

# *Assessment of Wastewater Treatment in the Paper Recycling Industry with Concurrent Bioelectricity Generation Using a Microbial Fuel Cell*

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**Abstract:** Paper industry is one of the largest polluting industries in the world. The treatment of recycled paper mill wastewater is a big challenge; the characteristics of effluent vary from one mill to another. The wastewater degradation pathway was identified as formation Volatile Fatty Acids (VFA) which breaks down in to intermediates like acetate and propionate. The mixed inoculum supporting the MFC reaction mechanism was identified as *Acinetobacter* species and *Pseudomonas* species. The maximum COD removal achieved by the MFC using FePc/MWCNTs catalyst was nearly equal to the Pt/C catalyst. However, cost of the treatment using this catalyst is much lower than precious metal catalyst. In addition that MFC technology revealed better electricity generation and wastewater treatment using non precious catalyst.

**Keywords:** MFC, Paper Industry, Microbial fuel cell, Waste water.

## **1. Introduction:**

Wastepaper recycling industry is one of the major polluting industries consuming large quantities of water for its various operations and also discharging relative proportion of wastewater. The percentage recycled content decides the strength of a wastepaper recycling mill wastewater (Huang & Logan 2008). Wastepaper recycling wastewaters contains lingo sulphonates, hemi-cellulose, organic soluble fatty acids and low concentrations bleaching products (Kirwan 2005). The effluent from paper mill can be cause considerable damage to the water bodies due to its high Chemical Oxygen Demand (COD) and its high toxicity (Noushdin Birjandi et al. 2014).

The wastepaper recycling process involves repulping, bleaching and paper making which generates substantial quantity of wastewater from each different stages of production. The wastepaper recycling wastewater characterized by Chemical Oxygen Demand (COD), Bio-chemical Oxygen Demand (BOD), Total Suspended Solid (TSS), Total Dissolved Solids (TDS), cellulose and slightly acidic pH. To minimize the pollution load to the environment several treatment techniques were developed such as adsorption, coagulation, filtration, oxidation and ozonation. But the conventional treatment schemes are having lot of drawbacks in the following operating parameters viz., pH, temperature, Organic Loading Rate, substrate characteristics and reactor design (Adrian Eugen Cioabla et al. 2012). In addition to, traditional

wastewater treatment technologies not effectively degrade the soluble organic matters and cellulose present in wastepaper recycling wastewater (Lens et al. 2002). Hence, the conventional treatment will be replaced by a new technology which will be efficient and economic than the previous system.

## **2. Microbial Fuel Cell and its Origin**

Microbial Fuel Cells (MFCs) are devices that uses bacteria to oxidize organic matter and generate current; Electrons produced by the bacteria from the substrate are transferred to the anode (positive terminal) and flow to the electron acceptor (negative terminal) linked by a conductive material containing a resistor.

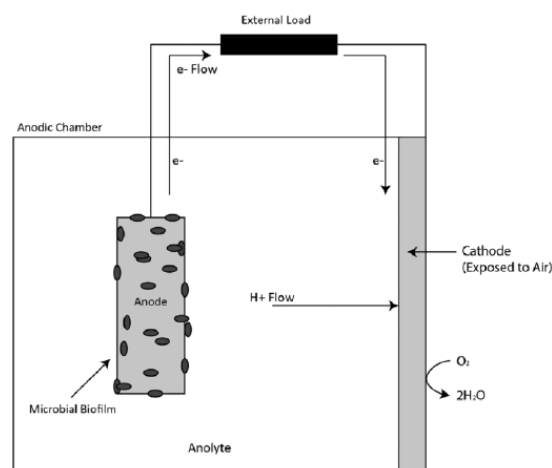
The first MFC was developed by Michel C Potter in 1911; bacterial culture was used as a medium in his study (Potter 1911). The current used in long Haul space flight in National Aeronautical and Space Administration (NASA) was generated from organic waste (Cohen 1931). In 1980's Luigi

Galvani identified that, frog legs connected with metallic conductor can produce bio electricity (Piccolino 1988). Benneto (1985), observed the performance of fuel cell with the effect of artificial electron mediators in pure culture. After that many researchers are attracted by MFC technology for treatment of wastewater as well as to reduce the energy crisis (He et al. 2006).

