A

PROJECT REPORT

ON

Simultaneous production of Electricity and Treatment of wastewater through Microbial Fuel Cell

Submitted in the partial fulfilment of the

Requirement for the award of the degree

Of

MASTER OF TECHNOLOGY

In

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abetment)

By

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INTRODUCTION

Microbial fuel cell (MFC) system, converts the chemical energy of organic biodegradable waste and wastewater to electrical energy with the catalytic activity of bacteria. Microbial fuel cell generally consists three parts i.e., cathode, anodic chambers and a proton exchanger. Degradation of organic substrates through microorganism takes place in anodic chamber that generates free electrons and H^+ ions under anaerobic condition.

In MFC electrons and protons travels through an external circuit and a salt bridge/PEM respectively. In anodic chamber electrons travels to the anode electrode surface through direct or indirect route or Direct route involves physical contact between MFC membranes with anode surface and electron transfer takes place through cytochrome, and in indirect route microbes excreted or externally added mediator is used.

Efficiency of MFC depends upon mainly anodic/cathodic pH, initial substrates COD concentration, temperature, material of electrodes, trace minerals and presence of mediator etc. However, higher or lower concentration of metal ions may responsible to enhance toxicity, sustainability of bacteria so that optimum values of these factors required for valuable performance of MFCs. Further, the coefficient of electron transfer from anode to catode may create difference in solution pHs because coefficient of no. Of H^+ ions or coefficient of electrons from anode to cathode through salt bridge/membrane may differ to same extent. In the anodic chamber, biodegradable organic substances are oxidized through microorganisms as equation (1) and transfer the electrons to anode electrode (negative electrode).

$$C_xH_xO_z + H_2O \rightarrow mCO_2 + nH^+ + ne^- \qquad (1)$$
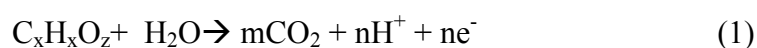
Electrons move along a circuit and tranfer to the cathode chamber (positive electrode), where oxygen [Gil, G. C et al 2003] or other chemicals such as ferricyanide [Rabaey, K et al 2003] accept these electrons. These electrons combine with protons that diffused from the anode chamber to the cathode chamber, form water (from oxygen) or ferrocyanide (from ferricyanide)[Boo kimin et al 2004].

Microbial fuel cell(MFC) consist of a proton exchange membrane (PEM) which separates cathodic and anodic chamber, protons in anode chamber moves through PEM and electron

through external circuit to the cathodic chamber. The putative cathodic process is given by reaction (2):

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O \qquad (2)$$
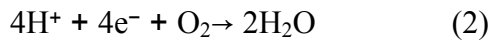
In MFC the coefficient of electron transfer from anode to catode may create difference in solution pHs because coefficient of no. Of H^+ ions or coefficient of electrons from anode to cathode through salt bridge/membrane may differ to same extent

1.1) Working of Microbial Fuel Cell (MFC):

The Microbial Fuel Cell (MFC) is divided into two halves, as shown in Fig.1, anaerobic and aerobic. In anaerobic chamber oxygen is not allow and it consist of a negatively charged electrode to act as the electron receptor for the bacterial processes. The aerobic is bubbled with oxygen and having a positively charged electrode. Both of these chambers are separated by a semi-permeable membrane to keep oxygen out from anaerobic half while still allowing hydrogen H^+ ions.

1. In anaerobic chamber bacteria decomposes the organic material and produce free electrons and H^+ ions.
2. The free electrons move from the bacteria towards anode electrode.
3. The electrons flow up from the anode onto the cathode through a wire. As free electrons flowing external circuit, an electrical current output can be used to perform the work.
4. The H+ ions moves through the proton exchange membrane to the cathodic chamber as well as electrons flow from external circuit.
5. The electrons in the cathode combine with the H+ ions and dissolved oxygen to form pure H_2O.
6. In cathodic chamber free electrons , H^+ions and oxygen are combine together to form water.
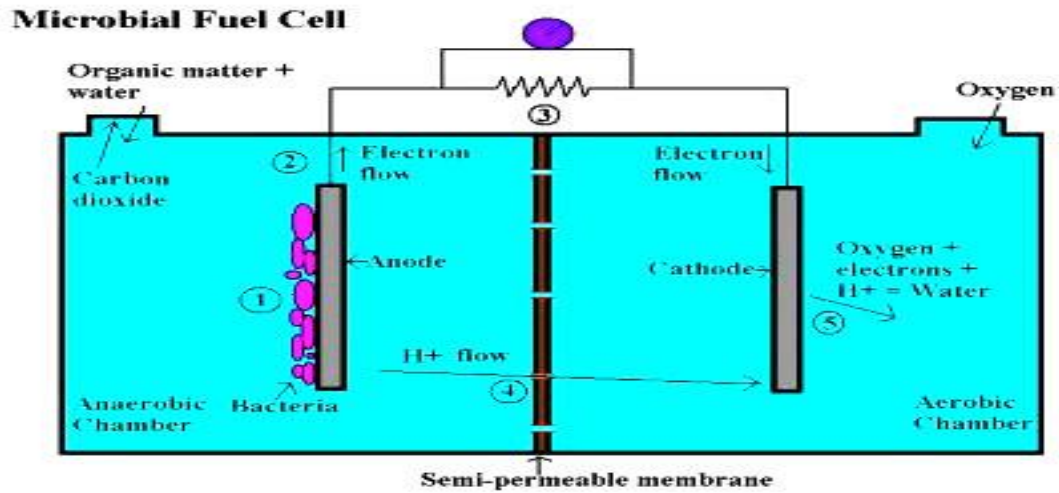
Microbial Fuel Cell

Organic matter + water

Oxygen

Carbon dioxide

② Electron flow

Electron flow

←Anode

Cathode→

①

Oxygen + electrons + H+ = Water ⑤

H+ flow

④

Anaerobic Chamber Bacteria

③

Aerobic Chamber

Semi-permeable membrane

Figure 1: A schematic of a microbial fuel cell.

1.2) Objectives:

1. Preparation and characterization of low cost proton exchange membrane for MFC.
2. Selection and characterization of microbes for microbial fuel cell.
3. To use the prepared low cost proton exchange membrane in MFC to determine its performance.
4. Optimization of process parameters.
5. Compare the Performance of MFC using Proton Exchange membrane and salt bridge.

LITERATURE REVIEW

Microbial fuel cell (MFC) is the system, that converts chemical energy of organic substrates and wastewater to electrical energy. (Shankar et al., (2013), Moon et al., (2006). It has the potential for simultaneous removal of pollutants from the wastewater and production of electricity.

Although, the electricity generation capacity of MFC is not much, it can be sufficient for small equipment such as biosensor (Kim et al., (2003)).

2.1) Basic components used in microbial fuel cell:

Basic component used in microbial fuel cell, like anode, cathode, PEM etc. and materials that most basically used for these components has given in Table 2.1:

Table 2.1: The basic components used for MFC:

Items	Materials	Remarks
Anode	Graphite, carbon-cloth, Pt, Pt black, graphite felt, carbon paper etc.	Necessary
Cathode	Graphite, carbon paper, carbon-cloth, Pt, Pt black, graphite felt, etc.	Necessary
Anodic Chamber	Polycarbonate, Plexiglas, Glass,	Necessary
Cathodic Chamber	Glass, Plexiglas, polycarbonate	optional
Proton exchange system	Proton exchange membrane: polyethylene.poly (styrene-co-divinylbenzene)Salt bridge, porcelain septum, Nafion, Ultrex, or solely electrolyte	Necessary
Electrode catalyst	Pt, Pt black, MnO_2, Fe^{3+}, polyaniline, electron mediator immobilized on anode	optional

2.2) Application of MFC in batch reactors for simultaneous removal of organics and electricity generation:

Fei Guo et al [2013] have been worked on *Mustard tuber wastewater treatment and simultaneous electricity generation using microbial fuel cells*. They have used Mustard tuber wastewater(MTWW) was utilized as fuel in the typical dual-chamber microbial fuel cells (MFCs) to recover bio-energy and to obtain effluent treatment simultaneously and generated a maximum power density of 246 mW/m^2.

Vanita Roshan Nimje et al(2012) investigated *Comparative bioelectricity production from various wastewaters in microbial fuel cells using mixed cultures and a pure strain of Shewanella oneidensis.*Using AWW (0.011 mA/cm^2; 0.0013 mW/cm^2) and DWW (0.017 mA/cm^2; 0.0036 mW/cm^2), FDWW produced a maximum current from MFC (0.037 mA/cm^2; 0.015 mW/cm^2), and confirmed the unsuitability of MFC at an alkaline pH.

Mostafa Rahimnejad et al (2011) worked on *Power generation from organic substrate in batch and continuous flow microbial fuel cell operations* and At HRT of 6.7 h, maximum current and power were 1210 mA m^{-2} and 283mWm^{-2}, respectively.

Mohanakrishna et al., (2010) investigated the multiple functions of MFC as a fuel generator and as an integrated wastewater treatment unit. MFC was operated at three substrate load conditions in fed-batch mode under acido-philic (pH 6) condition using anaerobic consortium as anodic-biocatalyst. MFC operation reduced COD, color, total dissolved solids as 72.84%, 31.67% and 23.96% respectively.

Zhu et al., (2009) demonstrated that a MFC not only can remove biodegradable organics and generate electricity, but also can remove bio-refractory pollutants like *p*-nitrophenol. They reported that in MFC, *p*-nitrophenol was completely degraded after 12 h, and about 85% TOC was removed after 96 h. simultaneously, a maximum power output of 143 mW /m^2 was generated.

Li et al., (2009) developed an overflow-type wetted-wall MFC (WWMFC) with air cathode to generate a stable voltage from acetate-based substrates. The maximum power density produced in the MFC from1000 mg/l acetate was 18.21 W/m^3 and the internal resistance was 400 Ω.

Zhang et al., (2008) examined a mediator-less MFC with aerobic bacteria as catalysts in the cathode for electricity generation from the microbial oxidation of glucose in the anode.

The microbial fuel cell could be started up after a short lag time of 9 days when anaerobic sludge and aerobic sludge used in the anode and cathode respectively. It generate a stable voltage of 0.324 V. A maximum volumetric power density of up to 24.7 W/ m^3 (117.2 A /m^2) was reached at an aeration rate of 300 ml/ min in the cathode.

Fikret Kargi et al (2007) laid emphasised on *generation of electricity   with simultaneous wastewater handling by a microbial fuel cell (MFC) with Cu electrodes.* After doing this he has been observed that power density (mW/m^2) increased with incease the COD content of the wastewater and with increasing of the electrodes surface area. Power density (mW) and the current density (mA) increased with time and reach maximum levels at the end of batch operation.More than 80% COD removal have been achieved in the aerobic chamber with voltage generation of 2.9mWm^{-2} at 6000mg/l initial COD concentration.

M.M. Ghangrekar et al (2006) have investigated the *Performance of microbial fuel cell membrane-less system to treat wastewater and to determine the effect of space between electrodes and effect of surface area of electrode on electricity production.* In this system Performance of membrane-less and mediator-less microbial fuel cell (ML–MFC) was evaluated to treat artificial wastewater and real sewage. The ML–MFC gave BOD andCOD removal efficiencies of 87% and 88%, respectively.

2.3) Application of proton exchange membrane microbial fuel cell for electricity generation:

Mostafa Ghasemi et al (2013) investigated the Effect of pre-treatment and bio-fouling of proton exchange membrane on microbial fuel cell performance. The maximum generated power and current density of the treated membrane was achieved 103mW/m^2 at 408.1mA/m^2, respectively.

Mostafa Ghasemi et al (2012) laid emphasised on new generation of carbon nano-composite proton exchange membranes in microbial fuel cell systems. The results reveal that the system is operated by the ACNF/Nafion membrane produce the highest voltage of 57.64 mW m^{-2}, while Nafion 112 produces the lowest power density (13.99 mW m^{-2}).

Bruce E. Logan et al (2009) worked on Exo-electrogenic bacteria that power microbial fuel cells and achieved generated power densities as high as 6.9 W per m^2 (projected anode area).

Shun'ichi Ishii et al (2008) research on Comparison of Electrode Reduction Activities of *Geobacter sulfurreducens* and an Enriched Consortium in an Air-Cathode Microbial Fuel

Cell and achieved current density reached a maximum of 1,530mA/m^2, and power density reached a maximum of 461 mW/m^2.

Bruce E. Logan et al (2005) have been worked on *generation of electricity from cysteine in a MFC* .In this system bottles were joined by a glass link containing a proton exchange membrane(PEM) (Nafion^{TM} 117, Dupont Co.) held through a clamp between the compressed ends of the two glass tubes (inner diameter=1.3cm) fitted with rubber gaskets. Over a period of few weeks, electricity production gradually increased to a maximum power density of 19 mWm^{-2} (700 or 1000Ω resistor; 385 mgL^{-1} of cysteine).

