, exacerbate environmental damage and accelerate global climate change. A whole new technology platform must be developed that produces clean energy, while at the same time reduces carbon dioxide emissions with a goal to meet 2050 energy needs on carbon neutral basis, **Lewis and Nocera, 2006.** Industrial processes generate a wide variety of wastewater pollutants. The characteristics and levels of pollutants vary significantly from industry to another. Pharmaceutical wastewater are characterized by high chemical oxygen demand (COD), containing a variety of organic and inorganic constituents, the most important are the priority pollutant and low biodegradable compounds or being inhibitory to conventional biological treatment systems, **Benitez et al, 1995. ,Davis and Cornwell, 2008.** Microbial fuel cell (MFC) technologies represent the newest approach for electricity generation from biomass using bacteria, which became of more interest and work on MFCs began to increase, **Allen and Bennetto, 1993.** Microbial fuel cell(MFC) is a type of fuel cell which converts the chemical energy contained in organic matter to electricity using microorganisms as a biocatalyst. In MFC, bacteria do not transfer their electron directly to their terminal electron acceptor, but, rather to a solid electrode and offers the possibility of directly harvesting electricity from organic waste and renewable biomass, **Rabaey and Verstraete, 2005. ,Lovley, 2006.** The basic components of MFCs are the anode, cathode compartments and cation exchange membrane (CEM). The electrochemically active bacteria in the anode compartment oxide the substrate and separate the electrons from protons. These electrons and protons transfer to the cathode, the electrons move through the external circuit and the protons diffuse through the anolyte and the cation exchange membrane (CEM), subsequently they combine at the cathode with oxygen to form water molecules, **Kim et al., 2008.**

Angelov et al.,2013 constructed a dual chambered laboratory scale microbial fuel cell (MFC) based on natural sulfate reducing bacterial consortium in electroactive biofilm on zeolite. The COD removal efficiency and power generation were 23% and 0.68 mW/m^2, respectively. The proposed design can be used for simultaneous sulfate purification of mining drainage wastewater and generation of renewable energy. **Karra et al., 2013** investigated the use of activated carbon Nano-fiber (ACNF) as anode material to enhance biofilm growth and improve MFC performance. Results showed that MFCs with ACNF and granular activated carbon (GAC) as an anode achieved power densities of 3.5±0.46 W/m^3 and 3.09±0.33 W/m^3, respectively. In addition, MFCs with ACNF achieved higher contaminant removal efficiency 85±4% than those with GAC of 75±5%, respectively. **Zhang et al., 2014** examined the effectiveness of refinery wastewater treatment using air cathode microbial fuel cell (MFC). It was configured with separator electrode assembly (SEA) or spaced electrodes (SPA). The MFC with SEA configuration produced a higher maximum power density 280±6 mW/m^2 than the SPA arrangement 255±2 mW/m^2 due to lower internal resistance. Both configurations produced lower power than domestic wastewater indicating poor bio-degradability of refinery wastewater.

The present study aimed to investigate the performance of a continuously operated two chambered air cathode microbial fuel cell (MFC) fueled with actual pharmaceutical wastewater and inoculated with anaerobic aged sludge mobilized on zeolite biofilm bearer for simultaneous wastewater treatment and power generation.

2. MATERIALS AND METHODS

2.1 MFC System

The experimental setup for the microbial fuel cell (MFC) system is presented in **Fig.1.** Microbial fuel cell (MFC) was fabricated of Perspex material with two different sized chambers. Dimensions of anode and cathode chambers were 20 cm*20 cm*26 cm and 10 cm*10 cm* 15 cm, respectively. The cathode chamber was fully submerged in the anode chamber with two opposite sides containing two pieces of cation exchange membrane (CEM) which was sandwiched between two perforated Perspex sheets with a net membrane area of 44 cm^2. The anode compartment contains three ports, one at the top for treated effluent outlet, two ports at the bottom, one for pharmaceutical wastewater inlet and the other for nitrogen flushing. The cathode compartment contains two ports, one for catholyte inlet and the other for air sparging. Two uncoated graphite rods were used as electrodes for each chamber. The graphite rods diameter was 1.8 cm and an effective length of 15 cm resulted in a surface area of 87.5 cm^2 for each electrode. Before the installation of electrodes in the MFC, graphite rods were abraded by sand paper to enhance bacterial attachment, they were soaked in deionized water for a period of 24 h. The electrodes in each chamber were pierced with copper wire extended outside the MFC to simply connected to an external circuit through which electrons were transported. Approximately, 60% of the volume of anode compartment was occupied with zeolite particles as a biofilm bearer and the remaining 40% was considered as a head space. Cylindrical shaped zeolite particles of 1.6 mm diameter and different lengths averaged 2-4 mm were used. The chemical composition of zeolite was as follows:39.5% SiO_2, 22.8% Al_2O_3, 1.65% Na_2O and 1.4% K_2O with a porosity of 57.5%.