Microbes can act as a biocatalyst in the anode chamber which converts the organic matter in to electricity (He 2007). Numerous works reported that, the performance of cathode plays a vital role MFC (Rismani Yazdi 2008). Logan has been reported that oxygen is a good electron acceptor by its easy availability and capability (Logan 2006). However the performance of MFC in ORR is poor without cathode catalyst (Zhao et al. 2006). In MFCs platinum is a commonly used cathode catalyst. Even though platinum as a universally used cathode catalyst, it has its own drawback due to high cost and sensitivity to poisoning (Rismini-Yazdi et al. 2008). Hence, the development of low cost cathode catalyst with higher ORR is necessary for better performance of MFC (Ming Ma et al. 2015).

### 3. Related Work:

Single chamber MFC (Fig 1) was tested for treating wastewater using acetate, lactate and glucose (Liu et al. 2004). COD removal was documented and reported. In total 8 nos of graphite electrodes were used in the study and one single air cathode was used. The MFC was fed with clarifier effluent of WTP which resulted in good power generation and simultaneously almost eighty percent of COD removal was reported. The HRT maintained was 3 hrs to 33 hrs and the organic substrate concentration was 50 to 220 ppm of COD. The optimum performance of MFC was obtained by the passive flow of air of 4.5 to 5.5 litres per min. The coulombic efficiency indicated that part of the organic matter did not participate in the energy production. It is concluded in the study that the treatment process is novel and it is found to be more economical compare to the conventional treatment systems.



**Fig 1 Typical Single Chamber MFC**

Further the challenges in operating the MFC was studied by Hong Kim et al. (2007). The metabolism of microbes is converting the stored energy to power. The potential of microbes for power generation to be increased and thus the optimization of the system is very much required. This covers an application of using MFC as biosensors for pollutants monitoring. The study listed down the major parameters affecting MFC and also suggested the points for improvement. The complete literature survey and the advances of MFC was studies by Du et al. in 2007. The conversion of chemical energy was described in the study. The main advantage of production of electricity and biogas ( $H_2$ ) without the emission of carbon dioxide is the main advantage of MFC. The application of using as biosensors also reiterated in the report. The energy generation and coulombic efficiency are affected by the dimensions and operating parameters. The practical application of MFC is limited because of the lower power generation. The detailed study is needed to improve the efficiency and energy generation of MFC.

The performance of MFC was tested for domestic wastewater with two different temperature conditions by Youngho and Logan in 2010. The ambient and mesophilic temperature conditions were studies. The mesophilic temperature was around 23 deg plus or minus 3 deg C. The configuration of the reactor was single chambered and air cathode system. The operating temperature was the deciding factor for degradation and energy production. The power production was around 420 mW/m<sup>2</sup> in a continuous flow reactor under mesophilic conditions. The temperature and flow

of the substrate were affecting the performance. The MFCs connecting with series perform much better with less production of sludge.

The sludge obtained from sewage treatment were tested in MFC as substrate by Guodong et al in 2012. Bio cathodes were used in the system. The MFC with abiotic cathodes (Fig 2) using platinum as catalyst. Additionally, hexacyanoferrate to be used as catholyte. In the present study, 3 chambered MFC with biocathodes were used to treat the sludge with maximum energy of around 13 W/m<sup>3</sup> which was higher than the previous such studies. The operating time for the reactor was 15 days. The COD removal and coulombic efficiency was achieved around 40 % and 20 % respectively. The internal resistance was reduced to the value of around 40  $\Omega$  and thus the power performance was increased. The microbial culture in the anode biofilm was studied by parallel sequencing technology and 454 pyrosequencing technique.

