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Application of Nano-Electrode Platinum (Pt) and Nano-Wire Titanium (Ti) for Increasing Electrical Energy Generation in Microbial Fuel Cells of Synthetic Wastewater with Carbon Source (Acetate)

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ABSTRACT: The microbial fuel cells (MFCs) are a kind of systems through which the anaerobic bacteria along with the oxidation of simple or complicated organic matter in the wastewater can generate the electric power. This is a modern approach used in generation of the clean and renewable energy. In this research, two pilot laboratories of double-chamber microbial fuel cells were made. One of them contained platinum electrode and simple nano-wire Titanium and the other had nano-electrode Platinum and nano-wire with equal volume of 1 liter. They were launched in 4 Hydraulic Retention Time (2.5, 3.5, 4.5 and 5.5 hrs.) and increased in 4 steps of organic loading rate with synthetic wastewater with carbon source (acetate) and temperature (20±5°C). The voltage and electric current was measured by means of digital multimetre. The performance of the two reactors in generation of electricity was investigated based on the polarization curve. Maximum voltage and current output were, respectively, 1425 mV and 13.1 mA, and the maximum power density and current density were, respectively 78 mW/m^2 and 67.3 mA/m^2 and columbic efficiency were achieved in 34.6% in reactor with nano-electrode Platinum and nano-wire Titanium (in HRT 4.5 hr and external resistance was 100Ω). In addition, the maximum removal rate of COD in organic loading rate 3.99 Kg COD/m^3.day is equal to 98.28% for nano-electric and nano-wire and 72.5% for simple electrode and wire.

Key words: Columbic Efficiency, Microbial fuel cell, Nano-Electrode Platinum, Nano-Wire Titanium, Synthetic Wastewater

INTRODUCTION

Given the increasing need for the energy in economic, industrial and scientific issues, the mankind has constantly been seeking to have access to a boundless and renewable energy source. The extensive and huge consumption of the fossil fuels, though it leads to the economic growth and advanced industrial countries, it causes the increase of CO_2, severe degradation of the environment, global change, increase of sea level and harms the human health (Logan *et al.,* 2008). The generation of the clean energy by means of renewable matter like biomass, on one hand, is conducive to the production of energy and, on the other hand, reduces the global emission of CO_2 (Giddey *et al.,* 2012). The renewable energies are actually in harmony with the environment and are not polluting substances (Rahimnejad *et al.,* 2011).

Biomass is the fourth biggest source of energy in the world and it provides 15% of the global energy consumption. The microbial fuel cell technology is the state of the art method for generation of bio electricity, which is produced from biomass containing bacteria (Qing *et al.,* 2009). The production of the first electric current with anaerobic bacteria was investigated by Potter in 1911. The microbial fuel cell is a bio electro chemical that produces electric current with the aid of cloning and bacterial reaction in the nature (Logan, 2008). The microbial fuel cell has special benefits such as high efficiency and application in conducive conditions (temperature, environment pressure, neutral pH). Additionally, the MFCs may change a wide variety of organic matter to electric energy (Junqiue *et al.,* 2010). These organic combinations are consisted of simple Carbohydrates as Glucose (Chaudhuri & Lovely, 2003), Acetate and