Hong Liu et al (2004) investigated the effect of *Electricity Generation Using an Air-Cathode Single Chamber Microbial Fuel Cell(MFC) in the Absence and Presence of a Proton Exchange Membrane.* Power density was found to be greatly greater than typically reported for aqueous-cathode MFCs, reaching a maximum of 262 ± 10 mWm^{-2} (6.6 ± 0.3mWL^{-1}; liquid volume) using glucose. Removing the PEM increased the maximum power density to 494 ± 21 mWm^{-2} (12.5 ± 0.5 mWL^{-1}).

Table 2.2: presents a list of polymeric proton exchange membrane that has been prepared for microbial fuel cell:

Table 2.2: Various polymeric Proton exchange membranes for MFCs:

Polymers used	Dissolving agent	Ion-exchange capacity	Proton conductivity	Operationg Temperature (^{o}C)	References
Polystyrene-butadiene rubber (PSBR)	1,2 dichloroethane	0.63mmol/g	10^{-3} S/cm	70 ^{o}C	A.S.Abdulkareem et al., (2010)
polystyrene	acetone	2.85 meq/g	2.57 µS/cm	(100 ± 5)$^\circ$ C	Nilar Win et al., (2008)
polystyrene	methyl ethyl ketone	3.215 meq/g	3.05 µS/cm	(90±2)$^\circ$ C.	Nilar Win et al., (2008)
Polystyrene-block-(ethylene-ran-butylene)-block polystyrene (PSEBS)	chloroform	0.02 meq/g	10^{-3} S/cm	10 ^{o}C	S. Elamathi et al., (2007)

2.4) Substrates used in MFCs:

In MFCs, substrate is the most vital biological factor that affects electricity production as we already know from introductory part. Table 2.3 presents a wide spread organic substrates that generally used in microbial fuel cell system. (Deepak Pant et al 2010)

Table 2.3: Different substrates used in microbial fuel cells (MFCs):

Type of substrate	Source inoculum	Current density(mAcm^{-2})	Reference
Arabitol	Pre-acclimated bacteria from Microbial fuel cell(MFC)	0.68	Catal et al. (2008b)
Azodye with glucose	Mixture of anaerobic and anerobic sludge	0.09	Sun et al. (2009a)
Carboxymethyl cellulose (CMC)	Co-culture of Clostridium Cellulolyticum and G. Sulphur reducens	0.05	Ren et al. (2008)
Cellulose particles	Pure culture of Enterobacter-cloacae	0.02	Rezaei et al. (2009b)
Ethanol	Anaerobic slush from wastewater plant	0.025	Kim et al. (2007)
Glucose	Mixed bacterial culture maintained on sodium acetate for 1 year (Rhodococcus and Paracoccus)	0.70	Catal et al. (2008a)
Glucuronic acid	Mixed bacterial culture	1.17	Catal et al. (2008a)

Lactate	Pure culture of S. oneidensis MR-1	0.006	Manoharand Mansfeld(2009)
Phenol	Mixed anaerobicand aerobic activate sludge (1:1, v/v)	0.1	Luo et al. (2009)
Propionate	Anaerobic sludge	0.035	Oh and Logan (2005)
Ribitol	Pre-acclimated bacteria from MFC	0.73	Catal et al. (2008b)
Sodium formate	Anaerobic digested fluid from a sewage treatment plant	0.22	Ha et al. (2008)
Phenol	Mixed aerobic activated sludge and anaerobic sludge (1:1, v/v)	0.1	Luo et al. (2009)
Starch	Pure culture of Clostridium butyricum	1.3	Niessen et al. (2004)
Sucrose	Anaerobic sludge from infected tank	0.19	Behera and Ghangrekar (2009)

2.5) Types of MFC:

Generally, there are five type of microbial fuel cell (MFC) that are discussed below:

2.5.1) Mediator-Microbial Fuel Cell [MMFC]:

This type MFCs are electro-chemically inactive so that some mediators such as methyl blue, humic acid, thionine, , methyl viologen, neutral red and so on are used to transfer the electron to the electrode surface. [Delaney et al 2008, Lithgow et al 1986].

2.5.2) Mediator-free microbial fuel cell [MFMFC]:

This type of Microbial Fuel Cell (MFC) does not require a mediator but utilize electrochemically active microbes to transfer electrons to the electrode (electrons are carried directly from the bacterial respiratory enzyme to the electrode). Among the

electrochemically active microbes, *Shewanellaputrefaciens*, *Aeromonashydrophila*, is one of them. [Strik, David et al 2008, web link 18,19]

2.5.3) Microbial electrolysis cell:

MEC's are work on reverse principle. In this type of cell hydrogen or methane are produced through an external current applying to the microbes to increase their voltage generation capacity by oxidation of organic compounds through bacteria and that sufficiently lead to the electrolysis of methane or the water production.[Nevin Kelly P et al 2010]

2.5.4) Soil-based MFC:

[SBMFC] work on basic MFCs principles as describe above, in which soil acts as the inoculum, the proton-exchange membrane (PEM) and the nutrient-rich anodic media.

2.5.5) Phototrophic bio-film microbial fuel cell [PBMFC]:

These are different type MFCs which use of anode with phototrophic bio-film containing photo-synthetic bacteria like chloro-phyta, cyano-phyta etc. [Elizabeth, Elmy et al 2012].

2.6) functional & operational advantages of Microbial fuel cell:

1. In MFC bacteria is worked as catalyst and organic material used as a fuel for bacteria.
2. Like Hydrogen Fuel Cells (HFC), MFCs do not call for highly regulated sharing systems.
3. Microbial fuel cells (MFCs) have high alteration effectiveness to compare to the Enzymatic Fuel Cells.

2.7) Applications of MFC:

Some of the applications of MFC are given below:

2.7.1) Wastewater treatment:

Recently MFCs in under serious consideration as system to simultaneous treatment of waste streams and electricity production through that wastewater streams that are out from many agricultural industrial and municipal areas [Shukla, A et al 2004]

2.7.2) Powering underwater monitoring devices:

. MFCs can also be used to provide control for such devices, mainly in river and deep-water environment where it is difficult to routinely contact the system to repair batteries. [Bond, D. R. et al 2002]

2.7.3) Power supply to remote sensors

With the progress of micro-electronics and discipline linked the necessity for power electronic devices has Considerably compact. General research budding toward reliable MFCs to this effect is determined to Selecting Appropriate mostly on organic and inorganic substances can be used as those sources of power. [Shantaram, A. et al 2006]

2.7.4) BOD sensing:

Another application of the microbial fuel cell equipment is to use as a sensor for pollutant analysis. BOD is the amount of DO necessary to provide for aerobic organisms in water rich in organic substance. The comparative relationship between the coulombic acquiesce of MFCs and the meditation of assailable organic impurities in wastewater make Microbial fuel cells as a probable method as BOD sensors. [Lovley, D. R. (2006).]

2.7.5) Hydrogen production:

MFCs are alternative option for Hydrogen production that operating on organic waste. In the cathode chamber, anaerobic circumstances are preserved and voltage aprrox 0.25 V is supplied after doing this. Such microbial fuel cells are known as bio-electro-chemically assist microbial reactor (BEAMR). [Liu, H., et al 2005]

2.8 Mechanism of MFC

In an MFC, microorganisms degrade (oxidize) organic matter and produce free electrons and H^+ ions in anodic chamber as described above. The H^+ ions are transported to cathode through hydrogen transfer membrane or through the filter media (in case of membrane less MFC). However, the electrons are transported to anode through various routes depending upon the nature of the microorganisms used (Huang et al., (2011)).

Two major routes i.e., direct and indirect routes for the electron transfer from bulk phase to anode surface in MFC have been reported (Sund et al., (2007), Huang et al., (2011)). Electrons are transfer to anode through direct route of microorganisms themselves through physical contact between bacterial cell membrane and the electrode surface via cytochrome

or putative nanowire structures, (Sund et al., 2007, Huang et al., (2011)). However, a soluble redox active compound (mediator) is responsible for electron transfer through indirect route (Bond and Lovley (2005); Turick et al. (2003); Chaudhuri and Lovley (2003); Reguera et al. (2006)). Some microorganisms can excrete redox-active compounds to carry out indirect electron transfer with electrodes (Huang et al., (2011)).

Both oxidative and fermentative metabolisms of microorganisms are observed in MFC. Some microbes having different types of metabolic paths and electron transport systems are reported in Table 2.4. As long as for current production conditions remain favourable by the anode-associated microbes, a MFC has the potential to produce electricity indefinitely.

Table 2.4 Some microorganisms with different metabolic paths and electron transport systems (Rabaey et al., (2005)

Metabolic type	Transfer type	Examples of organisms
Oxidative metabolism	Membrane-driven	*Rhodoferax ferrireducens*
		Geobacter sulfurreducens
		Aeromonas hydrophila
	Mediator-driven	*Escherichia coli*
		Shewanella putrefaciens
		Pseudomonas aeruginosa
		Erwinia dissolvens
		Desulfovibrio desulfuricans
Fermentative metabolism	Membrane driven	*Clostridium butyricum*
	Mediator driven	*Enterococcus faecium*

Electric current is generated in MFC in the same way as in chemical fuel cell but in MFC bacteria is worked as catalyst on anode surface. Without being changed catalysts increase the rate of a reaction and do not receiving energy from the reaction that catalyzed. In MFC,

bacteria received energy from oxidized organic substrates that's why microbe is not true catalyst for the same. (He et al., (2009)

2.9) Performance of MFC

The Colulombic efficiency of microbial fuel cell is the measured in coulombs recovered from the organic substrates that oxidise from bacteria present in MFC. Columbic efficiency of the MFC is dependents upon the microorganisms that are responsible for oxidation of substrates used. Bacteria need to be completely oxidized to generate electrons and to form carbon dioxide so that maximum theoretical amount of energy is obtained. (Zeng et al., (2010)).

Performance of MFC depends on types of micro organisms used, mediator concentration, types of hydrogen transfer membrane / system, operating conditions such as pH and temperature, substrate concentration and its nature, electrode spacing etc. (Ghangraker and Shinde (2007)). Type of reactor also influences the performance. It has been reported that MFC performs better in batch scale reactor than continuous reactor (Min et al., (2003)).

2.8) Research gaps:

None of the approaches cover the investigation including microbial fuel cell for Electricity production and simultaneously treatment of wastewater (mixture of glucose and glutamic acid) through microbial fuel cell with sulphonated polystyrene proton exchange membrane in previous researches, so that here we laid emphasized on this system and will determine how much power density enhancement we'll achieve for this system.

EXPERIMENTAL SET-UP AND INSTRUMENTATION

Present investigation is carried out to remove toxic organics in terms of COD removals from synthetic (glucose-glutamic acid solutions of mole ratio 1:1) wastewater and simultaneous electricity production. Removal of toxic organics from synthetic wastewater samples has been carried out in batch reactor for sulfonated polystyrene proton exchange membrane microbial fuel cells operations. In this Chapter, the design considerations, composition of synthetic wastewater samples, range of experimental parameters, details of setups, limitations of setups and specification of auxiliary and analytical instruments used have been described.

3.1) Design Consideration:

Design considerations of the batch studies to obtain accurate and reliable experimental data for the removal of toxic organics from synthetic (glucose-glutamic acid solutions) wastewater samples have been discussed below:

3.1.1) Batch study:

Batch study in MFC is carried out to study the simultaneous generation of electricity (reported as voltage, current density and power density generation) and deletion of COD from synthetic glucose-glutamic acid solution as well as to optimize the process parameters. Effect of individual process parameter on the removal of organics COD and generation of electricity (in case of MFC only) were studied to find out the optimum process conditions. In the present study for removal of organics (COD) and generation of electricity we have prepared a low cost proton exchange membrane for MFC.

3.2) Type of wastewater Treated:

In this present batch study synthetic wastewater of glucose-glutamic acid(abundantly available in distillery effluents) have been considered.

3.2.1) Synthetic glucose-glutamic acid solution:

The glucose and glutamic acid have been considered as model compounds to prepare synthetic solution since these are abundantly available in distillery effluents (Satyawali and Balakrishnan, (2008)). The above range of COD has been considered to make it suitable for

the application in MFC (Moon et al., (2006)). Glucose: glutamic acid ratio (1:1) has been considered to understand the process of MFC and compare the experimental data with literature where glucose: glutamic acid ratio has been considered as (1:1) (Moon et al., (2006)).