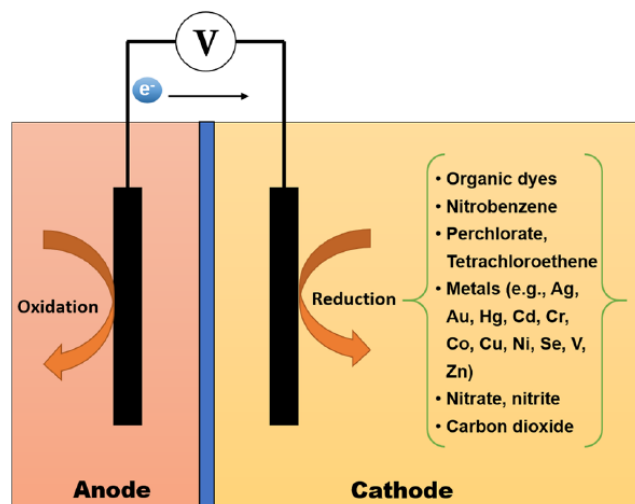


Fig 2: Abiotic cathode system

#### 4. Methodology:

The wastepaper recycling mill effluents have significant impact on the environment because they contain considerable amounts of fibers, fillers and toxic chemicals. Conventionally, the wastepaper recycling mill wastewater is treated using physico-chemical methods. The existing treatment system required more space and consumes high energy. Hence, the treatment of wastepaper recycling wastewater contains a complex organic compound, a promising way to perform the degradation of the substance is the application of Bio-Electro chemical system. Microbial Fuel Cell technique

appears to be one of the most popular treatment methods in BES. Microbial Fuel Cell (MFC) is a technology directly generating electricity from degradation of wastewater, simultaneously treating wastewater which solves energy crisis and environmental damage.

The methodology consisted of the following steps:

- Collection and characterization of real and simulated wastewaters.
- Fabrication of two lab-scale DCMFC reactors (250 mL capacity each) and conduct feasibility studies on bioelectro chemical process for treatment of wastepaper recycling wastewaters and simulated wastewater.
- Procurement of membrane, catalysts FePc, Pt/C, Ketjan Black and MWCNTs and its characterization.
- Electrode modification using catalysts viz., FePc/KB, Pt/C, FePc/MWCNTs and MWCNTs and characterization.
- Identification of best reactor configuration based on the performance and kinetic analysis.
- Study the effect of operating parameters viz., electrode material, electrode spacing, catholyte concentration, pH, composition of FePc and loading rate of the treatment of real and simulated
- wastepaper recycling wastewaters by MFC technique using catalysts viz., Pt/C, FePc/KB, FePc/MWCNTs and MWCNTs.
- Identification of degradation pathway, gas composition analysis and microbial community analysis for the optimized condition.
- Cost estimation.

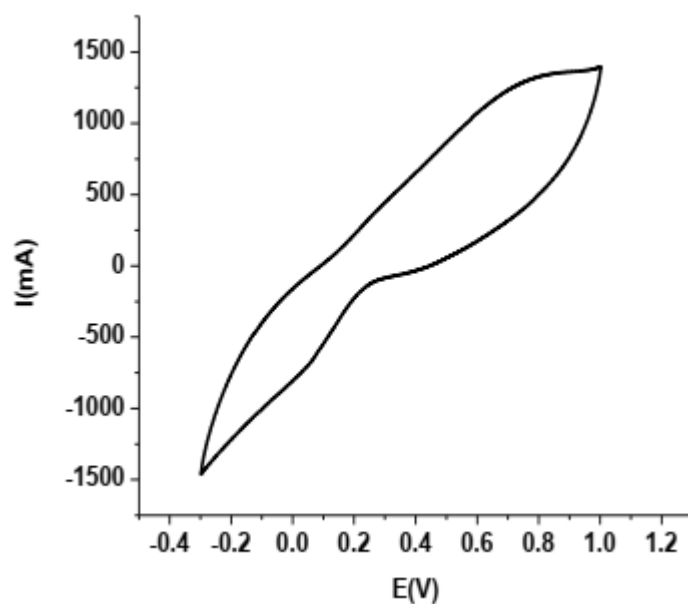
#### 5. Result and Discussion:

The simulated wastewaters (viz., SWW1 to SWW4) were prepared using cellulose as per the recipe obtained from the wastepaper recycling industry. The industrial wastewaters (viz., IWW1 to IWW5) were collected from a wastepaper recycling industry located near Chengalpattu, TamilNadu. Both the simulated and industrial wastewaters were characterized for various physico-chemical parameters including pH, EC,

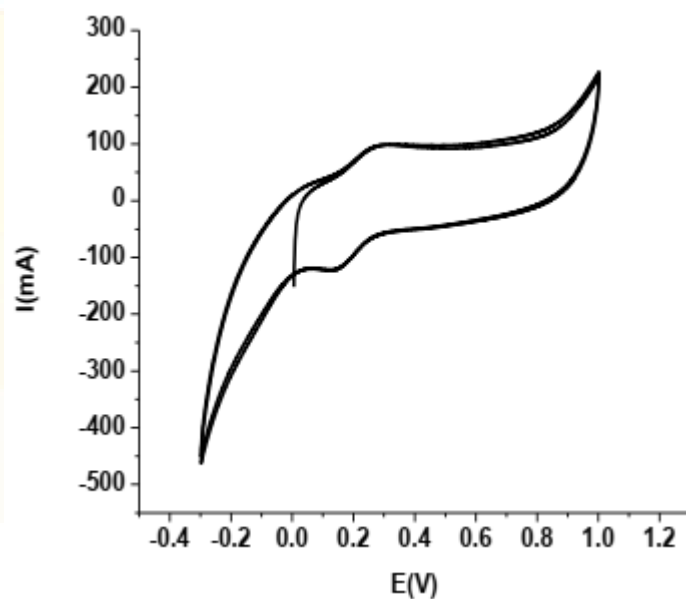
colour, COD, BOD and TDS and the results are discussed in the following sections.

The effect of cathode catalyst for the oxygen reduction reaction in MFCs, Cyclic Voltammetry (CV) tests were conducted in an O<sub>2</sub>-saturated PBS (100mM) solution with the potential window of -0.2 to 1.2V. The ORR performance of different catalysts viz., FePc/KB, FePc/MWCNTs, Pt/C and MWCNTs were compared by CV results, where the peak potential and current values varied. Figure 4.24 illustrates the ORR activity of the catalysts followed in the order of FePc/MWCNTs > FePc/KB > MWCNTs. Cyclic voltammograms recorded for MWCNTs supported FePc modified Graphite felt electrode has cathodic peak at 0.19V Vs (SCE) at the scan rate of 20 mV/s. Similar type of peak position has reported at 0.16 V for amino functionalized MWCNTs supported FePc composite catalyst.