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butyrate (Liu *et al.,* 2005), and Complex organic compounds for example domestic wastewater (Sunil *et al.,* 2009), (Qing *et al.,* 2009) livestock wastewater (Booki *et al.,* 2011), Chocolate Industry Wastewater, Beer wastewater (Logan *et al.,* 2008), (Youngho & Logan, 2010). The microbial fuel cell technology is a totally different way for treating wastewater. It may be used as a treatment process to produce electricity and hydrogen gas (Nigel, S., 2007). The researchers have recently sought to increase the electric current by means of different methods in microbial fuel cell. These methods includes use of different microorganism variety, change in substrate, change in the shape of the reactor, use of the successive reactors for increase of voltage, change in the membrane exchange proton (Logan *et al.,* 2008) and use of the anode and cathode electrodes with different material. In this research, the effect of platinum electrode with nano-structure as anode electrode and wire Titanium (transmission of the electron) nano structure was investigated on the increase of the generated electricity in the reactors of the microbial fuel cell. In the microbial fuel cell, the micro- organisms oxidizes the organic matter in the wastewater and produces electrons; these electrons passes through a number of breathing enzymes existing in the cells and produces energy for the cells in the form of ATP. Then, the electrons are released to the Terminal Electron Acceptors (TEA). The TEA absorbs the electrons and it is reduced. For example, the oxygen during the catalytic reaction may change with electrons and protons into water. The microbial fuel cells have a cathode chamber and anode chamber, which has been separated from special membrane. The existence of the oxygen in another chamber will restricts the generation of the electricity. Therefore, the system should be designed in a manner in which the bacteria are kept away from oxygen. In fact, the membrane of the Du Pont Corp Nafion-117 is porous in contrast to the protons produced in the anode chamber (Logan, 2008). Both chambers of the anode and cathode are linked by wire together. The bacteria grow in the anode chamber and oxidize the organic matter to produce the proton and electron. The electrons produced enter through external orbit and the protons enter through the membranes and reaches to the cathode. The protons in the cathode chamber along with the electrons transmitted by wire combine with oxygen to produce water. In cathode, the injected air provides dissolved oxygen for reaction (Logan, 2008), (Youngho & Logan, 2010). The figure (1) shows the schematic image and how the microbial fuel cells function.

MATERIAL & METHODS

In the research, two pilot laboratory of the microbial fuel cell were used. In the first reactor were used the simple electrode platinum and simple wire Titanium and second reactor nano-electrode platinum and nano wire Titanium in the anode chambers, and The impacts of electrodes and wires with nano-scale was investigated to increase absorbed electrons released from biochemical reactions resulting from performance bacterial and treatment of synthetic wastewater with carbon source (Acetate) in the anode chamber. Two reactors laboratory of microbial fuel cells with same volume 1000 liter, that each reactor was formed of 2

