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## Treatment of pulp and paper industry effluent and electricity generation by constructed wetland coupled with microbial fuel cell (CW-MFC)

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**Abstract**

Microbial fuel cells (MFCs) have got a remarkable consideration for its capability to perk up the degradation of some unmanageable pollutants and simultaneous electricity production. A microbial fuel cell coupled constructed wetland (CW-MFC) is a latest technology to treat the wastewater and produce energy which has more wastewater treatment volume and more easily to maintenance than others MFCs. In this work, the effects of hydraulic residence time (HRT), COD concentration on the electricity production of CW-MFC and the degradation characteristics of pulp and paper effluent were investigated. The highest electricity production was obtained when HRT was 5 day. The highest degradation rate for BOD was 97.86% in S2, COD 89.09%, 88.54% for chloride in S3 and voltage 26.33 mV, current 29 mA respectively, in the S2 was achieved. Further investigations are needed to optimize CW-MFC performance and explain the mechanism of bio refractory compounds degradation and electron motion in CW-MFCs.

**Keywords:** Wastewater treatment, Microbial fuel cell, Constructed wetland, Electricity generation, Alternate energy

**1. Introduction**

Constructed wetland (CW) is a man-made wetland which utilizes natural process to treat and improve the quality of water. CW is recognized as an eco-friendly technology and has been used as part of the wastewater treatment process in treating a wide range of wastewater like industrial wastewater [1], landfill leachate [2], agriculture wastewater [3], storm water, sewage and municipal wastewater [4] and acid mine drainage [5]. CW has been well acknowledged due to its important characteristics such as simple construction, low maintenance and cost effective [6-9]. In recent years, microbial fuel cell (MFC) technology has been explored extensively for their innovative features and environmental benefits [10-12]. A microbial fuel cell (MFC) is a bio electrochemical system which converts chemical energy into electricity by using biocatalyst, and it has been well thought-out as to be one of the promising and sustainable technologies for electricity generation as well as waste treatment [10, 13-15]. At the anode, organic co substrate is oxidized by electrochemically active microorganisms. Subsequently, the microorganisms transfer the electrons resulting from this oxidation to the anode via extracellular electron transfer which then passes through an external circuit to the cathode, thus producing current. Technology combining CW systems with microbial fuel cells (CW-MFC) has promise for both wastewater treatment and bio-electric production [16-18]. In this system approach, electricity is produced with biodegradable substances as bacteria oxidize organic or inorganic matter in wetland soils [18]. A microbial fuel cell coupled constructed wetland (CW-MFC) system is a new device that embeds the MFC into the constructed wetland (CW) to treat the waste water and produce energy.

Constructed wetland-microbial fuel cells (CW-MFCs) are novel devices with a delicate combination of artificial ecosystems (constructed wetlands) and bioelectrochemical techniques (microbial fuel cells), in which electricity generation can be enhanced on account of rhizosphere effect of wetland plant [19, 20] and contaminants in the wastewater can be efficiently removed due to the synergistic effect of the 2 units [21, 22]. Both of the constructed wetland and the microbial fuel cell possess anaerobic and aerobic zones, where reduction and oxidation processes take place, and these similarities are the bases of the combination of the two units.

The pulp and paper division presents as one of the energy demanding and highly polluting sectors within the Indian economy and is therefore of particular interest in the context of both limited and global environmental consideration. In India, around 905.8 million m<sup>3</sup> of water is consumed and around 695.7 million m<sup>3</sup> waste-water is being discharged annually by this sector.

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Indian paper industry accounts for 1.6% of the world's production of paper and paperboard.

The pulp and paper manufacturing industry is a chemical process industry with major impact on the environment. They make use of large amounts of water and produce equally large amounts of wastewater, which constitutes one of the major sources of aquatic pollution.

The study on MFC has been extensively explored while the integration of constructed wetland and MFC is still in its infancy. Therefore, the study of incorporation of MFC into existing wastewater technologies like constructed wetland is definitely worthwhile as it has great potential to treat wastewater and merits with simultaneous electricity generation. The aim of this study was to investigate the feasibility and effectiveness of MFC integrates with CW. The performance of wastewater treatment such as chemical oxygen demand (COD), biochemical oxygen demand (BOD) removal of the hybrid system was assessed whereas electricity generation was evaluated.

