

# Evaluation of paper recycling wastewater treatment accompanied by power generation using microbial fuel cell

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## Abstract

This study investigates the feasibility of using cathode catalyst (Iron phthalocyanine (FePc) combined multi walled carbon nano tubes (MWCNT) and compares the oxygen reduction rate under different conductivity of catholite solution (50 mM, 100mM) in double chamber Microbial Fuel Cell. Microbial fuel cell (MFC) research is going on for few decades to increase the power density and improve the removal efficiency. Iron phthalocyanine (FePc) combined multi walled carbon nano tubes (MWCNT) cathode catalyst showed the highest power density (9.34 W/m<sup>2</sup>) in 100 mM PBS than 50 mM (7.58 W/m<sup>2</sup>). The electrodes are characterized by scanning electron microscopy (SEM) and the electrocatalytic activity of the catalyst coated electrodes were examined by cyclic voltammetry(CV). The high power density indicates a potential alternative to precious platinum metal catalyst in treatment as well as electricity production Microbial Fuel cell.

**Keywords:** Iron phthalocyanine, Multiwalled carbon Nano Tubes, electrocatalytic, conductivity.

## 1. Introduction

Energy is the prime mover of economic growth of a country's economy. Future economic growth significantly depends on the extensive availability of energy sources. Previous works says the treatment efficiency is mainly limited wastewater conductivity (Bruce E Logan et.al., 2008). Different types of wastewater have been successfully treated by MFC (Velasquez-Orta, 2011). Bacteria in an MFC grow under anoxic condition which can benefit cellulose fermentation and degradation with the added benefits of electricity generation rather than power consumption (Logan et al., 2008). Wastewater contains lot of easily degradable organic matter which are metabolized by the active bacterial species present in wastewater itself and produces electricity during the course (Jang et al., 2004) In a double chambered salt bridge MFC, the sludge organic matter is oxidized with simpler compound in the anode chamber (Mohan et al., 2008) The fuel cell performance is based on the fuel transport to the microorganisms and metabolic activity and examined the

effectiveness of MFC using Membrane Electrode Assembly (MEA) (Lovely et al., 2003). A chamber MFC for anode material up gradation is an important parameter (Rabaey et al., 2006).

Performance of SCMFC on Nafion<sup>®</sup> 117 and SPSEBS (polymer) membrane are compared using Pt catalyst (Dharmalingam et al., 2012). The use of Manganese-polypropylene-carbon nano tube (Mn-PPY-CNT) has been demonstrated to have potential to replace platinum (Pt) in oxygen reduction rate (ORR) (Lu et al., 2013). However, platinum metal as an expensive catalyst while scale up the reactor, a more cost effective MnO<sub>2</sub> with activated carbon can replace Pt (Chandra et al., 2013; Zhu et al., 2013). Ammonia treated activated carbon presence of peat increases the nitrogen functional group improves the ORR activity (Logan et al., 2013). Polyaniline-Iron-carbon (PANI-Fe-C) having specific surface area (228.3 m<sup>2</sup>/g) lesser than Pt (733.9 m<sup>2</sup>/g) but power density is high due to its chemical structure (Li et al., 2013)

In present study shown, Pt free catalyst is chosen for economic point of view. Recently, use of MWCNT/FePc catalyst particle having significance of ORR in MFC. Electrocatalytic activity of the MWCNT supported FePc compared with bare graphite felt. Performance of the MWCNT/FePc catalyst in MFC was due to four electron path way (Yong et al., 2011). The composite catalyst having potential in ORR comparable to platinum & many researches have been conducted to develop a new non-noble metal as an electro catalyst to replace or reduce the amount of Pt (Zhao et al., 2005; Ahmed et al., 2012; Birry et al., 2011; Yong et al., 2011).

## 2. Materials and Methods

### 2.1 Electrode preparation

Catalytic ink is prepared by dispersing the catalyst in isopropyl alcohol solvent followed by mixing 10 % Nafion (5% wt Nafion from Sigma Aldrich) solution for total weight of catalyst to bind the catalyst with electrode. The catalytic ink is sprayed over the electrode and dried for 70 °C to evaporate the solvent. By the above said method graphite felt is modified as (FePc/MWCNT) catalyst coated electrode. Multiwalled carbon nanotubes (MWCNT (>80%

pure, Nano shell, USA), Iron phthalocyanine (FePc, Sigma–Aldrich) MWCNT has a surface area of 90–350 m<sup>2</sup>/g with a diameter of 20–30 nm and length of 5–1µm. FePc has a carbon and Nitrogen content of 67.3% & 19.5% respectively 657nm.