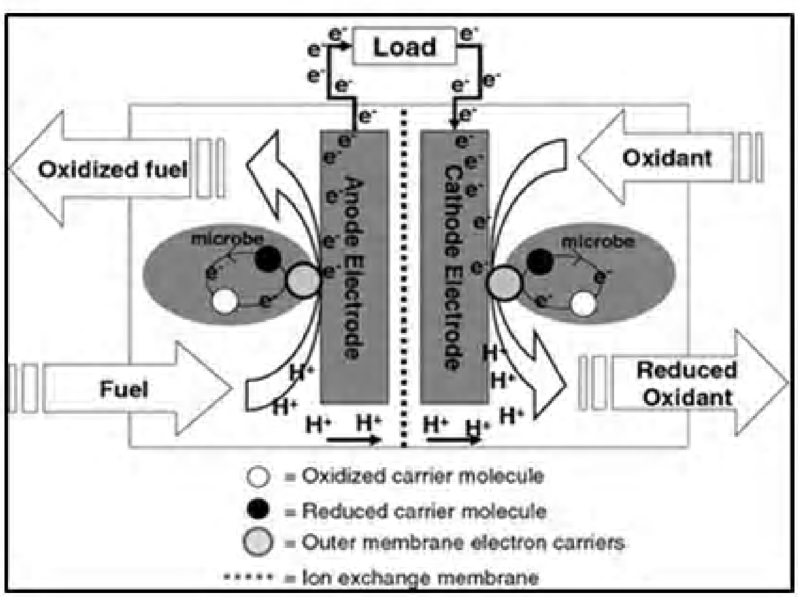

Fig.1. Schematic image of microbial fuel cells

chambers, anode chamber and cathode chamber. Dimensions of each chamber is (10×10×5cm), that chambers are separated with proton exchange membrane (PEM). Membrane used in most research is Nafion 117 that the thickness of this membrane is Equal to 0.019 cm. The reactors were made of Plexiglas and the two chambers of anode and cathode will be connected with empty space for fitting a membrane to each other. Anode chamber consists of raw wastewater inlet near to bed and wastewater outlet on the reactor. Cathode chamber consists of air inlet over the bed and catholyte solution inlet and gas outlet on the chamber. Air was injected to the cathode chamber by the diffuser via nozzle to supply continuous source of oxygen for effective reduction reaction. Electrode which was in anode chamber shall have great effective area for attachment of bacteria and transition of electron is more possible. In this case nano electrode platinum with low internal resistance was used. Material of electrode in cathode chamber shall have grate effective area to occur reduction reaction, so electrode graphite was used. In the first reactor simple electrode platinum was suspended by simple Titanium wire. In the second reactor nano electrode platinum was suspended by nanowire Titanium. Electrode graphite in the cathode chambers was suspended by cupper wire. Also for approaching required temperature for anaerobic bacteria (20±5°C), establishing equal condition and complete mix of synthetic wastewater whit microorganism inside anode chamber magnet and heater plate were used.

Synthetic wastewater was injected to the anode chamber inlet by peristaltic pump and the wastewater was distributed equally on the bed of the chamber. After the treatment by biological layer inside anode chamber the wastewater exited through outlet chamber via up flow. Technical specification of reactors is shown in Table (1).

In this research two microbial fuel cell each consists of two chambers (model H) made of Plexiglas has been used. Reactors consist of two anode and cathode chamber with capacity of 1 lit which are separated by proton exchange membrane (Nafion 117). In order of increasing the membrane porosity, the membrane has been placed in the deionized water, (0.5 M) Sulfuric acid solution and (30%) Hydrogen peroxide solution for one hour in (80°C) before using the membrane. Two electrodes made of carbon Graphite with dimension (2.1×4×0.4 cm) has been placed in each cathode chamber in each reactor and was connected to the copper wire of (8cm) length at its end. Electrodes have been placed in deionized water for 24 hours prior to use. Two electrodes one made of simple structure of platinum and the other one made of covered with nano

Table 1. Technical specification of bioreactors (MFCs)

Parameter	specification
material	Plexiglas
Anode chamber	500 ml
Cathode chamber	500 ml
Material of anode electrode	Nano-structure Platinum and simple structure Platinum
Material of cathode electrode	Graphite electrode
Material of connector wire	Nano wire of Titanium and simple wire Titanium
Direction of flow	Up flow
Thickness of walls	5 mm
Proton exchange membrane	Nafion 117

particle platinum based on Carbon Nano Tubes (CNTs) with density (0.06 gr/cm^2) the same dimension as Graphite electrode have been placed inside anode chambers. The platinum nano electrode was connected to the wire covered with nano particle Titanium at 8cm length with density (0.06gr/cm^2) and also Simple electrode platinum to the simple Titanium wire, at their ends.

Considering degradation and fermentation of organic matters steps in wastewater by anaerobic bacteria, synthetic wastewater with carbon source (acetate) has been selected for substrate that inlet organic loading rate into the reactors occur in 4 steps according to ascending increase, removal efficiency and electrical generation. Other materials have been added as required nutrients for bacterial cells to grow and reproduce besides metabolic activities. The used nutrients are shown in Table (2) (Logan *et al.,* 2008). Anaerobic microorganisms have been used from anaerobic digester chamber of Omid-e-Sabz district wastewater treatment plant for this research.

Table 2. Material and Required Nutrients for Microorganisms

Nutrient	g/l
K_2HPO_4	0.87
NH_4Cl	0.28
$MgSO_4.7\ H_2O$	0.1
$CaCl_2.\ 2H_2O$	0.1
NaCl	0.58
KCl	0.74
KH_2PO_4	0.68
Vitamin	1ml/l

They were injected per appropriate scale to the anode chamber to prepare anaerobic condition in the reactor.