## 2. Materials and methods

### 2.1 CW-MFC construction

The reactor of CW-MFC was designed and fabricated using cylindrical polyacrylic plastic chamber with diameter of 18 cm and height of 100 cm. This reactor was placed at net house of microbiology department of GB Pant University of Ag. & Tech., Pantnagar at average temperature of  $28 \pm 4$  °C. Glass beads with diameter of 10 mm were filled at the bottom of the column up to 10 cm to ensure even distribution of influent. In this study, there were four layers from the bottom to the top of the CW-MFCs. The bottom layer at a depth of 20 cm is filled with gravels with an average size of 0.157-0.31 inch, pebbles with an average size of 0.079-0.157 inch, sand with an average size of 0.010-0.020 inch and mud (silt) with an average size of 0.00015-0.0025 inch was introduced to make man-made wetland i.e., constructed wetland. The emergent plant employed in this study was reed (*Phragmites australis*). Carbon electrodes were used as anode and cathode respectively in the microcosm.

Finally, the cathode and anode were connected with insulated copper wire [16]. In order to ensure MFC function efficiently, it is important that the anode compartment maintains in anaerobic condition. Therefore, anode was positioned at the bottom of the reactor fulfilling the suitability of anodic reaction in MFC. While cathode compartment at rhizopheric zone, oxygen must be easily obtained as it will combine with protons from anode and electron from external circuit to complete the circuit.

### 2.2 Inoculation and operating conditions

Activated sludge collected from the Wastewater Treatment Plant (Uttarakhand, India) was used as the source of nutrient in the whole study. The systems were operated for several days until the reproducible maximum voltages were observed. Pulp and paper industry effluent was collected from Century Pulp and Paper Industry, Lalkua, Uttarakhand, India. In the experiments, the required amount of pulp and paper industry effluent was mixed with nutrient rich solution for making solution of setup 1 (S1) (100% pulp and paper industry effluent) likewise setup 2 (S2) (75% pulp and paper industry effluent and 25% tap water), setup 3 (S3) (50% pulp and paper industry effluent and 50% tap water), setup 4 (S4) (25% pulp and paper industry effluent and 75% tap water) and setup (S) (control without plant) volume concentrations. In the beginning of the experiments, inoculums was fed to the microcosm and kept for two weeks in order to be stabilized. For sampling purpose

at desirable time, desirable amount of wastewater was withdrawn.

## 2.3 Experiments

A series of experiments were conducted to investigate the pulp and paper industry effluent degradation and electricity production efficiencies when the systems running stable and reliable. The experiments were conducted as follows: the hydraulic retention times (HRT) were set at 1 day, 2 day, 3 day, 4 day and 5 day. Samples were taken at desirable time.

## 2.4 Analytical methods

The ability of the CW-MFCs to treat wastewater was examined in terms of removal efficiencies of biochemical oxygen demand (BOD), chemical oxygen demand (COD), chloride (Cl<sup>-</sup>), sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), total nitrogen (TN), sulphate (SO<sub>4</sub><sup>2-</sup>). Daily samples were taken and analyzed. [23]. The current (I) and voltage (V) can be measured using digital multimeter. Power ( $P = IV$ ) can be obtained from calculation. Current can be obtained from calculation; Ohm's Law is given by:

$$V = I R$$

Where, V is the potential difference between two points which include a resistance R. I is the current flowing through the resistance.

## 3. Results

### 3.1 BOD removal efficiency

The initial value of BOD of effluent was 621.53 mg/L and of tap water was 2.4 mg/L and there were 4 treatments namely 100% E with BOD load 621.53 mg/L, second 75% E and 25% TW of 466.74 mg/L BOD value, third 50% E and 50% TW having 311.96 mg/L BOD value and last 25% E and 75% TW which is having 157.18 mg/L BOD value. There is also a control which is fed with 100% E. The highest removal efficiency was observed in S2 i.e., 97.86 and lowest in S4 i.e., 94.40. The setup control has shown 75.64% removal efficiency. (Fig. 1) has shown the removal efficiencies of different microcosm in different HRTs.