3.3) Details of experimental set-up:

For batch study, requirement of the sample for the analysis of voltage, current and power generation, COD removal etc., 700 ml of the glucose-glutamic acid sample volume was taken for each experiment in batch MFC. For sufficient mixing the volume of the batch reactor was fixed as 800ml. Microbial species used in the study was collected from sewage treatment plant Jagjitpur Haridwar, Uttarakhand, India.

3.3.1) Set-Up for Batch scale PEM-MFC reactors:

Batch scale MFC was constructed with two chambers of Plexiglas material (10cm × 10cm× 10 cm) system which were connected by proton exchange membrane as shown in Fig.3.1.

The polymeric membrane that separates anodic and chathodic chambers has the diameter 3cm and 0.025mm thickness. Graphite rods 0.10m length and 0.015m dia was used for graphite electrodes in both of the chambers. A constant air flow rate of 40 - 50 ml/min was maintained through aquarium pump and External connections for transfer of electron were made with copper wire.
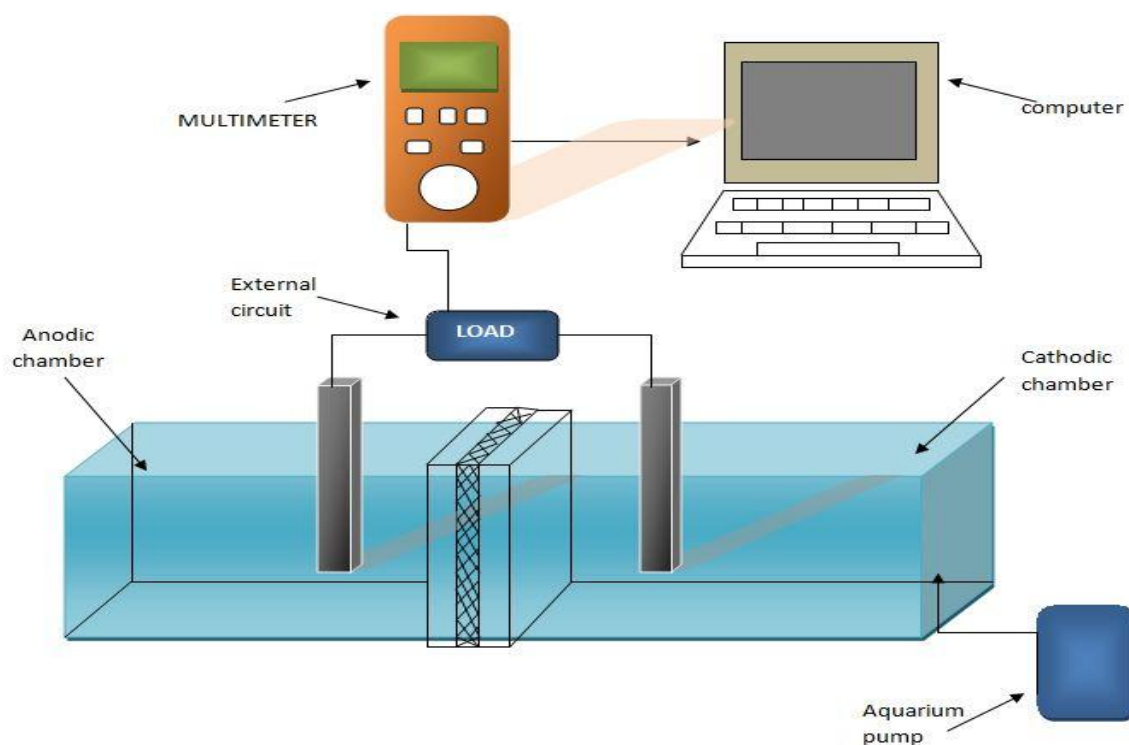

Fig. 3.1: Batch Microbial fuel cell

3.3.1.1) INSTRUMENTATION AND CONTROL:

Digital multi-meter model KROS-S DT830D was used to measure the voltage and current in the external circuit. Temperature was maintained at reactor chamber, and air flow maintained by aquarium pump.

3.3.1.2) AUXILIARY EQUIPMENT USED IN THE PRESENT INVESTIGATION

Auxiliary equipment using in the present study are autoclave, water bath, muffle furnace, distilled water plant, digital camera, weighing balance, multi-meter etc.

3.3.1.3) ANALYTICAL INSTRUMENTS USED FOR THE PRESENT INVESTIGATION

Analytical instruments use in the present study are, FE-scanning electron microscope (FE - SEM), and COD meter etc.

3.3.2 Set-Up for Salt-bridge MFC (Batch scale reactors):

Batch scale salt bridge MFC was contructed with two plastic bottles. Each bottle is of 7 cm height, 6 cm diameter, and connected via salt bridge as shown in Fig. 3.2. The salt bridge was prepared with a plastic tube. The internal diameter of salt bridge plastic tube is 2 cm and length is 5 cm and was filled with 10 % agar media of 3 M NaCl solution that is sterilized for 15 minute at 15psi pressure and $121^{O}C$ temperature. Graphite rod of 10 cm length and 1.5 cm diameter was used as electrode in both salt bridge MFC as well as PEM-MFC in both the chambers. A constant air flow rate of 40 - 50 ml/min was maintained through aquarium pump and External connections for transfer of electron were made with copper wire.
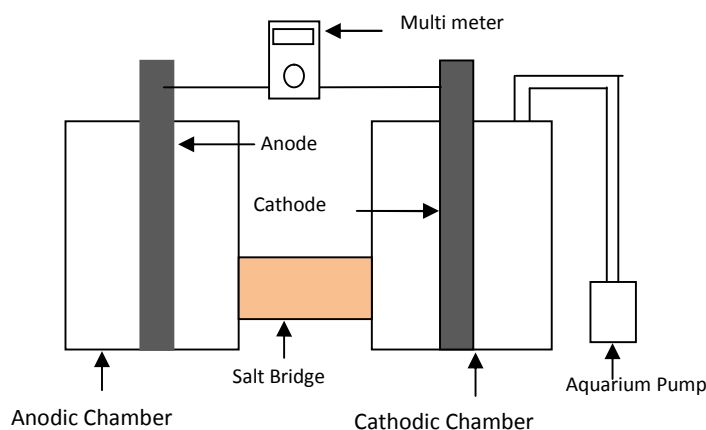
Fig. 3.2: Experimental setup for batch scale salt bridge MFC

EXPERIMENTAL PROGRAM AND DATA ACQUISITION

4.1) Preparation of proton exchange membrane for MFC:

A PEM is a semi-permeable membrane generally prepared from ionomers and designed to conduct protons while being rainproof to gases such as oxygen or hydrogen. This is their important function when integrated into a membrane electrode assembly (MEA) of a proton exchange membrane fuel cell or of a proton exchange membrane electrolyser : separation of reactants and transport of protons.

However, the high cost of perfluorinated Nafion membranes makes them inappropriate for low turnover margin for wastewater treatment systems. Sulfonated Polystyrene Membrane is highly performing thermoplastic that has good solvent resistance. The sulfonated derivatives of polymer offer low cost alternative to Nafion® membranes.

4.1.1) Preparation of membrane: Experimental method:

4.1.1.1) Preparation of Sulfonated Polystyrene Resins using Acetone:

Five grams of polystyrene beads were put into a 150 ml glass bottle and then 50 ml of acetone poured into the bottle and than well tapered. A jelly-like polymer pulp has been obtained after a time period of 48 hour. This jelly-like polymer used in further sulfonation practice. For sulfonation process, 50 ml of 95 % concentrated sulfuric acid was used as a sulfonating agent. Sulfonation temperature was maintained at $(105 \pm 5)°C$ and the time of sulfonation were limited to 15 minutes for SPR - 1 resin, 30min. for SPR - 2 resin and 60min. for SPR - 3 resin.

4.1.1.2) Preparation of Sulfonated Polystyrene Membrane:

Sulfonated polystyrene membranes were prepared from SPR - 2 resin that are shown in Fig 4.1: which had the highest cation exchange capacities. Sulfonated polystyrene solution was prepared by dissolving 1 gram of SPR - 2 resins in 10 ml of benzene and stimulated until a brownish yellow colored solution obtain; and then again poured into a Petri dish.

Fig:4.1 Sulfonated Polystyrene Resins using acetone(SPR-2)

To uphold slow evaporation, petri dish was covered with a aluminium foil with a few punch holes on it. Then dish was positioned on a flate surface in order to allow solvent evaporation at room temperature. After that petri dish with that dry film was weigh until to obtained constant weight .The film as shown in Fig.4.2 cut into circular shaped and kept in a storage place for further studies. The thickness measured nearly 0.025mm of diameter 5.8cm. The ion-exchange capacity and proton conductivity of the prepared polymeric membrane are 2.85meq/g and 2.57µS/cm.

Fig: 4.2) Membrane from SPR-2 resin:

4.1.1.3) Characterization of membrane:

The cation exchange capacity so obtained membrane was measured using titration method gives 2.85 meq/g at sulfonation time of 30min. The Conductance of SPR–2 (prepared resine) has been determined 2.57µScm-1 at 30min using time lag technique. Instruments/processes used for characterization of membrane are given in Table 4.1:

Table 4.1: Characterised parameters of Sulfonated Polystyrene Membrane:

Membrane Type	Polymeric(Sulfonated Polystyrene Membrane)	Instruments / processes used
Thickness	.025mm	Screw gauge
Cation exchange capacity	2.85 meq/g	Titration process
Conductance	2.57 μScm-1	Time lag Technique

4.2) PREPARATION OF SYNTHETIC WASTEWATER:

4.2.1) Synthetic Glucose-Glutamic Acid Solution

Synthetic glucose-glutamic acid solution was prepared with AR grade glucose and glutamic acid with mole ratio of 1:1. To prepare each litre of synthetic solution, 50 ml phosphate buffer (0.1 M, pH 5 - pH 8) and 10 ml trace mineral salt solution were added (Jang et. al., 2004). Each liter of trace mineral solution contained $(NH_4)_2SO_4$, 5.6 g; $MgSO_4 \cdot 7H_2O$, 2.0 g; $CaCl_2$, 0.15 g; $FeCl_3 \cdot 6H_2O$, 10 mg; $MnSO_4 \cdot H_2O$, 0.2 g; $NaHCO_3$, 4.2 g (Jang et. al., 2004).

4.3) Design of Experiments for fixing experimental conditions on the voltage generation and current density production from synthetic glucose-glutamic acid solution through MFC to develop empirical models:

A three factors three levels Box-Behnken design having total 17 number of experiment points as reported in Table 4.4was used to develop correlations among input parameters like initial COD(1000mg/l,1500mg/l,2000mg/l), initial pH (6,7,8) and mediator concentration(.2mM,.3mM,.4mM) and output parameters like voltage generation(in mV), current density(in mA) generation and % removal of COD from glucose-glutamic acid solution. Table 4.2 gives the design summary and Table 4.3 shows the coded values of experiment points.

Table 4.2: Design Summary:

Factor	Name	Units	Type	Minimum	Maximum	Coded	Values	Mean	Std. Dev.
A	substrate con	mg/l	Numeric	1000	2000	-1=1000	1.0 =2000	1500	343.00

| B | pH | | Numeric | 6 | 8 | -1= 6.00 | 1.0=8.0 | 7 | 0.69 |
| C | mediator | mM | Numeric | 0.2 | 0.4 | -1.0=0.2 | 1.0=0.40 | 0.3 | 0.07 |

Table.4.3: Three factor three level Box-Behnken design for preparing synthetic glucose-glutamic acid solution:

Sl no.	A:Initial COD(mg/l)	B: pH	C: Mediator conc.(mM)
1	-1	-1	0
2	0	0	0
3	-1	1	0
4	1	1	0
5	0	0	0
6	0	0	0
7	-1	0	1
8	0	1	-1
9	0	1	1
10	0	-1	-1
11	0	0	0
12	-1	0	-1
13	1	-1	0
14	1	0	1
15	1	0	-1
16	0	-1	1
17	0	0	0

The three levels for Initial conc.(A) are: 1 = 2000 mg/l, 0 = 1500 mg/l, -1 = 1000 mg/l. for pH (B) are: 1 = 8, 0 = 7, -1 = 6 and for initial mediator conc. (C)are : 1=.4mM, 0=.3mM,

-1=.2 .These experiment points were also used to generate data for finding optimum process conditions and interaction parameters among the process variables.

Design expert calculates the value of Std. Deviation, R-Squared, Adjusted R-Squared, Predicted R-squared and PRESS for various models i.e linear, quadratic, cubic etc. The model which exhibits low standard deviation, high adjusted R-squared value and low PRESS Value is chosen. Analysis of variance is done for the response parameters i.e. Voltage generation and Current density for the selected model. The software calculates coefficients for various factors by regression and thus the final model is obtained. With the help of final model, the final optimized point is thus obtained. The predicted voltage generation and current density values have been compared with the experimental values.