The cathode chamber reactor was filled with phosphate buffer solution ($KH_2PO_4.H_2O$, $K_2HPO_4.H_2O$) as a catholyte. This chamber was aerated continuously via air flow supplied by aquarium air diffuser (S18-A-3). The outlet flow of diffuser was adjusted to maintain the dissolved oxygen between 3mg/L to 4mg/L inside the cathode chamber. The anode chambers of both reactors were operated by anaerobic bacteria from anaerobic digester chamber of Omid-e-Sabz district wastewater treatment plant. The synthetic wastewater with carbon source (Acetate) as an organic matter was injected to the reactors continuously by a Peristaltic Pump (DLS model) with 4 different flows (2.2 l/day, 2.6 l/day, 3.4 l/day and 4.8 l/day) and with different hydraulic retention times.

As anaerobic bacteria had effective role in degradation of acetate the wastewater PH was maintained to 6 to keep acidophilic bacteria alive. Initially the reactors were operated with synthetic wastewater (acetate) with COD concentration of 350 mg/L and this condition was continued for one week to adapt the bacteria in the synthetic wastewater. After that in every cycle of increasing organic matter load three times of reactor operating time was given to bacteria to adapt. For analyzing and comparison of nano particle influence on power increase of electron transition from platinum electrode surface covered with platinum nano particles and Titanium nano wire the amount of voltage output and removal of organic matter in the two reactors have been considered as function evaluation indexes. Free current voltage (Volt), Current (Ampere I) have been measured by digital multi-meter in four organic loading steps and in four hydraulic retention times and different external resistance. The output power (mW) has been obtained from equation (1). The power density mW/m^2 has been obtained dividing power into anode area (equation 2). The current density mA/m2 has been obtained dividing the current into anode area (equation 3).

$P = V^2/R$ (Equation 1)
Power Density = P/A (Equation 2)
Current Density = I/A (Equation 3)

Columbic efficiency has been defined as ration (percentage) of gained electrons from current to total electric load existing in the substrate that is measurable. COD and PH of treated wastewater from anode chamber outlet in starting and finishing of each step was analyzed per standard method and the results was analyzed and evaluated based on descriptive statistics (APHA *et al.,* 1992).

RESULTS & DISCUSSION

According to results the maximum produced voltage in microbial fuel cell reactor with nano electrode platinum and nano wired Titanium in COD concentration of (750mg/l), organic loading rate of (3.99 Kg COD/m³.day) and hydraulic retention time of 4.5 hour was obtained 1425 mV and in microbial fuel cell reactor with simple electrode platinum and simple wire Titanium in COD concentration of (750mg/l) organic loading rate of (3.27 Kg COD/m³.day) and hydraulic retention time of 5.5 hour was obtained 960 mV. According to fig. 2 and 3 the rate of produced voltage and current is shown respectively in 4 steps of organic loading rate. The rate of produced current has a great decrease with increasing of the external resistance in each step.The rate of the produced current was (13.1 mA) at the maximum produced voltage when external resistance was 100 Ω in the nano structure reactor. While the rate of produced current was (4.76 mA) at the same condition in simple structure reactor. By comparing and observing the different produced voltages in which nano structure reactor was (348 mV) more than in simple structure reactor it was concluded that particles in nano dimensions causes the increase of effective area for more transition of electrons form electrode surface and conductor wire.

As columbic efficiency has been defined as ration (percentage) of gained electrons from current to total electric load existing in the substrate that 8 Mole of electrons were released by complete oxidation of Acetate. According to figs 4 and 5 relation between efficiency of removal organic rate and columbic efficiency changes, was obtained that the changes in efficiency of organic matter removal and in columbic efficiency doesn't have logical relation with increase or decrease of external resistance. The columbic efficiency changes has a direct relation with percentage of organic matter removal, so more substrate degraded by anaerobic bacteria causes more electron generation in anode chamber. In microbial fuel cell reactor with nano structure the maximum percentage of organic matter removal was obtained 98.28% and the maximum columbic efficiency was obtained 34.6% while maximum voltage producing.

In microbial fuel cell reactor with simple structure the maximum percentage of organic matter removal was obtained 72.5% and the maximum columbic efficiency was obtained 41.3% at the same condition.