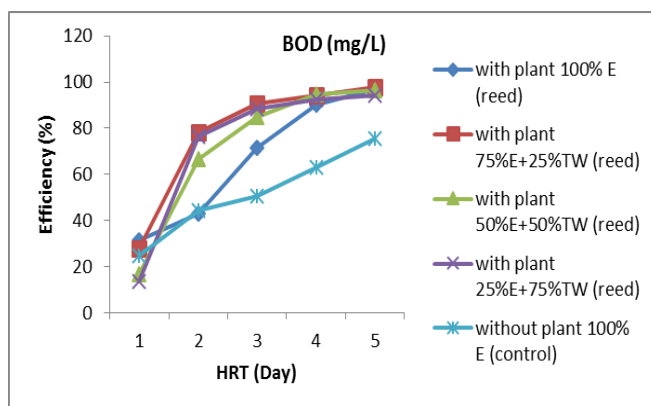


Fig 1: Removal of BOD from different concentration

### 3.2 COD removal efficiency

The initial value of COD in 100% E was 1958.3 mg/L and in other treatments it was 1470.04 mg/L (75%E and 25%TW), 981.8 (50%E and 50%TW) and 493.55 mg/L (25%E and 75%TW). The COD value of TW was 5.3 mg/L. As shown in Fig. 2, there was a drastic reduction of COD. A total of 89.09% of COD reduction occurred in S2. The COD reduction was contributed by microbes in anodic chamber, where microbes oxidized organic substrate as carbon sources to support microbial activity [24, 25].

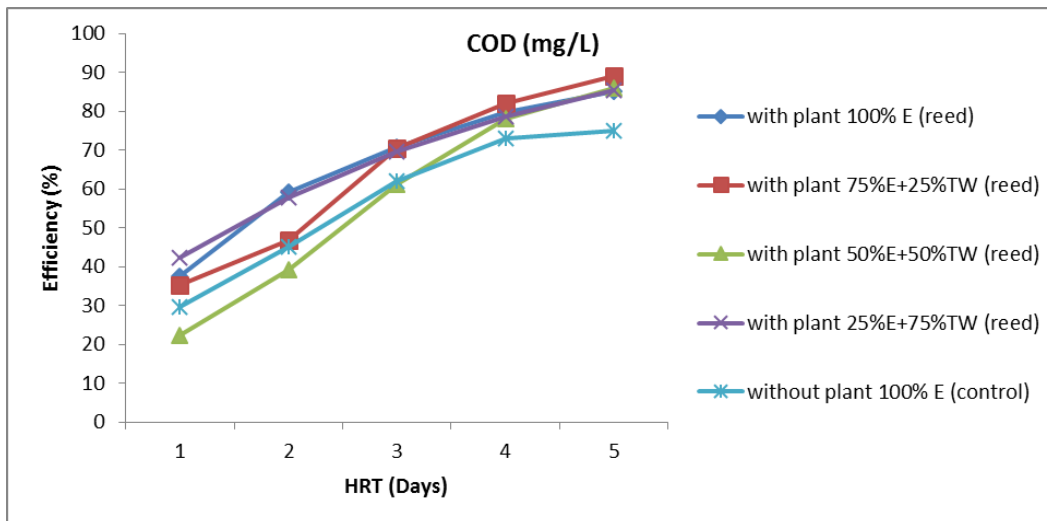


Fig 2: Removals of COD from different concentration

### 3.3 Chloride removal efficiency

The percentage of BOD at different concentration containing wastewater was found to be in the range of 731.6 mg/L to 189.95 mg/L. The highest removal efficiency was observed in

S3 is 88.54% and lowest was found in control is 43.09% at day 5. As shown in (Fig. 3) there was a drastic reduction of chloride.