4.4) Simultaneous Generation of Electricity and Removal of Organics from Synthetic Glucose-Glutamic Acid Solution through MFC:

Experiments were conducted for simultaneous generation of electricity and removal of organics from synthetic glucose-glutamic acid solution in batch MFC. In the batch study selection of microorganisms was done, which was followed by optimization of process conditions through variation in individual parameter as well as multi parameters and modelling of the process for the simultaneous generation of electricity and removal of organics. It also includes the improvements in voltage generation due to the addition of mediator in the MFC. Detail procedures are as follows:

4.4.1) Selection of microorganisms:

On the basis of literature and availability the *E.coli MTCC42* and *Pseudomonas fluorescence MTCC 103* were preliminary indentified as suitable microorganisms and procured from MTCC Chandigarh, India. The activated sludge collected from municipal wastewater plant at Jagjitpur, Haridwar was also used as a source of microorganisms.

4.5) Batch reactor study for proton exchange membrane microbial fuel cell:

In this case only *(MW-AS)* was used as microbial source. Conditions used for various experiments for optimization of process parameters through variation of individual process parameters are provided in Table 4.4.

Table.4.4) Conditions for various experiments conducted for variation in individual process parameters for batch MFC study with glucose and glutamic acid solution:

Experiment	Values of variable parameter	Values of fixed parameters
Effect of anodic pH	5, 6, 7, 8	Initial COD 1500 mg/l, temperature 35 ± 1 ^{O}C, microbes from (*MW-AS*), time 8 days
Effect of initial COD (mg/l)	500, 1000, 1500, 2000	Anodic pH 7 ± 0.2, temperature 35 ± 1 ^{O}C, microbes from (*MW-AS*), time 8 days
Effect of mediator, Methyl blue (mM)	0,0.2, 0.3, 0.4	Anodic pH 7 ± 0.2, temperature 35 ± 1 ^{O}C, initial COD 1500 mg/l, microbes from (*MW-AS*), time 8 days

For multivariable optimization and modelling of the process total 17 nos. of experiments, as shown in Table 4. were conducted. The experimental data were used to regress mathematical expressions correlating voltage generation and current density production with the process parameters and to find out a suitable expression through ANOVA using Design Expert software as well as to get the optimum conditions. Errors on generation were computed.

RESULTS AND DISCUSSION

This chapter covers the discussion and interpretation of results of the present investigation.

In this chapter we determined the effect of initial COD concentration, effect of initial pH, and effect of mediator concentration on production of electricity and wastewater treatment and optimization of these parameters also have been discussed through Design of experiment.

5.1) Effect of process parameters on the production of electricity and removal of organics:

The effects of initial COD concentration, pH and mediator concentration on the simultaneous generation of electricity and COD removal are described below:

5.1.1) Effect of initial COD on the production of electricity and %COD removal:

Experiments were carried out to find out the effect of initial COD concentration on the simultaneous production of electricity and COD removal from synthetic wastewater. The results on the electricity generation and COD removal are shown in Figure.(a),(b),(c) and (d).
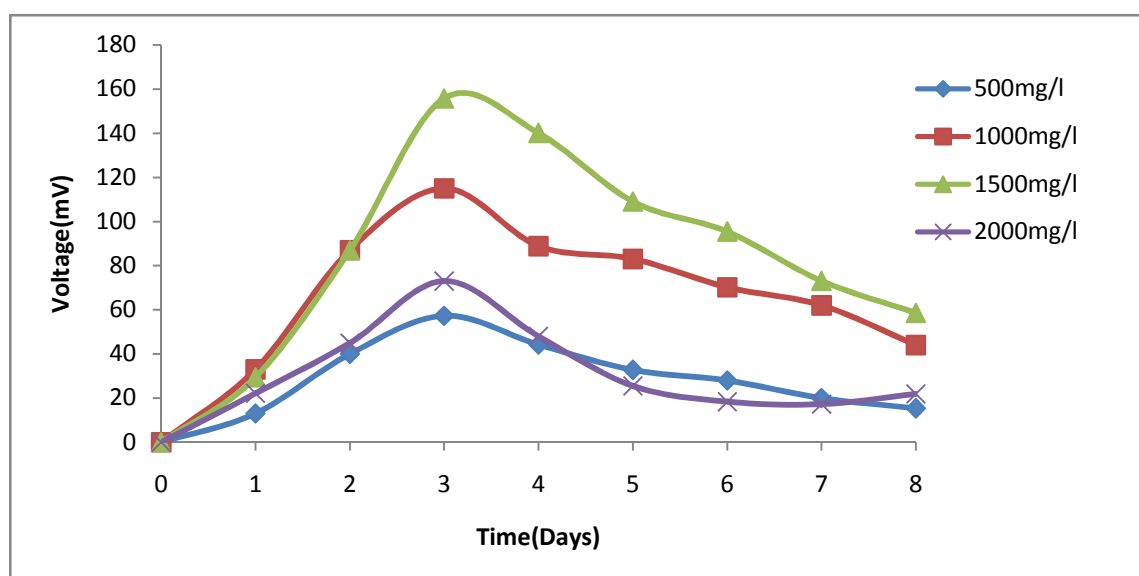
Fig. (a)
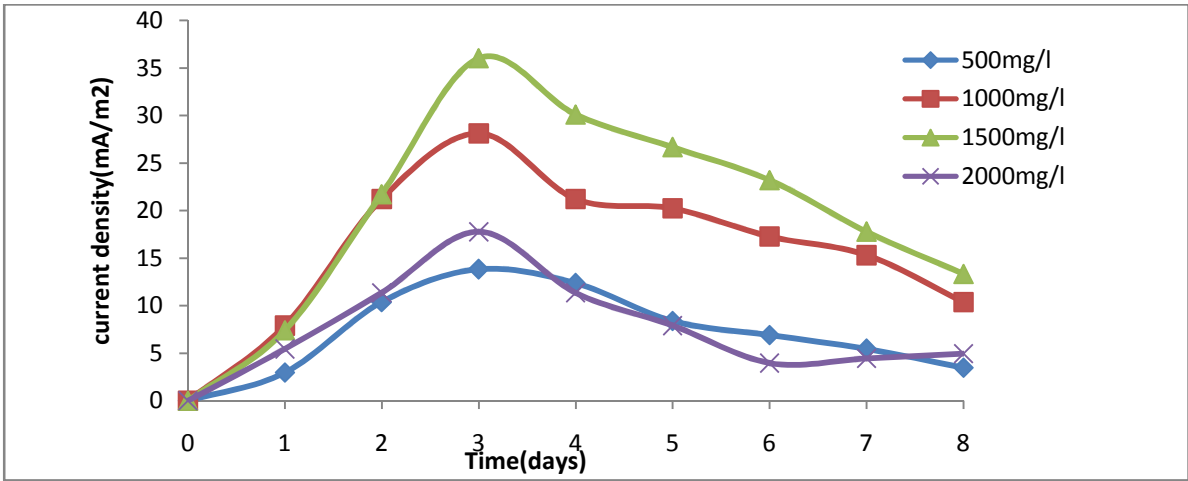
Fig (b)
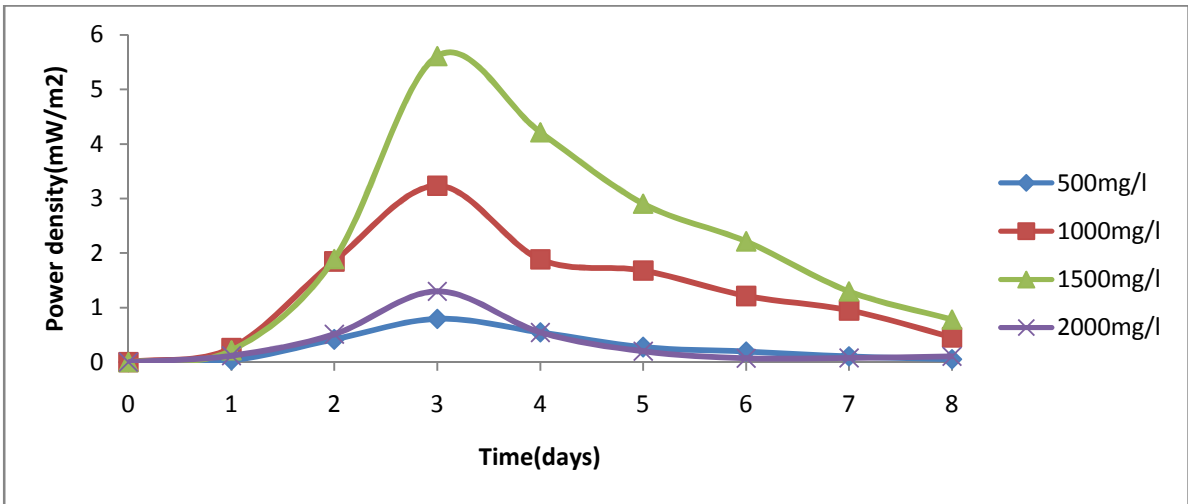
Fig (c)
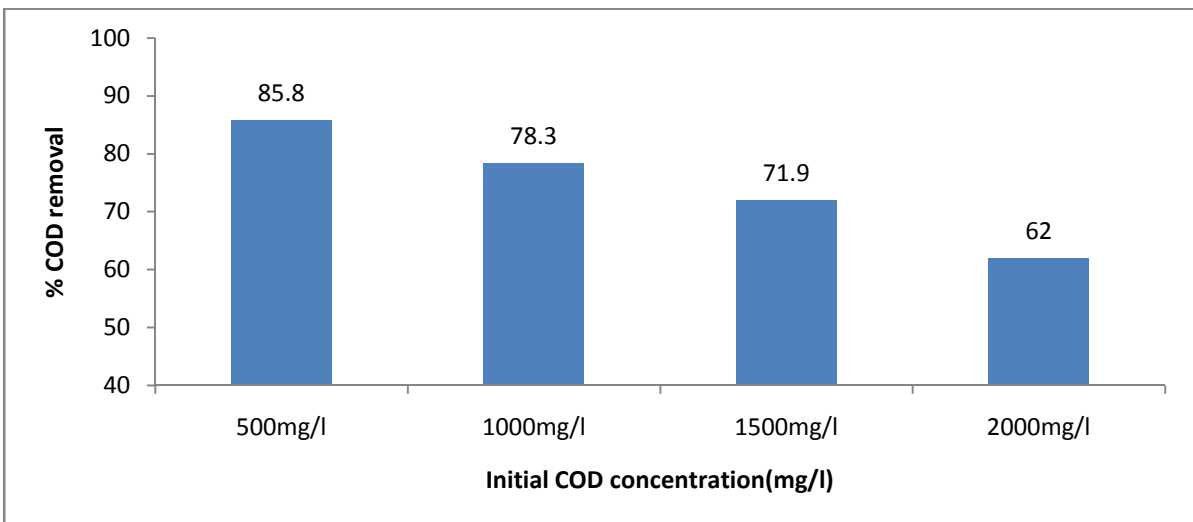
Fig (d)

Fig.5.1:Effect of initial COD on electricity generation and simultaneous removal of COD, (a) voltage generation, (b) current density generation, (c) power density generation, (d) %COD removal (Conditions: anodic pH 7 ± 0.2, temperature 35±1^OC, microbes from(*MW-AS*))

From above Figures the following points are evident.

(i)   Initial COD concentration of around 1500 mg/l gives maximum voltage, current density and power density.

(ii)   For all the initial concentration of COD voltage, current density and power density generation increase with increase in time and become maximum at around 3-4 days of operation and decrease thereafter.

(iii)   With increase in initial substrate concentration the % removal of COD deceases.