Polarization Curve is using for assessment of relevance between resistance and current during system operation steps (Logan *et al.,* 2008), (Chaudhuri & Lovely, 2003) Polarization curve resemble how voltage and power density varies by the change of current density. This curve is using for determining the effect of resistance in the microbial fuel cell function and determining optimum external resistance for maximum power density. In this research polarization curves were drawn for both reactors by changing

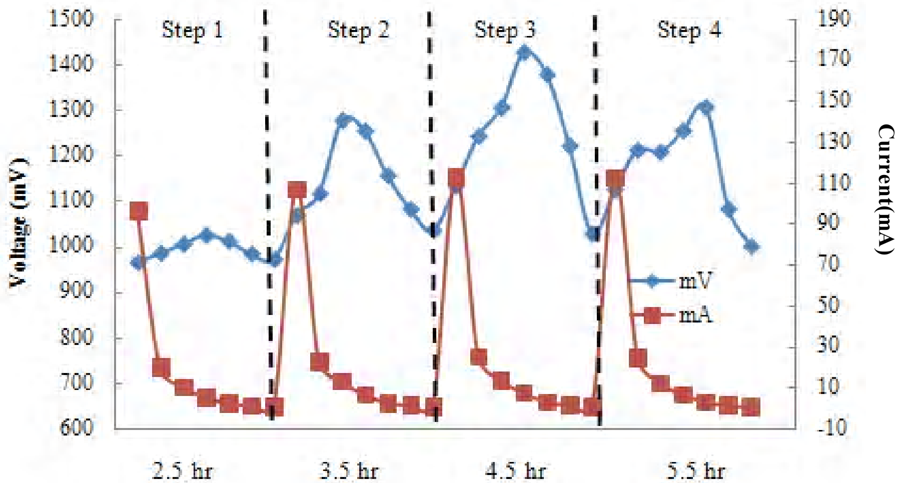

Fig. 2.Method of Produced Current and Voltage Changes in 4 Steps of Microbial Fuel Cell Performance Nano-Structure in External Resistance of 100 Ω

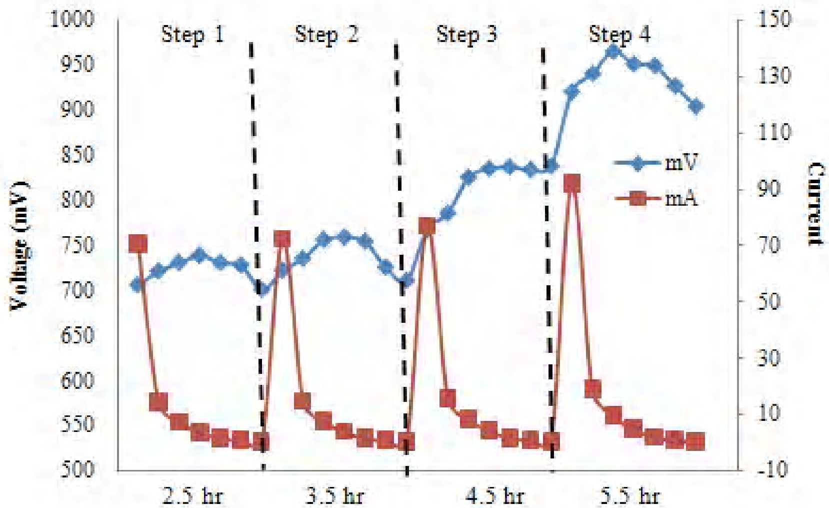

Fig. 3. Method of Produced Current and Voltage Changes in 4 Steps of Microbial Fuel Cell Performance Simple Structure in External Resistance of 100Ω