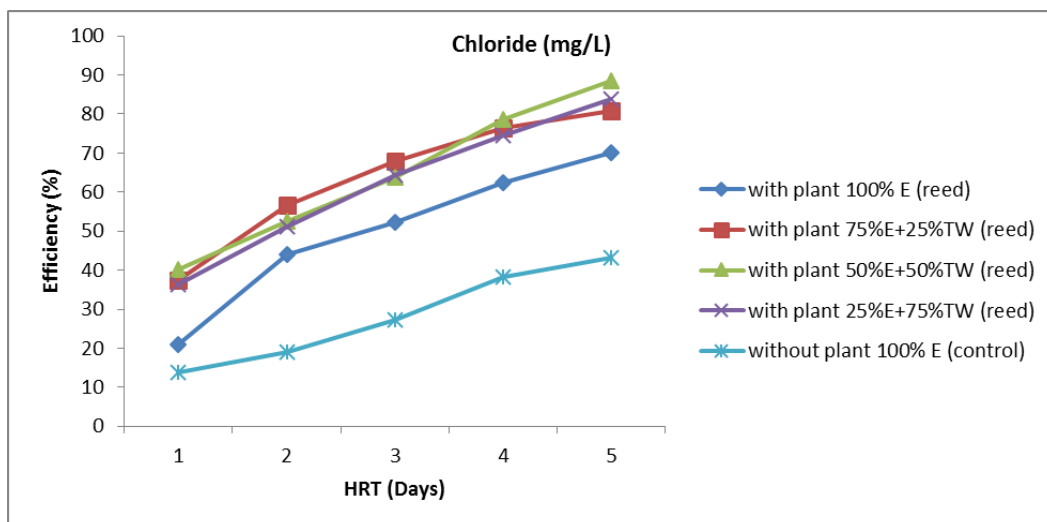


Fig 3: Removals of chloride from different concentration

### 3.4 Potassium removal efficiency

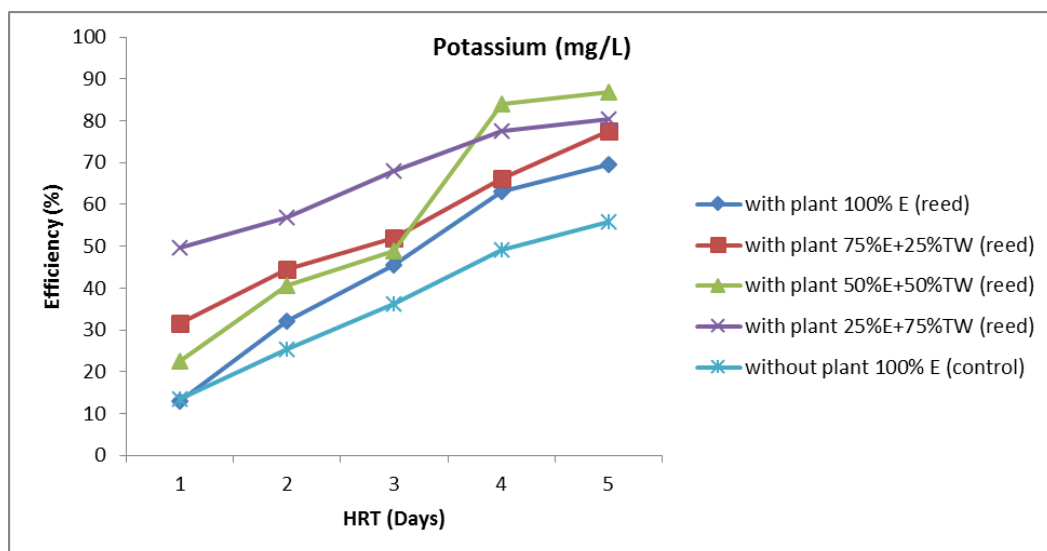


Fig 4: Removals of potassium from different concentration

As shown in Fig. 4, the removal rate of potassium was increased as the HRT increases. The efficiency was highest (86.72%) when S3proportion was 50% E and 50% TW. The efficiency was increased to 22.56%, 40.52%, 48.85% and 83.94% when S3 proportion was 50% E and 50% TW. Lowest was in control with only 55.93%.