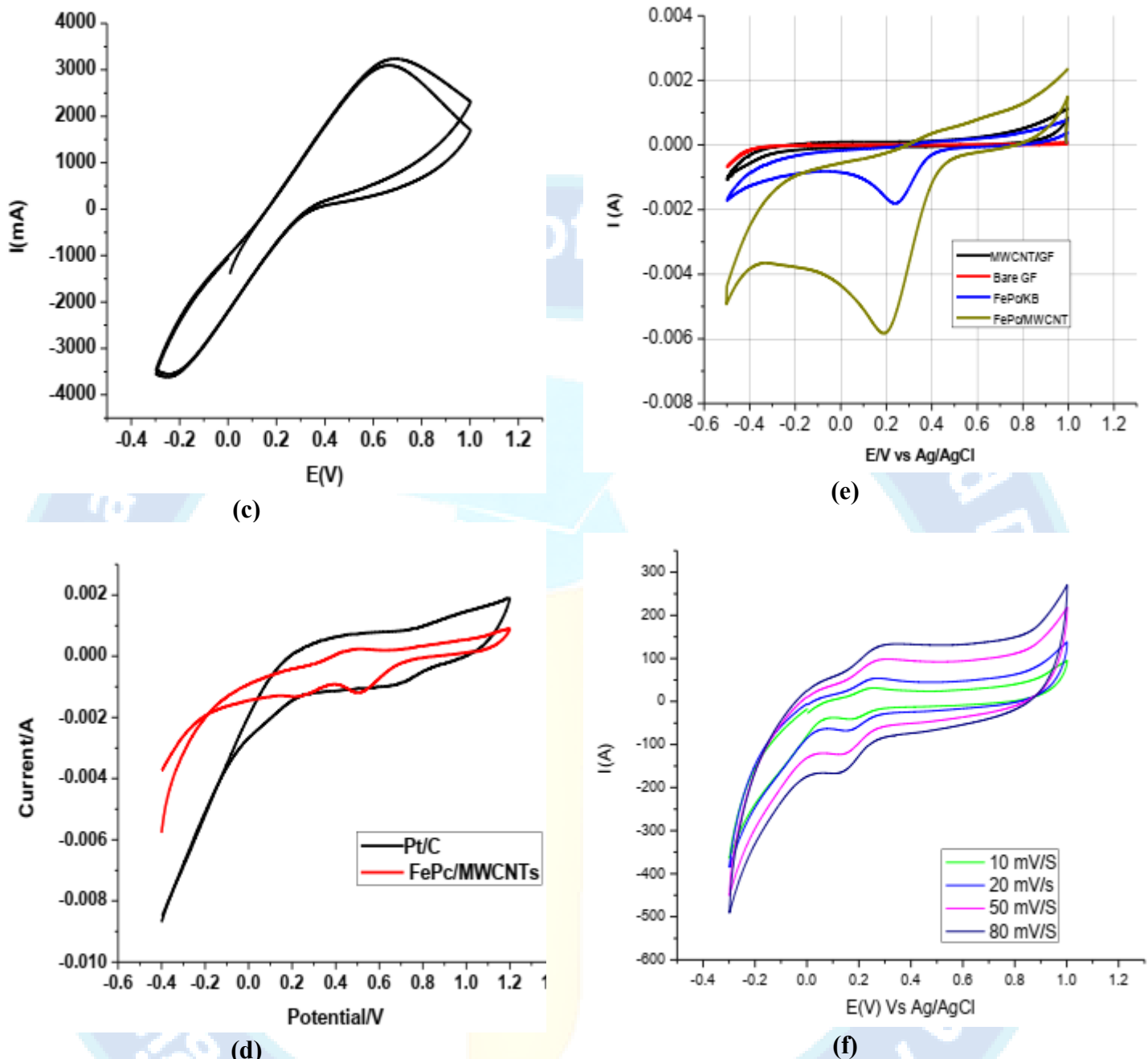
In addition there is no significant peak can be identified on the CVs of MWCNTs modified and bare graphite felt electrodes, suggesting that FePc was responsible for those peaks. The CV result of FePc/MWCNTs catalyst proved that successful attachment of FePc catalyst over electrode surface. Cyclic voltammograms of MWCNT/FePc with different scan rates from 10 to 80 mV/ as shown in Figure 3f. In addition, CV results of FePc/KB and FePc/MWCNTs highlighting the significance of supporting material which enhancing the ORR catalytic activity of FePc catalyst. Larger specific surface area of MWCNTs is an important factor to enhance the catalytic ORR for FePc/MWCNTs composite catalyst compared with FePc/KB and MWCNTs. The electrocatalytic activity of Nitrogen doped carbon nanotubes had better ORR than other catalyst. Especially, pyridinic and pyrrolic type nitrogen was responsible for the ORR enhancement. From the XPS results evidenced the presence of pyridinic-N and pyrrolic-N at 395.9 eV and 397.58 eV with the atomic weight % of 83.75 and 16.25 respectively.



(a)



(b)



**Fig. 3.** Cyclic voltammetry of different catalyst using 100 mM PBS (pH=6.8) under oxygen atmosphere (a)-(c), CV comparison plot for Pt/C and FePc/MWCNTs (d) catalyst comparative CV and (e) and CV for FePc/MWCNTs for different scanning rate (f).

## 6. Conclusion:

The treatment of wastepaper recycling wastewaters and simultaneous electricity generation using PEM based fuel cell with composite catalyst (FePc/MWCNTs) was found to be feasible technique to overcome the various drawbacks of

conventional methods. Therefore, this research work exhibited better performance in terms of electricity generation as well as wastewater treatment.

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