## 2.2 MFC construction and operations

Double chambered Microbial fuel cell (DCMFC) is constructed as reported previously (Limson *et al.*, 2014). Anodic and cathodic chambers are separated by PEM (Nafion<sup>®</sup>117, Dupont & co) membrane of size 2.5 cm diameter (Area 4.906 cm<sup>2</sup>), both chambers are made of borosilicate in cylindrical shape with volume of 250 ml each. PEM is held by clamp between two flattened chamber Interspace with air tight gasket. The spacing between anode and cathode are maintained as 12 cm. Anode carbon cloth (3cm x 3cm) and cathode graphite felt (3cm x 3cm) (sienergy fuel cell store, India) connected by copper wire with an external resistor 66 Ω to the multimeter. Anolite of Paper recycling wastewater with inoculum and catholyte of PBS (50 mM, 100mM) with

**Table 1.** Characteristics of paper recycling wastewater

Parameters	Units	Average value
BOD <sub>5</sub>	mg/l	615
COD	mg/l	1792
Chlorides	mg/l	257
Oil and Grease	mg/l	78
pH		7.12
TSS	mg/l	158
TDS	mg/l	1428
Sulphates	mg/l	85
Colour		Turbid

## 2.3 Analysis

Cyclic voltammetry is recorded at a scan rate of 50 mV/s over the potential window from +0.5 to -0.5 V. Electrochemical tests of the electrodes are done using 3 electrode setup by using Pt working electrode and Ag/AgCl reference electrode. The voltage across the external resistor is monitored with 10 hrs intervals using multimeter. Surface morphology is done by SEM analysis for catalyst coated and bare graphite felt. Power density and substrate degradation are considered as the two Main parameters to estimate the performance of fuel cells. Current production is calculated by Ohms law  $V=I \times R$  where I-Current in ampere, V-Voltage in volts, R-Resistor in Ω, Power output (P) = I x V where power in Watts, Current density (C.D) =  $I_{max}/A$ , Power Density (P.D) =  $P_{max}/A$  where A-surface area of the electrode. Columbic efficiency (CE) is calculated from the formula given below

$$CE = \frac{8 \cdot \int_0^t I dt}{F \cdot V \cdot \Delta COD} \quad (1)$$

Where F is the Faraday constant, I is the harvested current, V is the volume anode, and 8 are the grams per electron in oxygen. Chemical Oxygen Demand (COD) was measured from wastewater by standard methods (APHA) open reflux

potassium permanganate are used. The pH is maintained as 6.9 by adding NaOH or HCl. Paper recycling wastewater collected from the collecting tank after primary clarifier and stored below 4 °C until its use. Characteristics of wastewater are summarized in Table 1. Mixture of Sludge and soil collected from the paper recycling mill is used as an inoculum. Every time the reactor solution should be replaced, when the voltage dropped 50 mV and some quantity should be left in the reactor to inoculate the next cycle wastewater treatment. Anode and cathode chambers are maintained in anaerobic condition and aerobic condition respectively. The cathode chamber is aerated by fish tank aerator. The total setup was operated at room temperature at 29 °C in a fed batch mode. Before starting up the experiment both compartments are sterilized by autoclave for 20 minutes. The Nafion<sup>®</sup>117 membrane is pretreated with hydrogen peroxide solution followed by distilled water each one hour and the electrodes are pretreated by soaking in 1M HCl followed by 1N NaOH for whole night before giving a catalyst coating.

method. Total dissolved solids total solids are also measured according to standard methods (Rabaey *et al.*, 2006) and Biochemical Oxygen Demand were measured by the standard methods.