2.2 Substrate, Inoculum and Chemicals

Actual pharmaceutical wastewater samples were collected from the inlet pipe of the aeration tank in the biological treatment unit of the State Company for Drug Industry, Samarra(SDI, Samarra). The characteristics of the actual pharmaceutical wastewater are given in **Table. 1** The MFC was inoculated with anaerobic aged sludge which was used as a biocatalyst in the anodic compartment of MFC.

To enrich microbial growth in MFC, mineral salts medium(MSM) was prepared according to the procedure outlined by **Ghangrekar et al., 2005.** The MSM solution was prepared by dissolving 0.56 g/L $(NH_4)_2SO_4$, 0.20 g/L $MgSO_4.7H_2O$, 15 mg/L $CaCl_2$, 1mg/L $FeCl_3.6H_2O$, 20 mg/L $MnSO_4.H_2O$ and 0.42 g/L $NaHCO_3$ in deionized water, then the solution was autoclaved at 121 ^oC for a period of 20 min and cooled under oxygen-free space using nitrogen gas flushing.

The catholyte solution was used as an oxidant at the cathode compartment of MFC. The catholyte was a phosphate buffer solution (PBS) composed of 32.93g/L $K_3Fe(CN)_6$, 20.75 g/L Na_2HPO_4 and 3.1167 g/L NaH_2PO_4.

2.3 Set Up of MFC

Before the construction and set up of MFC, the system components were cleaned well with an appropriate detergent, then repeatedly rinsed with tap water and deionized water. Cation

exchange membrane (CEM) was subjected to a course of preconditioning by immersing in 5% sodium chloride solution for 24 h to allow for membrane hydration and expansion, and then washed with deionized water.

2.4 Operation of MFC

To start up and operate the MFC, anaerobic aged sludge was placed in the anode chamber and was sparged with nitrogen gas for a period of 10 min to maintain anaerobic environment. After 10 days, the MFC was fed with a primarily treated actual pharmaceutical wastewater at a constant rate of 3 ml/min corresponding to a hydraulic retention time (HRT) of 32 h. An air compressor with a maximum flowrate of 10 ml/min was connected to the cathode chamber to supply oxygen in a continuous manner. Oxygen concentration was monitored continuously in the anodic chamber, the absence of oxygen was observed. This means that the anodic compartment can be considered as anoxic environment. Also, pH of the solution in the MFCwas monitored continuously and adjusted to 7-7.2 using buffer solution. MFC system was operated at a temperature range of 28-30 ^{o}C.

2.5 Analytical Techniques and Calculations

2.5.1 Wastewater and treated effluent analysis

Chemical oxygen demand (COD), dissolved oxygen (DO), pH and TDS tests were conducted by the researcher on a daily basis. Other tests such as nitrate, sulphate, chloride and phosphate were carried out weekly according to the procedure outlined in the standard methods, **,APHA, 2005.** Instruments and measuring devices used in this study were; COD reactor (model: RD 125, Lovibond, Germany), COD photometer (model: multi direct, Lovibond, Germany), dissolved oxygen meter (model: senso direct oxi 200, Lovibond, Germany), pH meter (model: portable HI-83141, HANNA, Romania), electrical conductivity meter (model: portable HI-99300, HANNA, Romania), voltage data logger (model: Lascar EL-USB-3, USA), multimeter (model: 175 TRUE RMS, FLUKE, USA), variable peristaltic pump (model: 77200-62 Cole-Parmer, USA), air pump (model Rs-610 China), and resistance box (100-10000 Ohm).