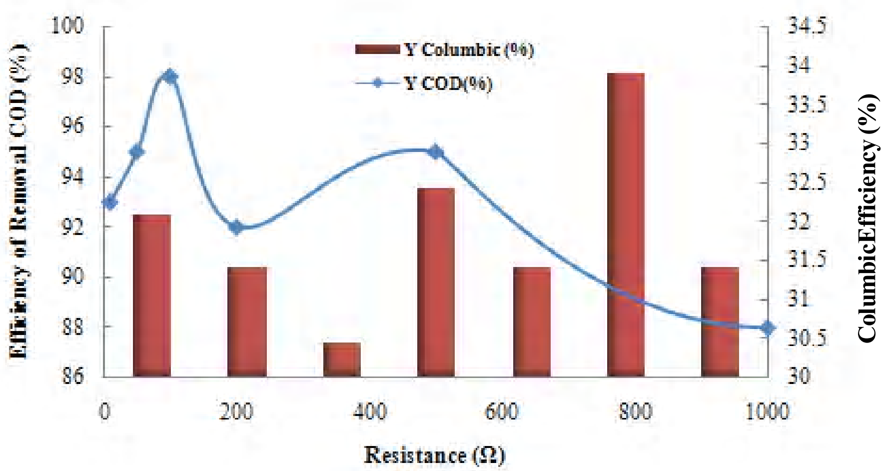

Fig. 4. Relevance between undulation of organic matter omission percentage and Columbic Efficiency for maximum voltage output period, in the Nano-structure reactor by the Hydraulic Retention Time of 4.5 hours

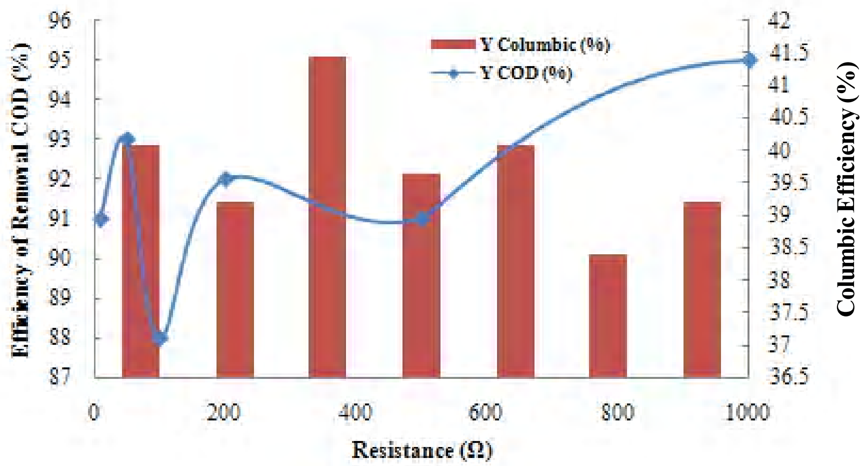

Fig. 5. Relevance between undulation of organic matter omission percentage and Columbic Efficiency for maximum voltage output period, in the Simple-structure reactor by the hydraulic extension time of 4.5 hours

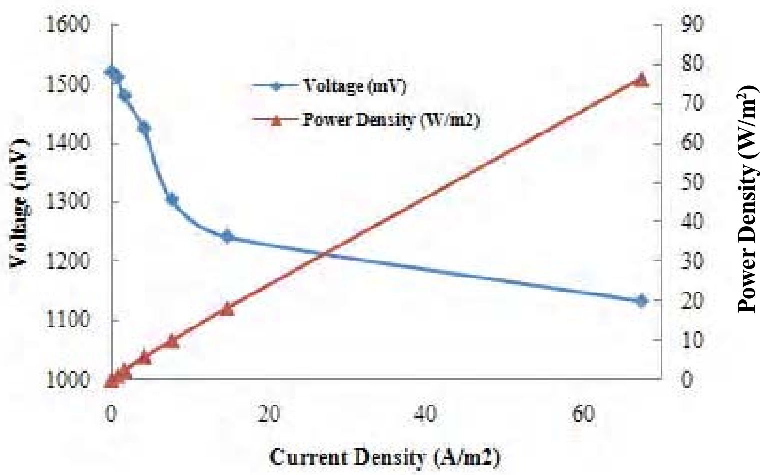

Fig. 6. Polarization curve at maximum output voltage in the Nano-structural reactor by external resistance of 10 ohm to 10 KΩ

external resistance from 10 Ω to 10 KΩ and recoding voltage, by extension time of 4.5 hours. The figs 6 and 7 show the relevance between produced voltage, current density and output power density. With increasing of resistance, output current decrease, and voltage stabilizing was observed in the upper resistance. Accordant to the experiment result and due to figs 6 and 7 polarization curves, this curves divided to three levels. Activation polarization, Ohmic wastage and polarization concentration (Wu *et al.*, 2012). In the first level where current is partly low, decreasing of resistance playing an important role and cause voltage decreasing. Because of activation potential in this level voltage decreasing gradient is high. By increasing of current, polarization curve resemble a linear relevance between voltage and current, which is named Ohmic polarization and is result of ionic and electronic resistance.