The increased biomass can reduce the conductivity of the solution due to the more consumption of trace ions from the solution. Through SEM images of electrode and FESEM images of proton exchange membrane shown in Fig. 5.2 and Fig. 5.3, it seems that some layer of biomass is formed on the electrode surface.
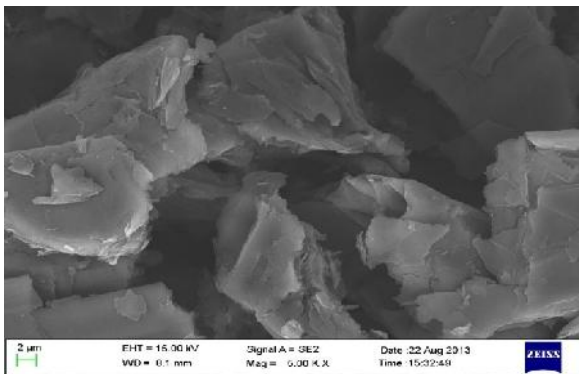
Fig. (a)
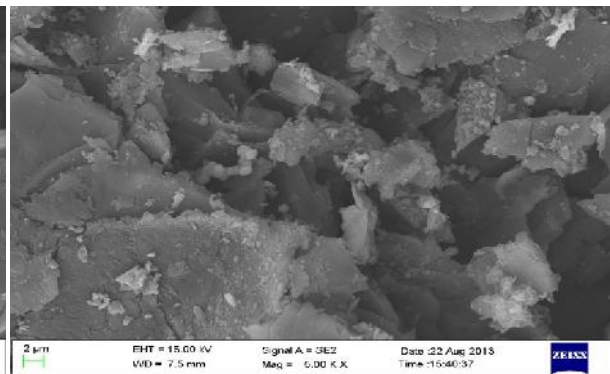
Fig. (b)
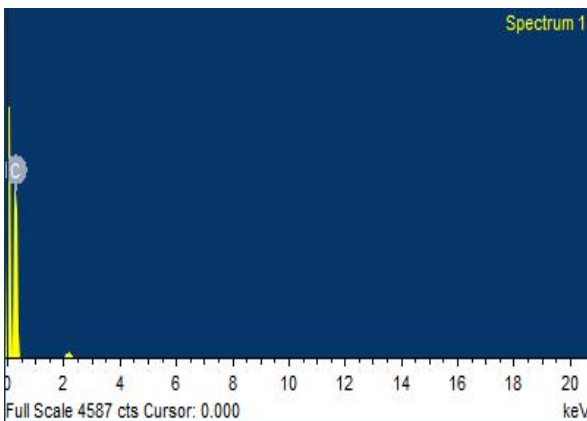
Fig.(c)
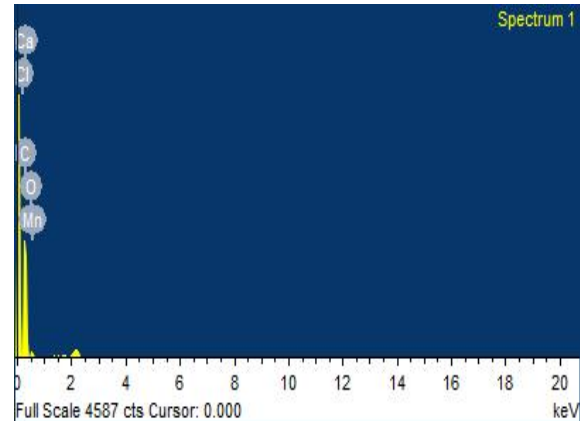
Fig. (d)

Fig. 5.2: SEM and EDAX spectra of the electrode (a) SEM before application, (b) SEM after application, (c) EDAX spectra before application , (d) EDAX spectra after application.
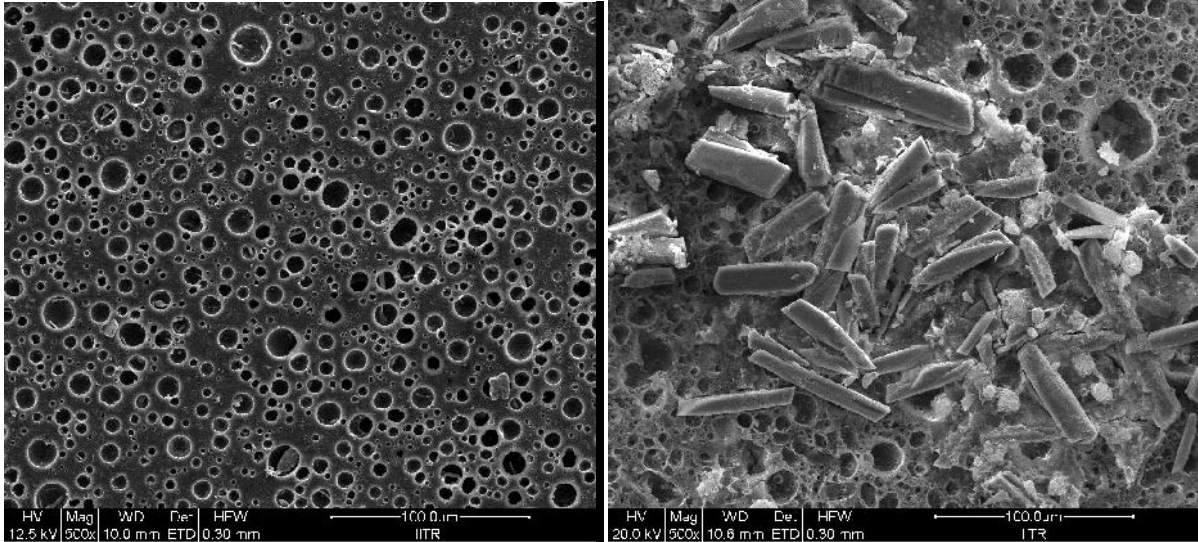

Fig. (a)

Fig. (b)
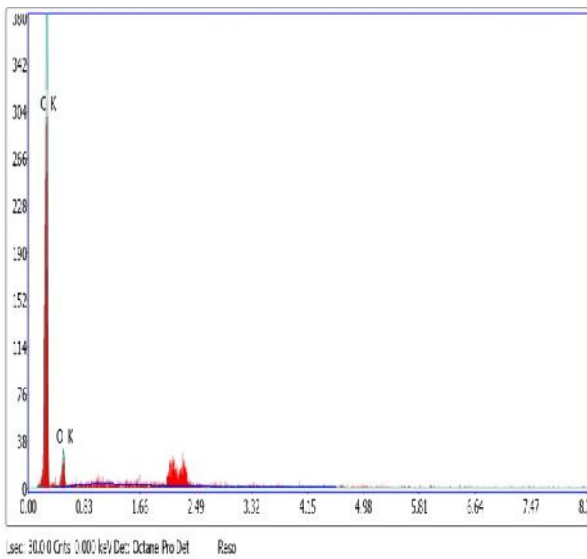
Fig. (c)
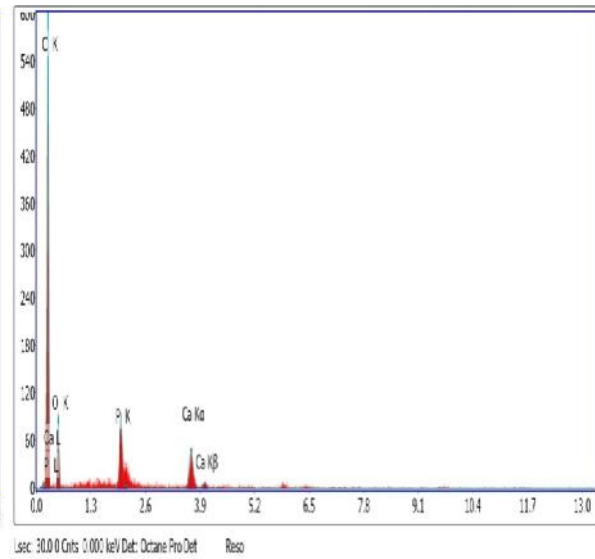
Fig. (d)

Fig.5.3: SEM and EDAX spectra of the membrane (a) FESEM before application, (b) FESEM after application, (c) EDAX spectra before application , (d) EDAX spectra after application.

Comparison of the EDAX spectra of the electrode before and after utilization in MFC as shown in Fig.5.2 (c) and Fig.5.2 (d) and EDAX spectra of proton exchange membrane before and after utilization shown in Fig.5.3(c) and in Fig5.3(d) respectively show the attachment of constituent of trace minerals and buffer solutions with the biomass on the surface of the electrode and proton exchange membrane. Due to the increase in electron and H^+ ion production at higher COD value and also the increase in resistance due to decrease in conductivity as well as increase in biomass.

5. 1.2) Effect of initial pH on the electricity generation and %COD removal

Experiments were carried out to find out the effect of initial pH on the simultaneous production of electricity and COD removal from synthetic wastewater. The results on the power generation are shown in Fig. 5.2.1 (a), (b), (c) and (d) are shown below:
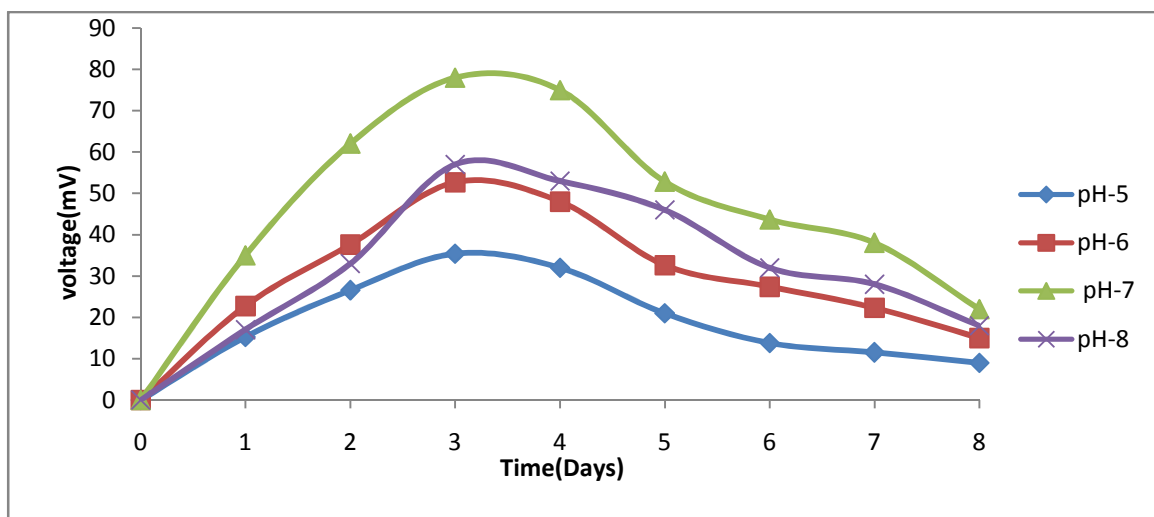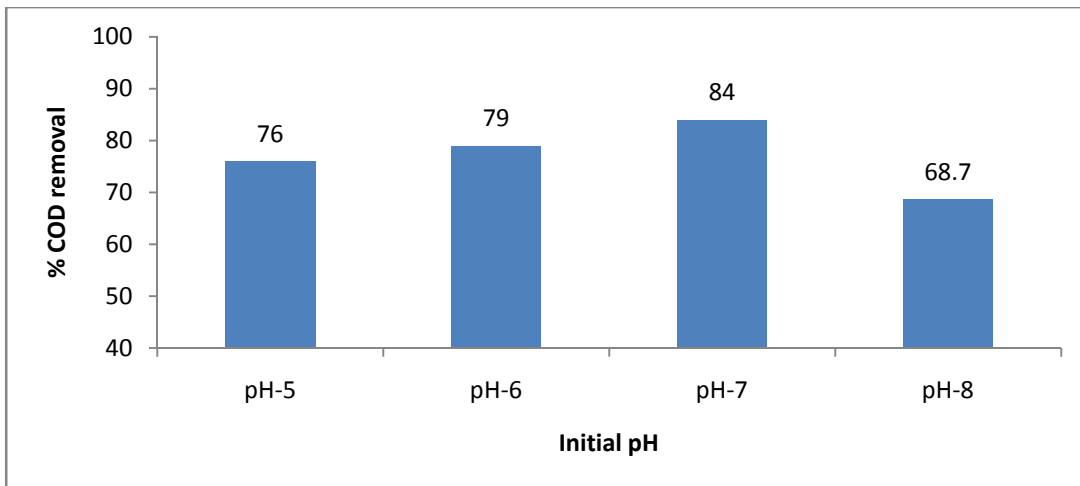