2.5.2 Power density

Power density is the product of voltage and current per unit of anode surface area, **Liu et al, 2005.**

$$P = \frac{V_{Cell*I}}{A_{An}} = \frac{(V_{Cell})^2}{R_{ext*}A_{An}} \quad (1)$$

$$I = \frac{V_{Cell}}{R_{ext}} \quad (2)$$

Where:P= power density (W/m^2), V_{Cell}=cell voltage(Volt), I=current (Amp), R_{ext}=external resistance and A_{An}=Anode surface area(m^2).

2.5.3 Polarization curve

The polarization was used to characterize the current as a function of voltage by changing external resistance (load), a new voltage and current values can be obtained.

3. RESULTS AND DISCUSSION

3.1 COD Removal Efficiency

The profile of COD removal for actual pharmaceutical wastewater is given in **Fig. 2.** The COD removal efficiency was observed for 45 days. A relatively steady state condition was achieved after 20 days. Maximum COD removal efficiency was observed to be 66% with an average of 44%. The organic loading rate was 0.563 kg/m^3/d. Fluctuation in COD removal efficiencies were attributed to the variation of inlet COD in the real wastewater from the source most likely due to unstable operational conditions at the pharmaceutical manufacturing plant. Results of COD removal efficiency for MFC were 3 times higher than COD removal efficiency of 23% which was previously reported by **Angelov et al., 2013,** for a microbial fuel cell inoculated with sulfate reducing bacteria mobilized on Zeolite bed**.**

3.2 Current Generation

MFC exhibited zero current generation during the first 13 days because the biomass requires an acclimation period, especially to this type of wastewater which can be characterized with recalcitrant nature associated with toxic chemicals and low biodegradability. Rapid increased for the following 4 days up to 172 mA/m^2 maintained for a period of 10 days. However, a notable decline in the generated current was observed upto 32 days of continuous operation, generated current stabilized at 30 mA/m^2 until the end of operation as given in **Fig. 3.** The open circuit voltage drop was 0.46 Volt across an external resistance of 100 Ω as shown in **Fig. 4.**

3.3 Polarization Curve

It summarized the behavior of microbial fuel cell at various external resistances ranged from 50-3000 Ω as depicted in **Fig. 5**. Maximum power and current densities were 2.4 mW/m^2 and 10mA/m^2, respectively obtained at external resistance of 1400 Ω. However, these results were potentially favorable compared to current densities observed at a range of 0.008-0.3 mA/m^2 as previously reported by **Niessen et al.,** and **,Liu et al., 2009,** for MFCs operated with starch, and glucose as substrates, respectively.

4.CONCLUSIONS

This study evaluated the performance of an upflow dual chambered microbial fuel cell for simultaneous pharmaceutical wastewater treatment and power generation. Significant relationship between COD removal and power generation was obtained. Higher COD removal efficiency up to 66% and current density 172 mA/m^2were obtained. A drop in voltage can be attributed to the increase of TDS concentration as a result of zeolite existence and expected release of ions such as sodium ions which inhibit and hinder biofilm growth because strong electrolyte alters the osmotic pressure of bacterial cell membrane. It is recommended to regenerate the zeolite bed to decrease TDS concentration of anolyte resulting in a better microbial biofilm growth.