## 3. Results and Discussion

### 3.1 Electrode Morphology

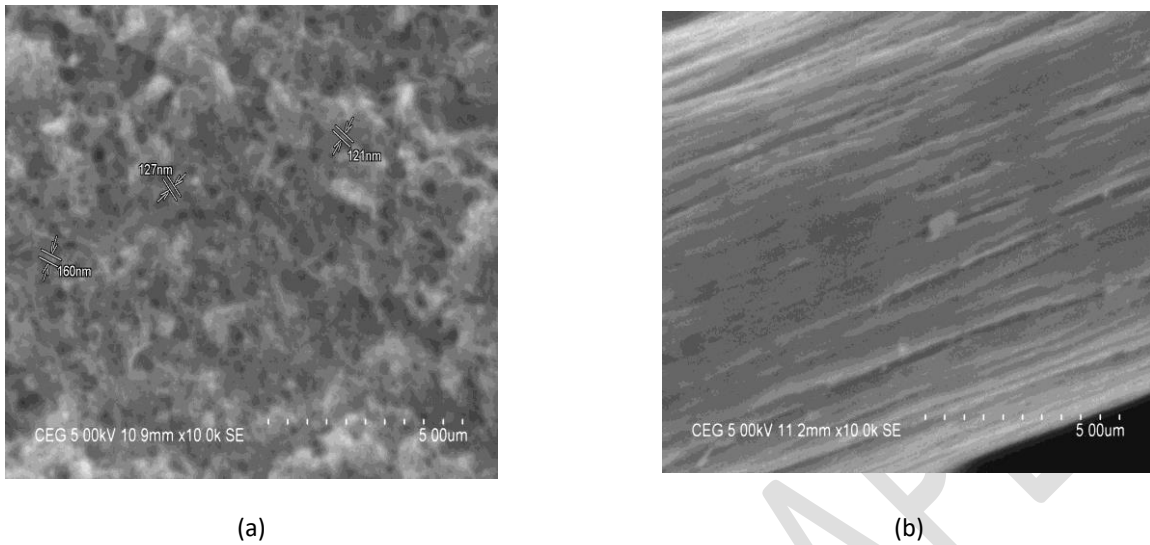
Surface morphology of catalyst coated electrode is analyzed by scanning electron microscope (SEM) at 5 KV. From the SEM images, The FePc is dispersed over the MWCNT at the external pores of coatings indicated in the Fig. 1a. Surface of bare graphite felt is very smooth (shown in Fig. 1b). MWCNT powders absorbed on the surface of FePc coated electrodes which improves the oxygen reduction rate. Different types of bacterial attachment are identified, which acts as a biocatalyst and assist the transfer of electrons from anolite to electrode.

### 3.2 Electrocatalytic characterization

From the readings of Cyclic Voltammetry (CV) is an enhancement in the electrocatalytic properties of various electrodes. Fig 2 shows that the CV of different nano composite electrodes at the scan rate of 10 mVs<sup>-1</sup>. In the present study compare the Electrocatalytic activity of FePc/MWCNT and bare graphite felt (GF) are compared in

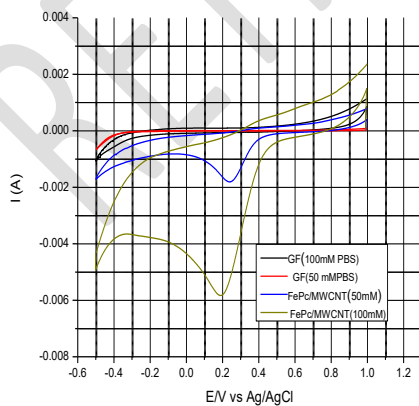
100 mM and 50 mM PBS with 5 Mm. Potassium permanganate electrolyte are compared under oxygen saturated condition. The electrode FePc/MWCNT produced maximum of peaks on CV, with +0.18V in 100

mM PBS at the scan rate of  $10 \text{ mV s}^{-1}$ , the peaks were not present in bare GF and MWCNT. The peaks may be due to PcFc effect.



**Figure 1.** SEM images of (a) FePc/MWCNT coated electrode (b) Bare Graphite felt

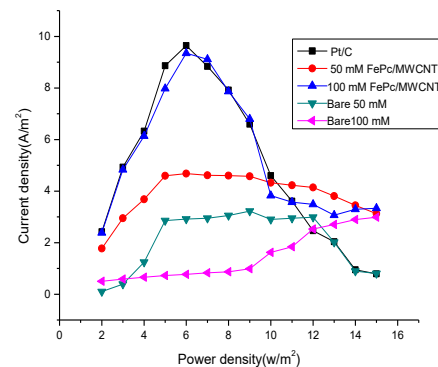
From the previous study the first peak is at +0.12 V and the second peak is at -0.51 V to the CNT on Pt (CNT/Pt) was greater than CNT alone (Ghamesi *et al.*, 2013). The first peak is due to ligands of PcFc and the second peak is due to redox reaction (Ha *et al.*, 1999). MWCNT/FePc produced two peaks, but the peaks were not present in MWCNT (Yuan *et al.*, 2011). The peak potential of +0.19 V for FePc is more positive potential than other electrodes, which proves that the FePc/MWCNT had most effective ORR activity. Electrochemical activity of electrodes is greatly enhanced by associating nitrogen groups in the CNT (Gong *et al.*, 2009). MWCNT enhance the promising ORR activity, however the oxygen reduction potential is further improved by introducing MWCNT with FePc (Yuan *et al.*, 2011).