(a)
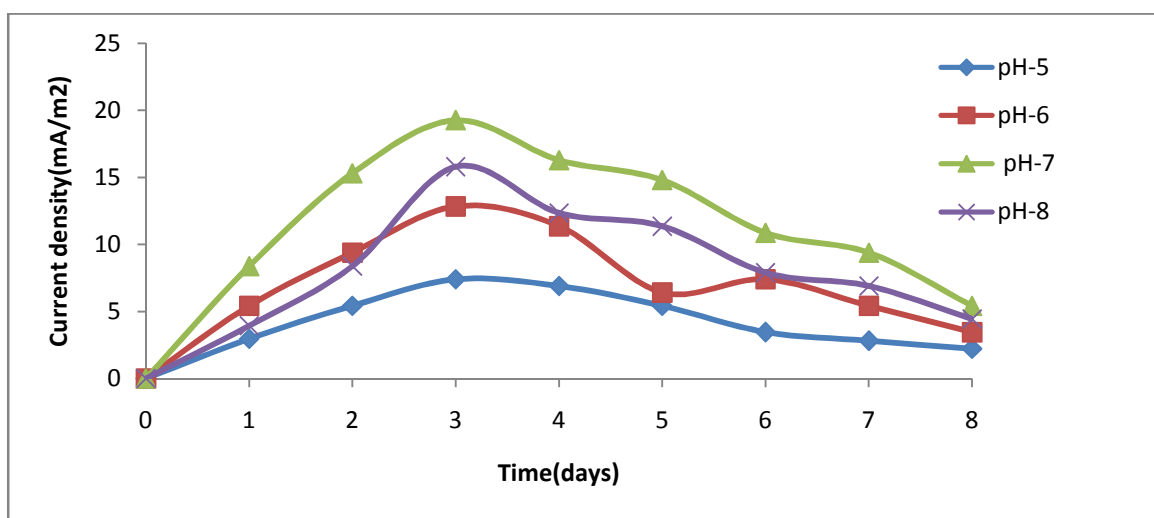
(b)
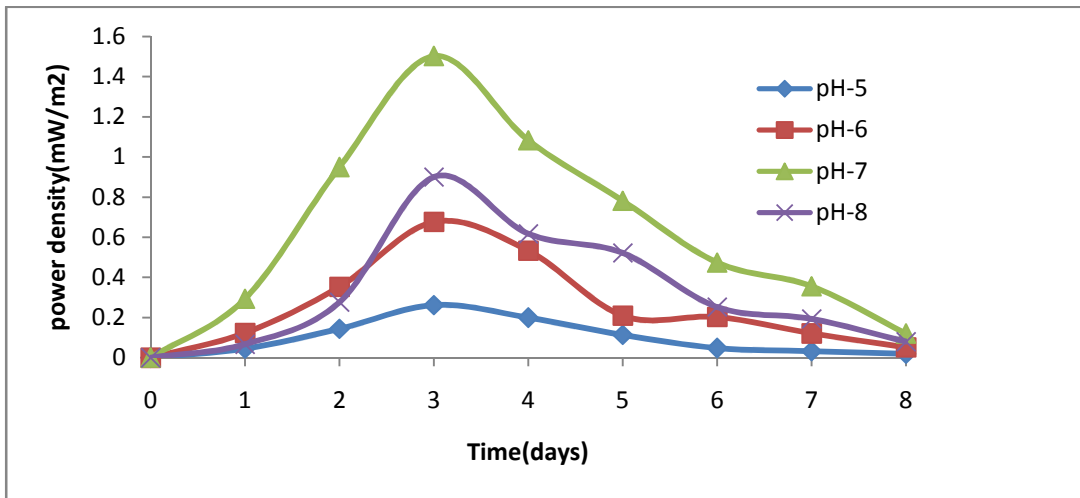
(c)

(d)

Fig:5.4 Effect of initial pH on (a) Voltage (b) Current density (c) Power density (d) COD reduction and pH difference between anodic chamber (Conditions: Initial COD 1500 mg/l, temperature $35 \pm 1^{O}C$, microbes from (MW-AS))

From Fig.5.4 the following observations are noted.

(i)   Initially voltage, current density and power density generation gradually increases with increase in pH, reaches maximum value at the anodic pH value of around 7 and decreases thereafter. Expect pH 7 the voltage, current density and power density generation does not sustain after 3-4 days of operation.

(ii)   % removal of COD increases with increase in pH and reaches maximum value at the pH value of 7 and decreases thereafter.

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Observations reported in points attributed to the fact that microbial growth is highly susceptible to solution pH. The favourable pH for the growth of microbes present in the *(MW-AS)* seems to be around 7. The *Pseudomonas stutzeri* and *Micrococcus species* can survive in the pH range of 5-11 and 7-11 however the pH for optimum growth of these microorganism is 6-8 respectively.
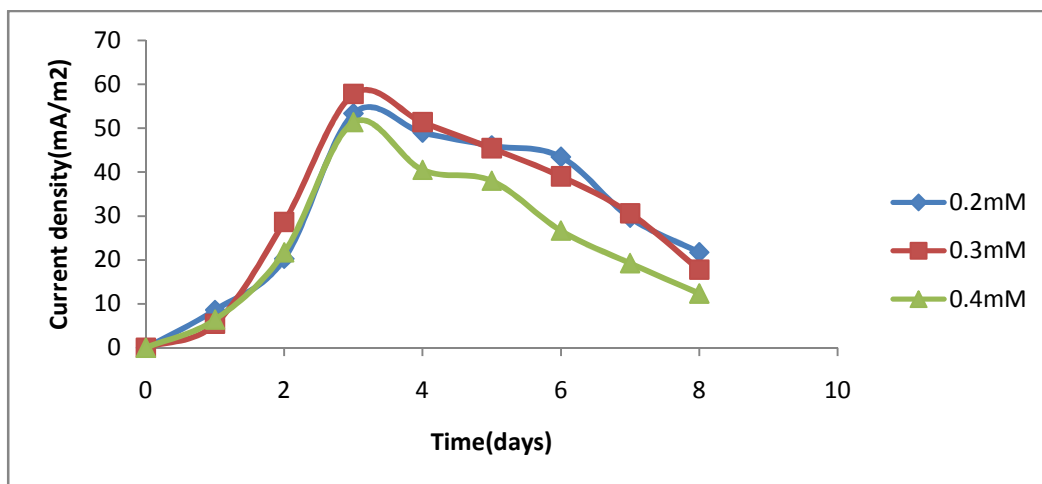
5.1.3) Effect of mediator concentration on the electricity generation and COD removal:

Experiments were carried out to find out the effect of mediator concentration on the simultaneous production of electricity and COD removal from synthetic wastewater.
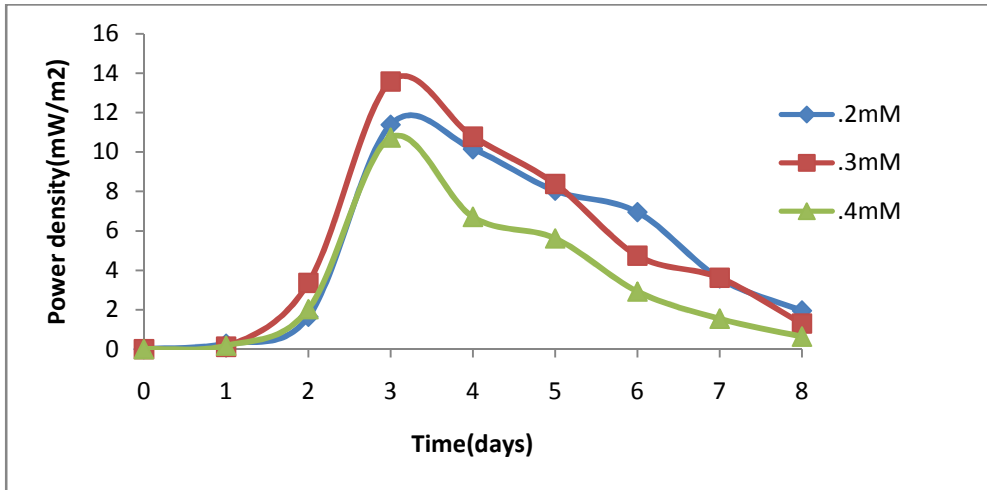
The results on the voltage and power density generation are shown in Fig.5.5 (a), (b), (c) and (d). From Fig. 5.5 the following observations are evident:
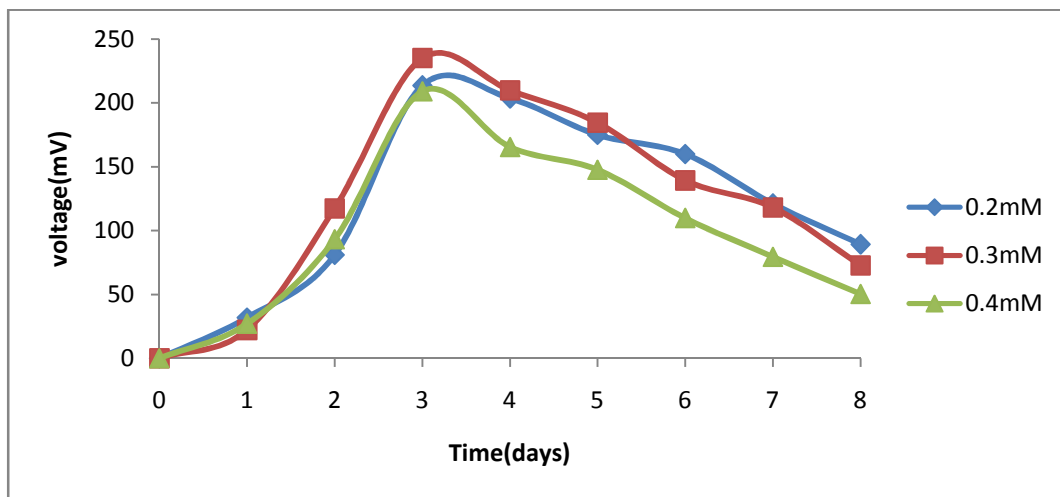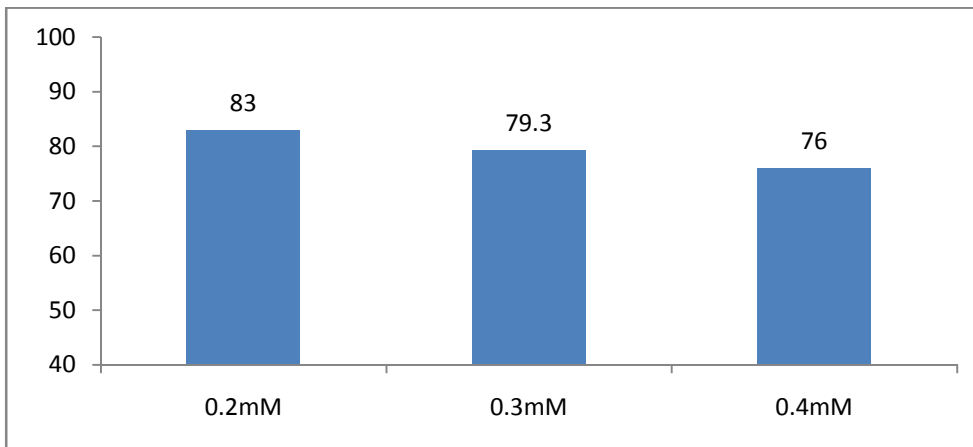

(a)

(b)

(c)

(d)

Fig. 5.5: Effect of mediator concentration on batch scale MFC (a) Voltage (b) Current density (c) Power density (d) COD reduction (Conditions: initial COD 1000 mg/l, anodic pH 7, microbes from (MW-AS)).

(i) Maximum generation of voltage and power density takes place with mediator concentration of 0.3 mM, whereas % removal of COD decreases with increase in mediator concentration.

Mediator facilitates the transfer of free electron produced during the oxidation of organics in MFC, which results increased voltage. Further, the mediator may be used as additional food for the growth of the microbes if the concentration is low and at higher concentration it may have some toxic effects to the microorganisms present in the wastewater and may show some

negative impact on the growth of the microorganisms, which may vary depending upon the concentration of the mediator.

5.2) Optimization of process parameters and modelling of the process:

For optimization, 17 experiments were conducted as per Box- Behnken method as discussed in chapter 4. The results are shown in Table 5.1. Fig.5.3.1 to Fig5.3.6.shows the response surface for variation in voltage production yield (=R1) and current density yield(=R2) with initial COD conc. (=A), initial pH(=B) and mediator conc. (=C).

Table: 5.1: voltage production and current density generation for optimization of reaction condition:

Run	A: substrate concentration	B: pH	C:Mediator (mM)	R1: voltage Generation (mV)	R2:current density (mA/m^2)
1	1000	6	0.3	136	79.0
2	1500	7	0.3	202.68	87.9
3	1000	8	0.3	170.44	80.5
4	2000	8	0.3	136.12	59.7
5	1500	7	0.3	203	87.9
6	1500	7	0.3	203	87.9
7	1000	7	0.4	175.22	67.6
8	1500	8	0.2	167.2	81.9
9	1500	8	0.4	140	75.5
10	1500	6	0.2	166.66	81.9
11	1500	7	0.3	203	90.3
12	1000	7	0.2	178.16	82.9
13	2000	6	0.3	121.63	57.7
14	2000	7	0.4	140.8	58.7
15	2000	7	0.2	143.88	62.7
16	1500	6	0.4	163.76	66.1
17	1500	7	0.3	203	87.9

Tables.5.2 and Table.5.3 shows the model summary statistics, which shows the reason for choosing quadratic model over any other model. The model having the maximum value for adjusted R-squared and predicted R-squared will be our choice.