REFERENCES

- Allen, R. M. and Bennetto, H.P., 1993, *Microbial Fuel Cells: Electricity Production From Carbohydrates*. Applied Biochemical Biotechnology. 39, 27-40.
- Angelov, A. Bratkova, S. and Loukanov, A.,2013, *Microbial Fuel Cell Based on Electroactive Sulfate-Reducing Biofilm.* Energy Conversion and Management. 67, 283-286.
- APHA ,2005, *Standard Methods for Examination of Water and Wastewater*. American Public Health Association. 20th ed. Washington, DC
- Benitez, J., Rodriguez, A. and Malaver, R. ,1995, *Stabilization and New Dewatering of Wastewater Using Hollow Fiber Membrane. Water* Science Technology. *29*: 2281-2286
- Davis, M.L. and Cornwell, D.A. ,2008, *Introduction To Environmental Engineering*, 4thed, McGraw Hill Inc.
- Ghangrekar, M. M., Joshi, SG. and Asolekar, S. R., 2005, *Characteristics of Sludge Developed Under Different Loading Condition During UASB Reactor Start-Up*. Water Research. 39, 1123-1133.
- Karra, U., Manikam, S. S., Jeffrey, R. M., Patel, N. and Li, B., 2013, *Power Generation and Organics Removal from Wastewater Using Activated Carbon Nanofilter (ACNF) microbial fuel cell.International* Journal of Hydrogen Energy. 38, 1588-1597.
- Kim, I.C., Jung, Y.C., Choi, M.J. and Verstraete, W., 2008, *Microbial Fuel Cell: Recent Advances, Bacterial Communities and Application Beyond Electricity Generation.* Environmental Engineering Research. 13, 51-65.
- Lewis, N. S. and Nocera, D.G.,2006, *Powering the Planet: Chemical Challenges in Solar Energy Utilization.* PNAS 10343,15729-15735.
- Liu, Z., Liu, J., Zhang, S. and Su, Z., 2009, *Study of Operational Performance and Electrical Response on Mediator-Less Microbial Fuel Cells Fed with Carbon and Protein-Rich Substrate.* Biochemical Engineering Journal. 45, 185-191.

- Lovley, D. R., 2006, *Harvesting Electricity with Microorganisms*, National Research of Microbiology, 4,497-508.
- Niessen, J., Schroder, U. and Scholz, F., 2004, *Exploiting Complex Carbohydrates for Microbial Electricity Generation, Bacterial Fuel Cell Operating on Starch,* Electrochemical Community. 6, 955-958.
- Rabaey, K. and Verstraete, W., 2005, Microbial Fuel Cells: *Novel Biotechnology for Energy Generation.* Trends of Biotechnology. 23, 291-298.
- Zhang, F., Ahn, Y. and Logan, B. E.,2014, *Treating Refinery Wastewaters in Microbial Fuel Cells Using Separator Electrode Assembly or Spaced Electrode Configurations.* Bioresources Technology. 152, 46-52.

Table.1 Characteristics of actual pharmaceutical wastewater.

Constituent	Average value	Units
Biological oxygen demand (BOD_5)	40	mg/L
Chemical oxygen demand (COD)	810	mg/L
Total suspended solids (TSS)	118	mg/L
Total dissolved solids (TDS)	355	mg/L
pH	7.27	------
Chlorides (Cl^-)	10	mg/L
Sulphate(SO_4^{-2})	138	mg/L
Nitrate (NO_3^-)	7.23	mg/L
Phosphate (PO_4^{-3})	2.13	mg/L
Zinc	Nil	mg/L
Chromium	0.05	mg/L
Copper	0.37	mg/L

Figure. 1. Microbial fuel cell system.