**Figure 2.** CV characterization of FePc/MWCNT and Bare Graphite felt in 100mM and 50 mM PBS

### 3.3 The performance of MFCs with power density production

Bioelectricity is successfully obtained from a Double chambered Microbial Fuel Cell by using different cathode catalyst inoculated with soil and sludge collected from paper recycling mill premises. Power density versus current density is plotted in graph as shown in Fig 3.



**Figure 3.** Power density versus current density for various electrolyte solutions

The power density of  $9.3 \text{ W/m}^2$  from FePc/MWCNT at 100 mM PBS in a composite catalyst coated is higher than bare electrode. The power density of 50 mM PBS gives  $501 \text{ mW/m}^2$  which is improved by 100 mM PBS to  $672 \text{ mW/m}^2$  and explained the effectiveness of electricity production as well as the treatment of paper recycling wastewater using MFC (Logan *et al.*, 2008). Solution conductivity is a main factor for treatment of paper recycling effluent (Feng *et al.*, 2008). Power density of FePc/MWCNT is comparably equal to the Pt/C cathode catalyst. From the result MWCNT/FePc

will be an excellent alternative to Pt in MFCs. Power density of FePc/KB was higher than FePc/vulcan-XC and slightly higher than Pt also (Yu *et al.*, 2007). Power density obtained from FePc/MWCNT>Bare graphite felt, it shows the MWCNT as a good supporting material than Ketjan Black. Power density of MWCNT/FePc is much higher than the KB/FePc (Yong *et al.*, 2011).

### 3.4 COD removal and columbic efficiency

To analyse the effectiveness of the catalyst in bio-electricity production by using paper recycling wastewater CE and

percentage of COD removal are shown in Fig. 4. The maximum COD removal (73%) and CE (8.4 %) are achieved from FePc/MWCNT deposited electrode. Due to longer operating time the bacteria will migrate from anode to cathode which affects the performance of fuel cell (Lefebvre *et al.*, 2011). By increasing the initial concentration, the COD removal efficiency can be improved (Mohan *et al.*, 2008). This study reveals that the COD removal rate is also slightly higher for FePc/MWCNT than other electrodes.

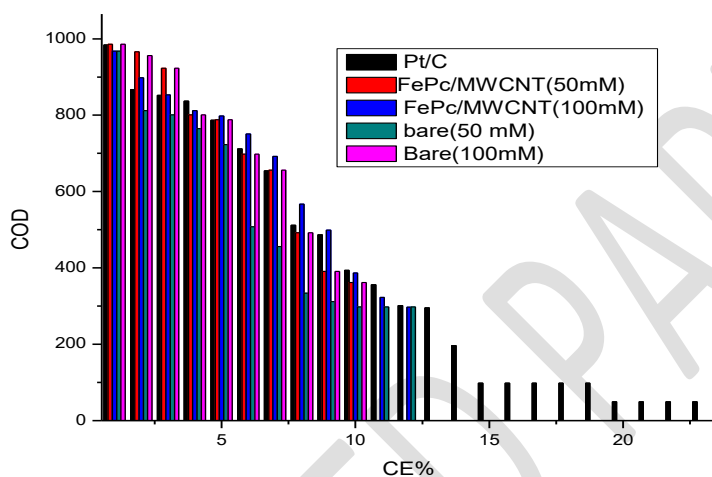


Figure 4. Effectiveness of the catalyst in bio-electricity production

## 4. Conclusion

This work conclude that the conductivity is increased by phosphate buffer solution by increasing the concentration from 50 mM to 100 mM. The results exhibit that solution conductivity and buffer capacity are significant factors that can limit the amount of power generated from paper recycling effluent. Adding a phosphate buffer (100 mM PBS, 10.5 mS/cm) demonstrate that the achievable power density produced by MWCNT/FePc is 9.34 W/m<sup>2</sup> was slightly lesser than Pt/C (9.64W/m<sup>2</sup>). In addition that long term stability and reasonable cost of MWCNT/FePc indicates it is a best alternative cathode catalyst in MFC.

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