Table: 5.2: Model summary statistics for voltage generation:

Model	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	
Linear	28.57132	0.156454	-0.03821	-0.29567	
2FI	32.19478	0.176098	-0.31824	-1.27883	
Quadratic	**10.51064**	**0.93853**	**0.937498**	**0.906578**	**Suggested**
Cubic	0.143108	0.999993	0.999974		Aliased

Table 5.3: Model summary statistics Current density:

Model	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	
Linear	0.201642	0.402352	0.264434	0.079186	
2FI	0.225011	0.427538	0.084061	-0.56846	
Quadratic	**0.042594**	**0.98564**	**0.967178**	**0.932894**	**Suggested**
Cubic	0.022361	0.997739	0.990955		Aliased

From Table.5.2 and Table.5.3, it is shown that quadritic model has maximum adjusted R-squared value, and maximum predicted R-squared value. Also, quadratic model has predicted R-squared value of **0.906578** and **0.932894** for voltage production and current density which shows much deviation from linear model value. So quadratic model was the chosen as it exhibits low standard deviation and high adjusted R-squared value (near to 1).

Table.5.4 and Table.5.5 shows the estimated values of regression coefficients for various factors for voltage production and current density generation respectively.

Table 5.4: Estimated values of regression coefficients for various factors

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	202.936	1	4.700503	191.8211	214.0509	
A- substrate con	-14.6738	1	3.716074	-23.4609	-5.88663	1
B-pH	3.21375	1	3.716074	-5.57337	12.00087	1
C-mediator	-4.515	1	3.716074	-13.3021	4.272119	1
AB	-4.9875	1	5.255322	-17.4144	7.439362	1
AC	-0.035	1	5.255322	-12.4619	12.39186	1
BC	-6.075	1	5.255322	-18.5019	6.351862	1
A^2	-30.8893	1	5.122255	-43.0015	-18.777	1.005882
B^2	-30.9993	1	5.122255	-43.1115	-18.887	1.005882
C^2	-12.5318	1	5.122255	-24.644	-0.41954	1.005882

Table.5.5: Estimated values of regression coefficients for various factors for current density production:

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	1.79	1	0.019049	1.744957	1.835043	
A- substrate con	-0.18	1	0.015059	-0.21561	-0.14439	1
B-pH	0.0325	1	0.015059	-0.00311	0.06811	1
C-mediator	-0.105	1	0.015059	-0.14061	-0.06939	1

AB	0.0025	1	0.021297	-0.04786	0.05286	1
AC	0.0575	1	0.021297	0.00714	0.10786	1
BC	0.0475	1	0.021297	-0.00286	0.09786	1
A^2	-0.27875	1	0.020758	-0.32783	-0.22967	1.005882
B^2	-0.10875	1	0.020758	-0.15783	-0.05967	1.005882
C^2	-0.13375	1	0.020758	-0.18283	-0.08467	1.005882

Final Equation in Terms of Coded Factors and Actual Factors for Response R1(voltage generation) shown below:

Equation (1) is Final Equation in Terms of Coded Factors:

R1=202.936 + -14.6737 * A + 3.21375 * B + -4.515 * C + -4.9875 * AB + -0.035 * AC + -6.075 * BC + -   30.8893 * A^2 + -30.9993 * B^2 + -12.5317 * C^2 .... (1)

Equation(2) is Final Equation in Terms of Actual Factors :

R1=-1904.37 + 0.411358 * substrate con + 470.391 * pH + 1133.05 * mediator + -0.009975 * substrate con * pH + -0.0007 * substrate con * mediator + -60.75 * pH * mediator + -0.000123557 * substrate con^2 + -30.9993 * pH^2 + -1253.18 * mediator^2.......................... (2)

Final Equation in Terms of Coded Factors and Actual Factors for Respons R2(current density):

Equation (3) is Final Equation in Terms of Coded Factors:

R2 =1.79 + -0.18 * A + 0.0325 * B + -0.105 * C + 0.0025 * AB + 0.0575 * AC + 0.0475 * BC + -0.27875 * A^2 + -0.10875 * B^2 + -0.13375 * C^2 .... (3)

Equation (4) Final Equation in Terms of Actual Factors:

R2 =-5.05625 + 0.002605 * substrate con + 1.405 * pH + 1.925 * mediator + 5e-006 * substrate con * pH + 0.00115 * substrate con * mediator + 0.475 * pH * mediator + -1.115e-006 * substrate con^2 + -0.10875 * pH^2 + -13.375 * mediator^2 .... (4)

Table 5.6 and Table 5.7 shows % Error in predicted value of voltage generation and current density obtained using the model as shown in Fig:5.1 and Fig:5.2

Table.5.6: % Error in predicted value of voltage production obtained using the model

Run	Predicted Value	Actual Value	% Error
1	147.52	136	7.809111
2	202.94	202.68	0.128117
3	163.92	170.44	-3.97755
4	124.6	136.12	-9.24559
5	202.94	203	-0.02957
6	202.94	203	-0.02957
7	169.715	175.22	-3.24367
8	173.2	167.2	3.464203
9	152.04	140	7.918969
10	154.64	166.66	-7.77289
11	202.94	203	-0.02957
12	178.665	178.16	0.282652
13	128.16	121.63	5.095194
14	140.305	140.8	-0.3528
15	149.395	143.88	3.691556
16	157.76	163.76	-3.80325
17	202.94	203	-0.02957

% Error = 100*(Actual value - Predicted value)/Actual value

The predicted values are plotted against actual value in the Figure below. Error % varies between -7.772% to 7.918969.
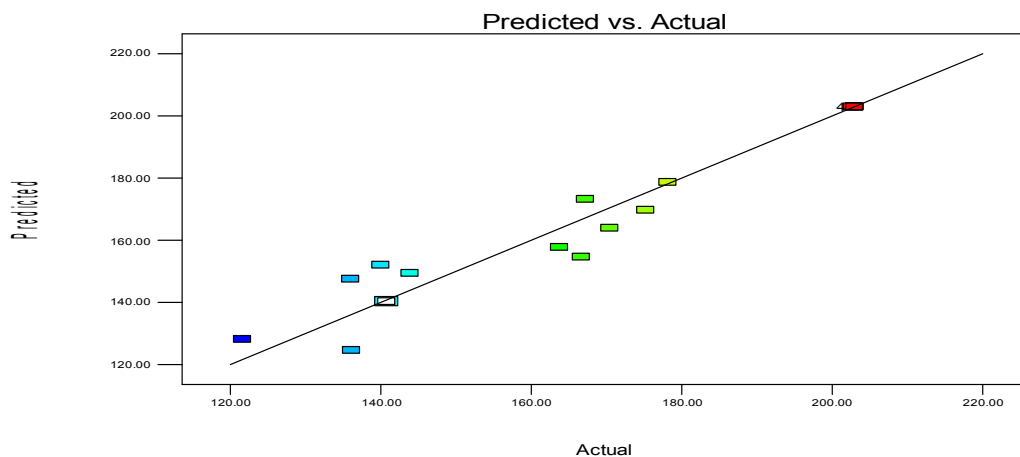
Figure 5.1: Predicted value vs. Actual value

Table.5.7: **% Error in predicted value of current density obtained using the model:**

Run	Predicted value	Actual value	% Error
1	1.5505	79.0	-3.193
2	1.79	87.9	0.559
3	1.6095	80.5	-1.274
4	1.2545	59.7	3.547
5	1.79	87.9	0.559
6	1.79	87.9	0.559
7	1.403	67.6	2.352
8	1.635	81.9	-1.529
9	1.529	75.5	-0.065
10	1.665	81.9	0.300
11	1.79	90.3	-2.235
12	1.717	82.9	2.155
13	1.1855	57.7	1.307
14	1.157	58.7	-2.852
15	1.243	62.7	-2.172
16	1.371	66.1	2.261
17	1.79	87.9	0.559

The predicted values are plotted against actual value in the Figure5.16. %Error varies between-3.193% to 3.547 %.
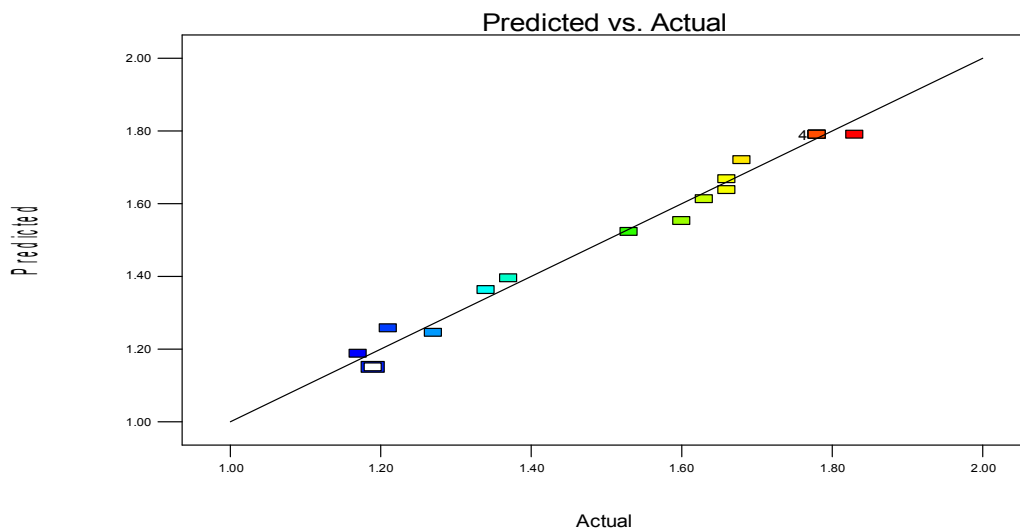
Figure 5.2: Predicted value vs. Actual value

5.3)   3-D response surfaces of voltage generation and current density are given in section 5.3.1 and 5.32 respectively.

5.3.1) 3-D Response surfaces for voltage generation (Response:R1):