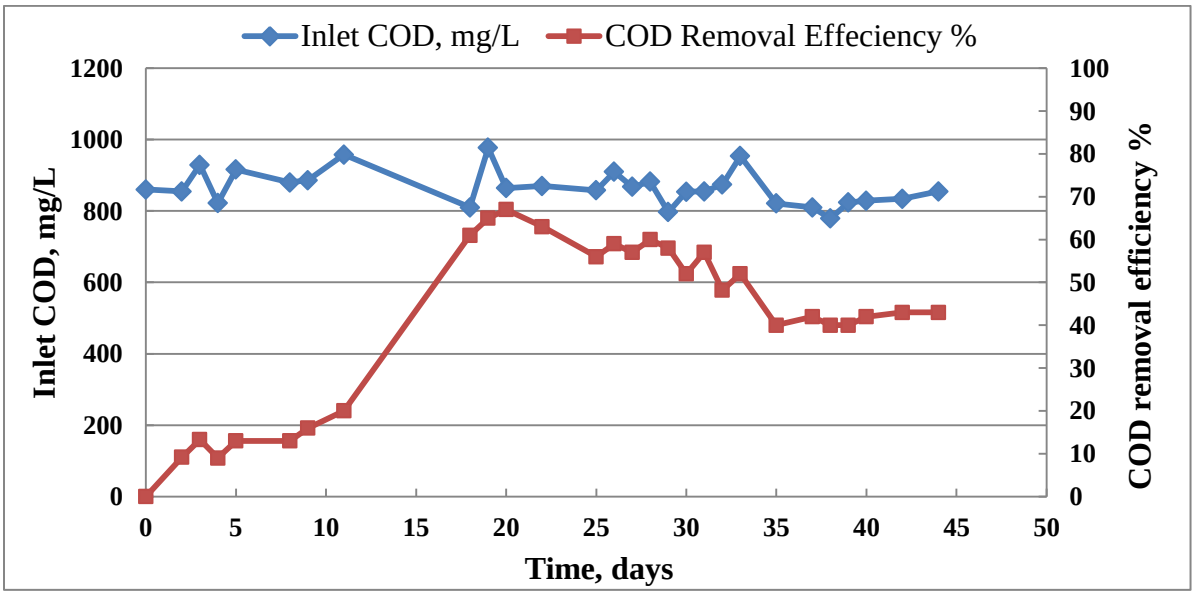

Figure 2. Profile of COD removal.

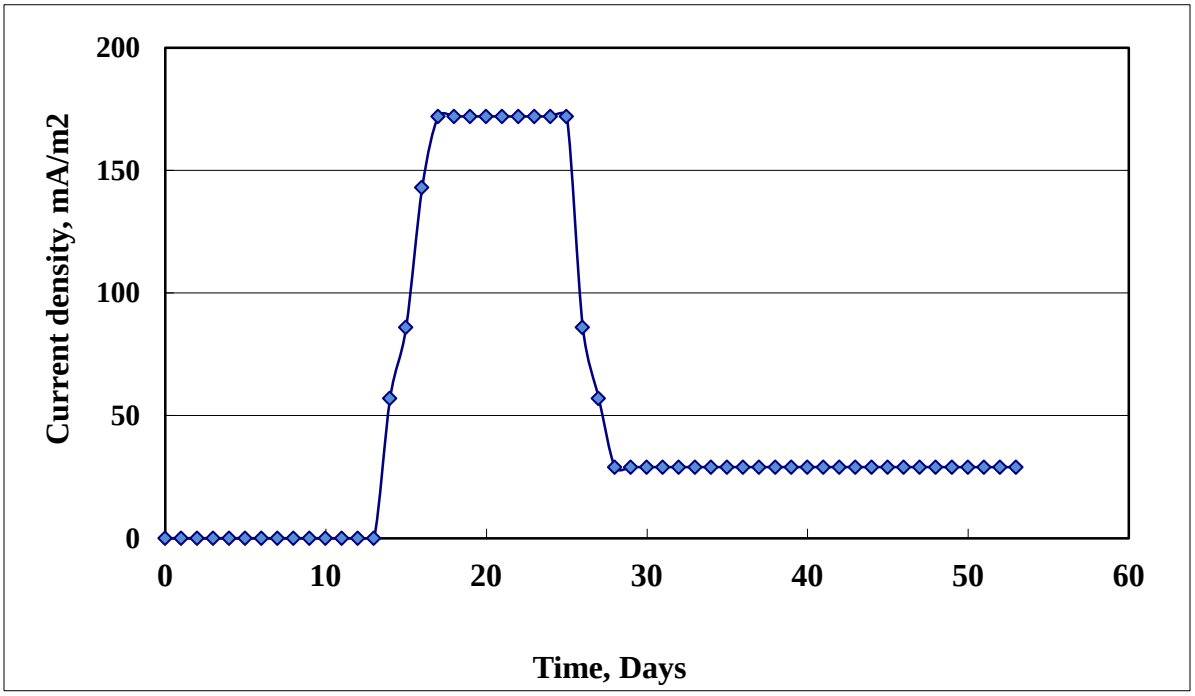

Figure 3. Profile **o**f **c**urrent generation.