In this level when internal and external resistance are equivalent, non-Ohmic polarization is also generating, which in this state power density is maximum accordant to the Ohm's law (Wu *et al.*, 2012). In the reactor with platinum electrode and Nano Titanium wire the maximum of power and current densities respectively generated 78 w/m^2 and 67.3 A/m^2 ,also in the reactor with simple platinum electrode and simple Titanium wire, generation were respectively 35.08 W/m^2 and 45.7 A/m^2 both in the 100Ω resistance. In 2013 Wan and association used TiO2 nanoparticles-decorated carbon nanotubes for significantly improved bioelectricity generation in microbial fuel cells that generated the maximum current density of 3.10 ± 0.03 A/m^2 (Wen *et al.*, 2013).

Also in 2011 Hoa and association could reach to 750mV voltage enhancement by using of Structural assembly effects of Pt nanoparticle–carbon nanotube–

polyaniline Nano composites on the enhancement of bio hydrogen fuel cell performance (Hoa *et al.*, 2011).In 2012 Xiao and association used Carbon/iron-based Nano rod catalysts for hydrogen production in microbial electrolysis cells, that in this research they achieved to 0.8 V at 10&Ω resistance and current density of 2.60 ± 0.07 A/m^2 and maximum columbic Efficiency of 43.6 ± 0.8% (Xeio *et al.*, 2012).In 2010 Priscilla and association used nickel powder cathode catalysts in microbial electrolysis cells for hydrogen production and achieved to hydrogen production of 1.2-1.3 $m^3H_2/m^3/d$ in comparison of 1.6 $m^3H_2/m^3/d$ production by platinum (Selembo *et al.*, 2010).

In a Bio-hydrogen fuel cell with anode covered by platinum, Nano composite nuclei and Carbon Nano Tubes they achieved to maximum power density of 613.5 mW/m^2, current density of 2.55 A/m^2 and output voltage of 0.24 V.

Groups of bacteria that can be electrochemical and interactional active inside a microbial fuel cell are Geobacters and Shewanella (Liu *et al.*, 2005) which in a research by Kim and association in 2007, 83% of anode chamber bacteria population were α- and β-Proteobacteria, Dechloromonas, Azoarcus and Desulfuromonas. In this research in both reactors after microbial sampling, culture and Gram-Stain were done, and then at the end by a microscope with 100 magnitude pictures of the fixed bacteria on the slide were taken. Which figs 8 and 9 show variety of bacteria with bacillus and cocci Shapes and red and pink colors that these colors demonstrate the negative gram of bacteria consortium, diversity of active anaerobic bacteria in the anode chambers is similar in both reactors.

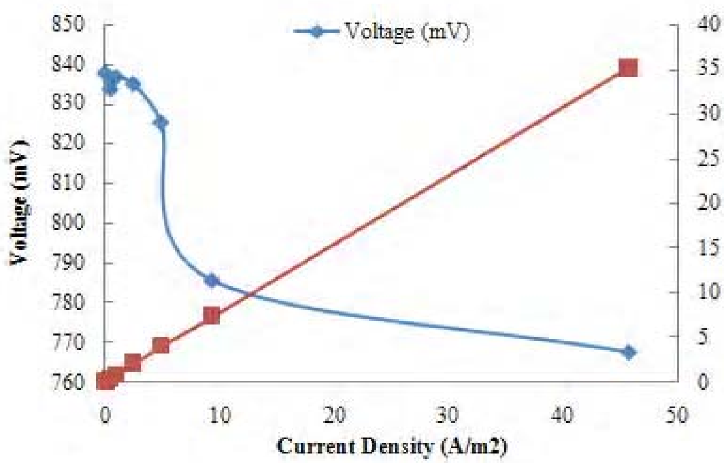

Fig. 7. Polarization curve at maximum output voltage in the simple-structural reactor by external resistance of 10 ohm to 10 KΩ