3-D Response surface parametric interactions for voltage generation and current density from synthetic glucose-glutamic acid solution for multi-parameter variation are shown below:
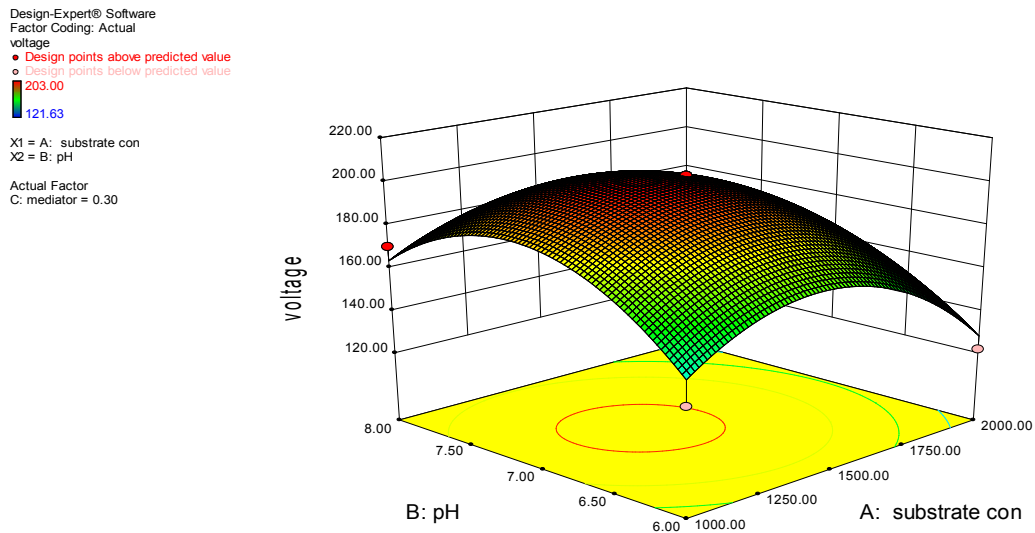
Figure: 5.1: Response surface for variation in voltage generation with respect to pH and substrate conc. at mediator conc. = .30
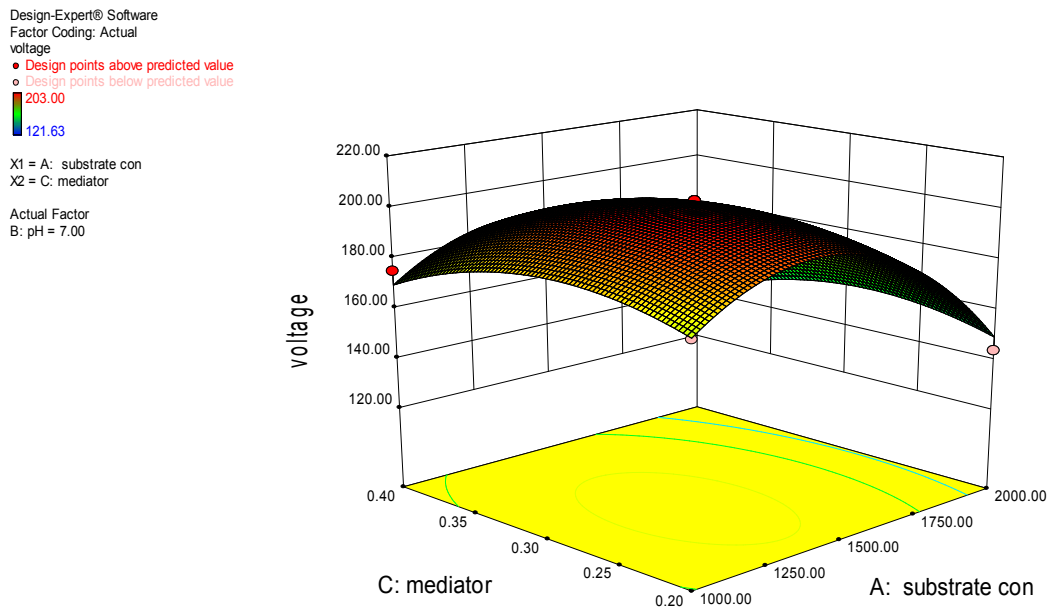
Figure 5.2.: Response surface for variation in voltage generation with respect to Mediator conc. and substrate conc. at pH=7.0
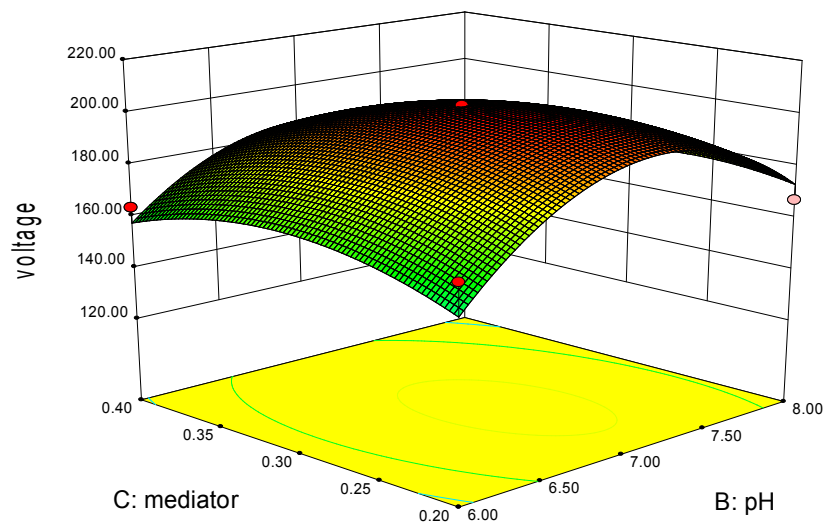
Figure 5.3: Response surface for variation in voltage generation with respect to
Mediator conc. and pH at substrate conc.:1500

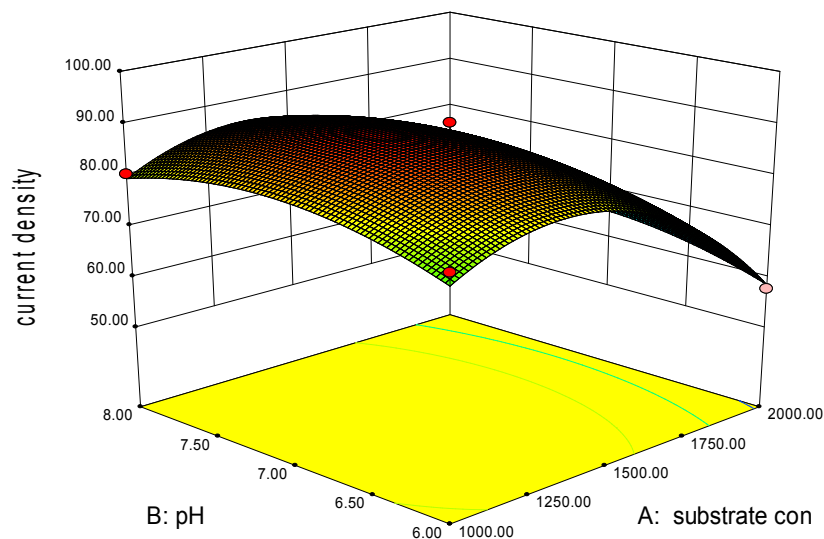### 5.3.2)   3-D Response surfaces for Current generation (Response: R2):

Figure 5.4: Response surface for variation in current density (mA/m^2) with respect to
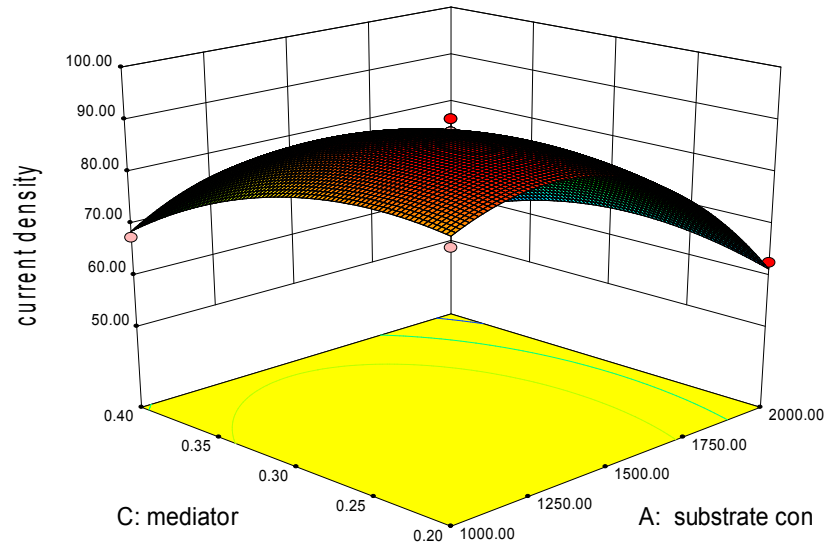pH and substrate conc. at mediator conc. 0.30

Figure5.5: Response surface for variation in current density (mA/m^2) with respect to pH and substrate conc.(mg/l) at pH=7
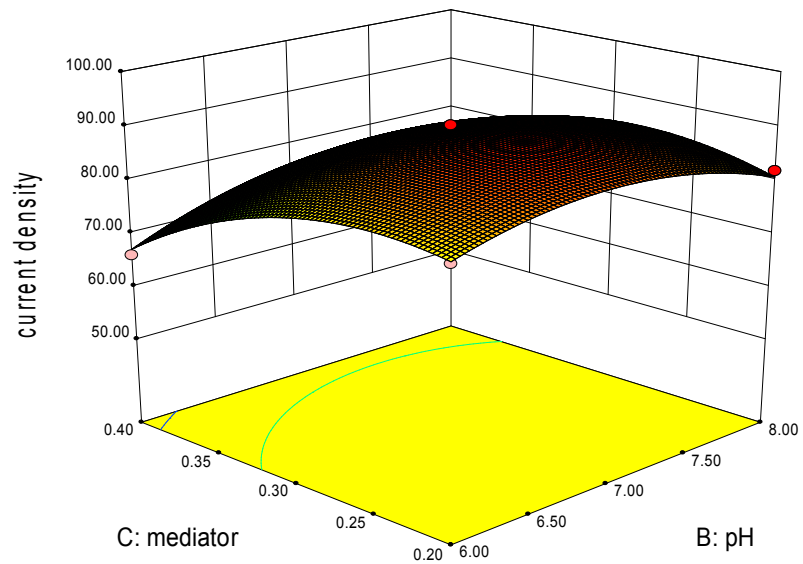

Figure5.6: Response surface for variation in current density (mA/m^2) with respect to Mediator conc. and pH at substrate conc. 1500mg/l

5.4: Comparison between voltage generation through PEMMFC and salt bridge MFC:

Values of voltage production through PEM-MFC and MFC using salt bridge for given parameter shown in Table: 5.8 below:

Table: 5.8 Comparison between PEM-MFC and salt bridge-MFC for voltage production:

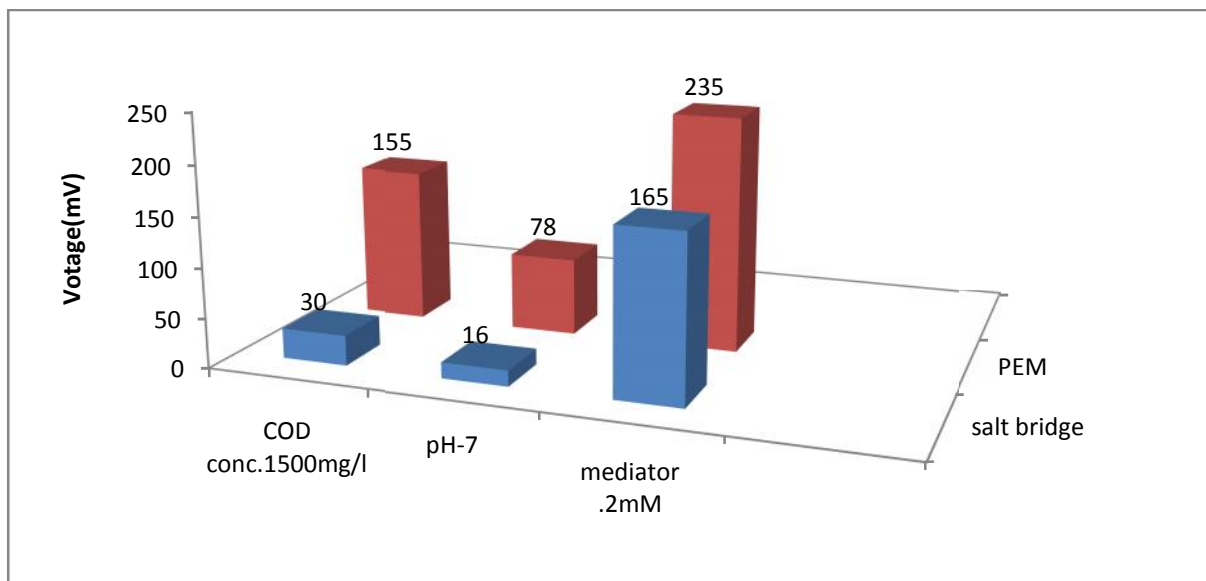|	Mediator conc. (= .2 mM)	Initial COD conc. (=1500mg/l)	pH (7)
Salt-bridge	165mV	30mV	16mV
PEM	235mV	155mV	78mV

Fig: voltage production through salt bridge MFC and proton exchange membrane fuel cell at constant initial COD conc.(1500mh/l), pH(7) and mediator conc.(.2).

Data from above table showing that voltage production through salt-bridge MFC is less than that of the PEM-MFC at constant process parameters, because the internal resistance of salt-bridge system is much higher than that of the PEM-MFC.

CONCLUSION AND RECOMMENDATION

6.1) Conclusion

Performance of proton exchange membrane MFC from synthetic wastewater was investigated in this experiment.

- The cation exchange capacity and conductivity of prepared low cost sulfonated polystyrene membrane of thickness 0.025mm after characterization have been determined 2.85meq/g and 2.57μScm^{-1} respectively.

- Microbes present in municipal wastewater sludge (MW-AS), collected from JagJitapur, Haridwar, can produce more electricity than *E-coli MTCC 42* and *Pseudomonas Fluorescence 103*.

- Addition of 0.3mM methyl blue as extraneous mediator improves the electricity generation capacity of the glucose-glutamic acid MFC.

- The optimum values of process parameters have been determined 1500mg/l for initial COD concentration, 7 for pH and 0.3mM for mediator concentration.

- The maximum % COD removal efficiency at optimum value of process parameters have been achieved 85.7%, 83.4% and 84.6% at an external resistance of 50 Ω for Initial COD concentration, mediator concentration and Initial pH difference respectively.

- At optimum values of process parameters the maximum voltages output of 155mV, 78mV and 235.6mV and a maximum power density of 5.6 mW/m^2 , 1.5mW/m^2 and 13.57mW/m^2 have been achieved for Initial COD concentration (1500mg/l), Initial pH(7) and at Mediator concentration(.3mM) respectively.

6.2) Recommendation:

On the basis of present search it will be useful, for the promotion of knowledge, if the following investigations are carried out:

- Investigation on the improvement in electricity generation for series connection of batch MFCs.

- Column study for same process parameters for same polymeric membrane.

- Investigation on batch/column system with Electrode modification.