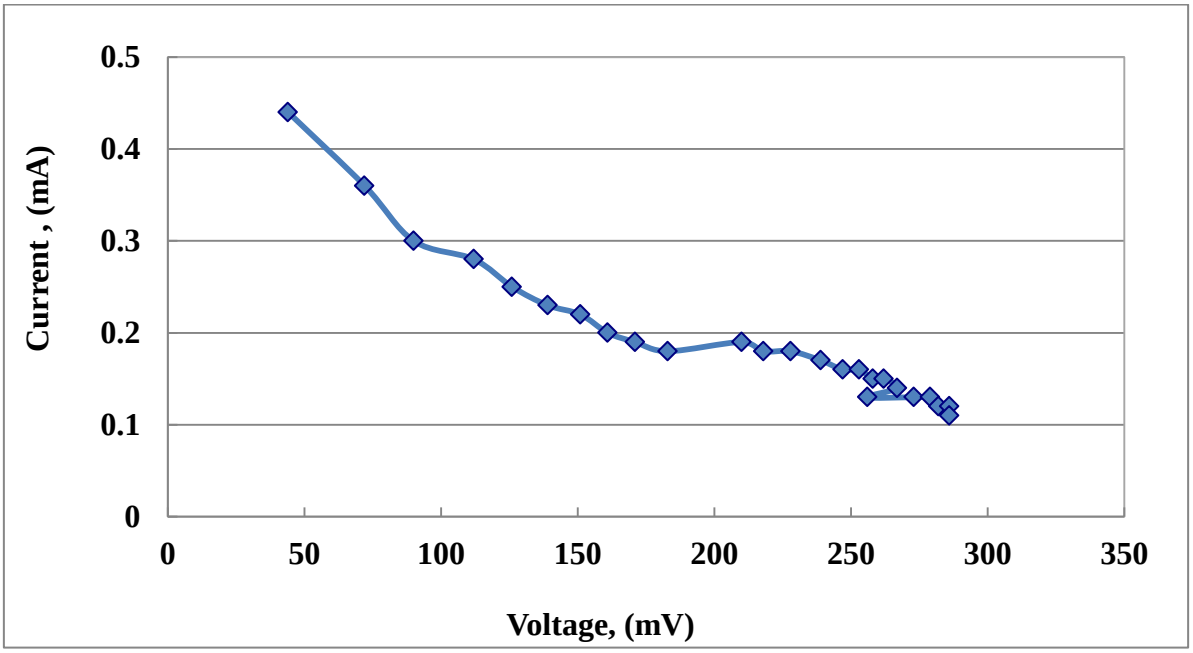

Figure 4. Current-voltage relationship at different resistances.

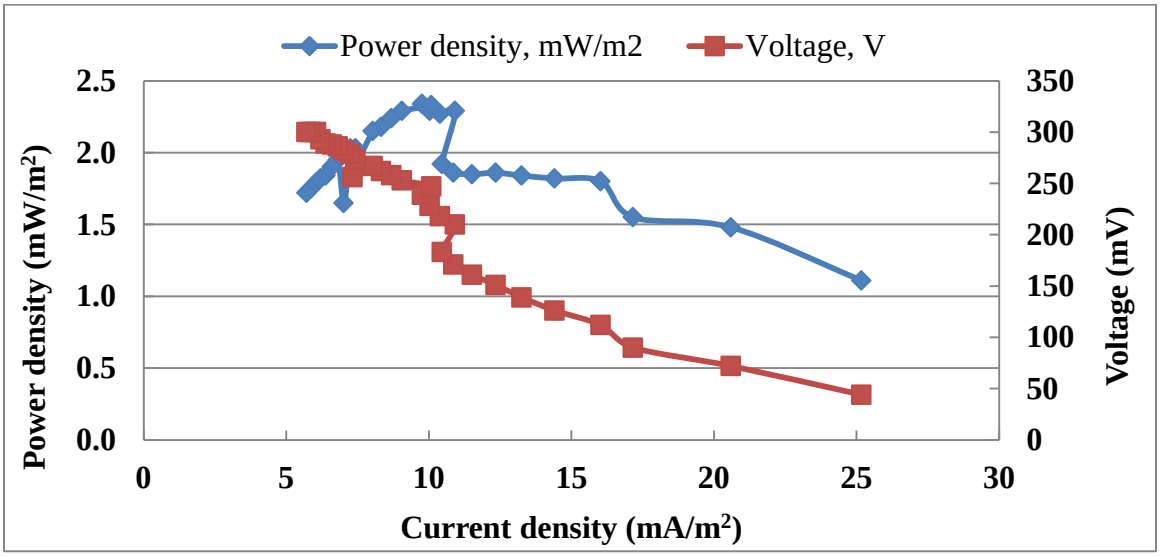

Figure 5. Profile **o**f polarization curve.