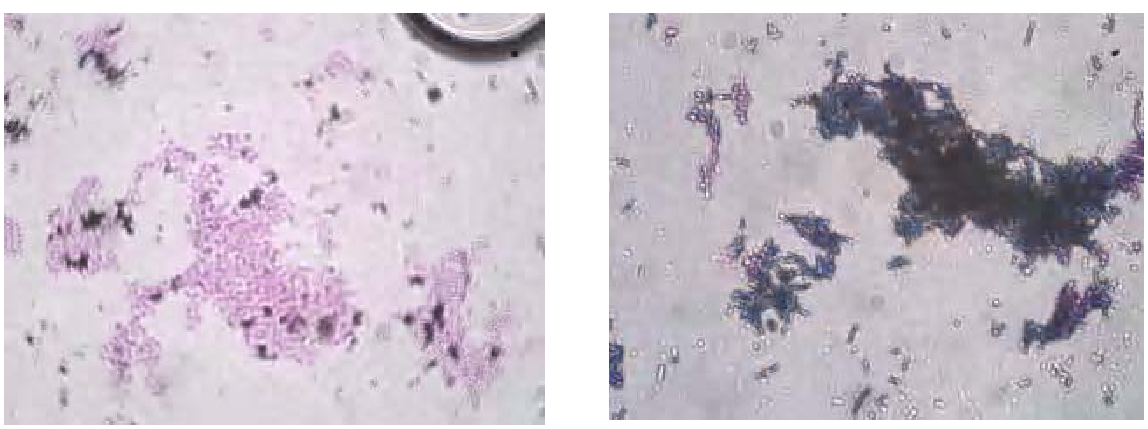

Fig. 8. Images of cocci and bacillus shapes anaerobic bacteria from the Nano-structural reactor

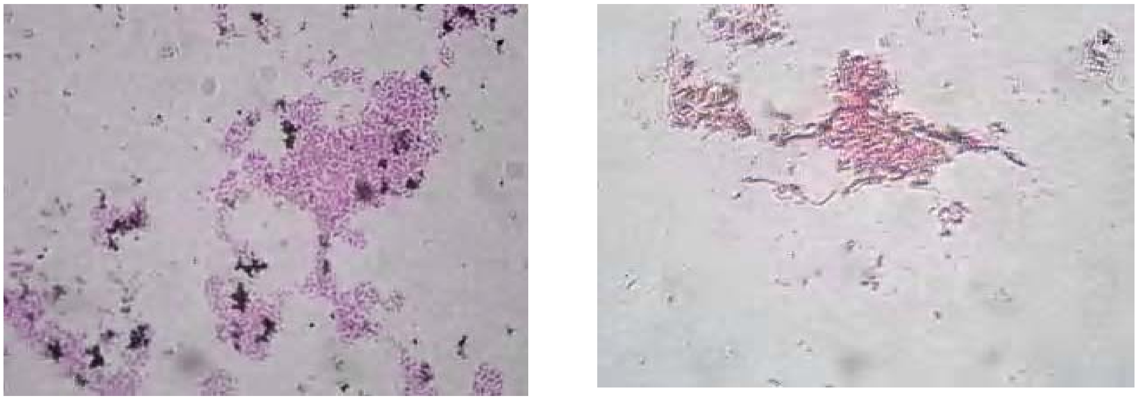

Fig. 9. Images of cocci and bacillus shapes anaerobic bacteria from the Simple-structural reactor

CONCLUSION

Considering achieved results in this research by an equivalent loading scale and hydraulic detention time, Nano-structural reactor with a 348 mV voltage production difference compare to Simple-structural reactor, discovers the effect of increasing specific surface and ability of more electron transition from the electrode surface and conductive wire in Nano dimensions.

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