### 3.5 Sodium removal efficiency

According to Fig. 5, the CW-MFC showed the highest sodium removal rate of about 80.53%, in comparison with 54.73% in the non-planted CW-MFC. The initial concentration of sodium was 624.15 mg/L.

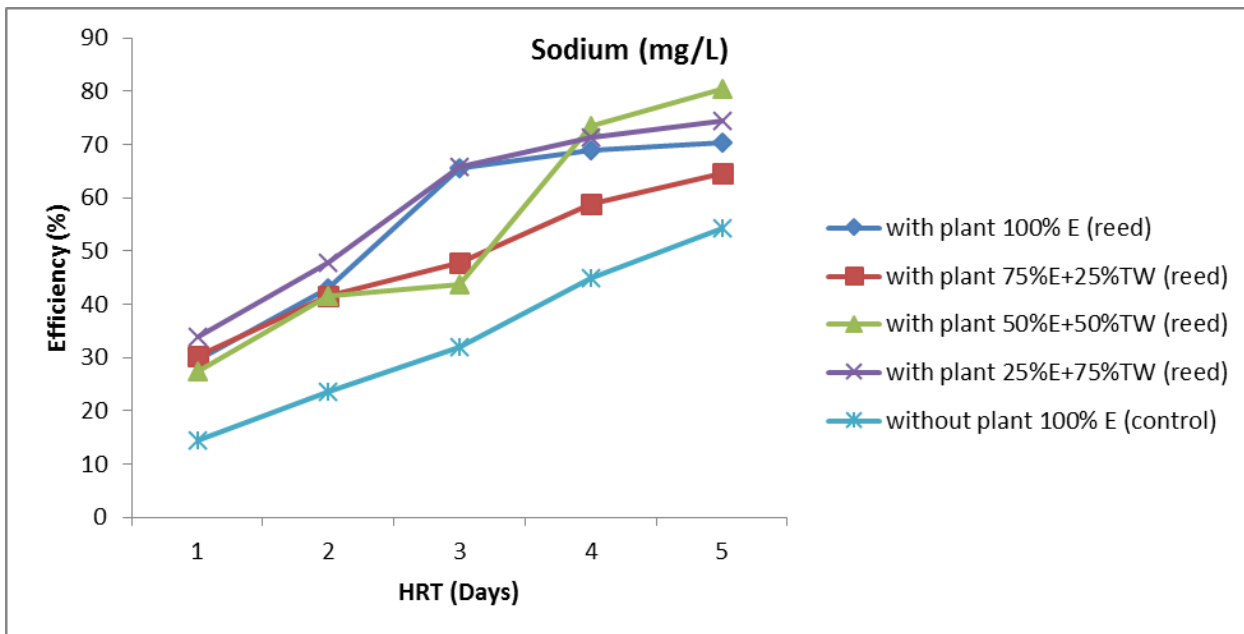


Fig 5: Removals of sodium from different concentration

### 3.6 Bioelectricity production

To investigate the effect of plants on electricity generation, a series of comparative studies were done to analyze the electricity generation from CW-MFCs. The plants significantly affected the power density. The electricity generation of the MFCs operated for several days. Results showed that the voltage was maximum when the HRT was 3 days i.e., 25.33 mV and the concentration was 75% effluent and 25% tap water. Similarly current is maximum at 2<sup>nd</sup> day HRT time with the same concentration i.e., 29 mA.

So high concentration of oxygen in the cathode can promote this reaction, and then strengthen the cell reaction. On the other hand, higher concentration of oxygen can enhance the

cathode potential. Therefore, the electricity generation of planted CW-MFC had been promoted.

Although the redox mediator allow bacteria to use remote anode and kinetically promote the extracellular electron transfer from bacteria to anode, this process was limited by other factors such as electron donor concentration, substrate conversion rate and diffusion limitations imposed by thick biofilm [26]. As shown in Fig. 6, 7, 8 & 9 there is increase in voltage, current, power density and current density. Based on the power density curves, the power generated by the MFCs was 1029.2 mW/m<sup>2</sup> and current density was obtaining 39.08 mA/m<sup>2</sup>.

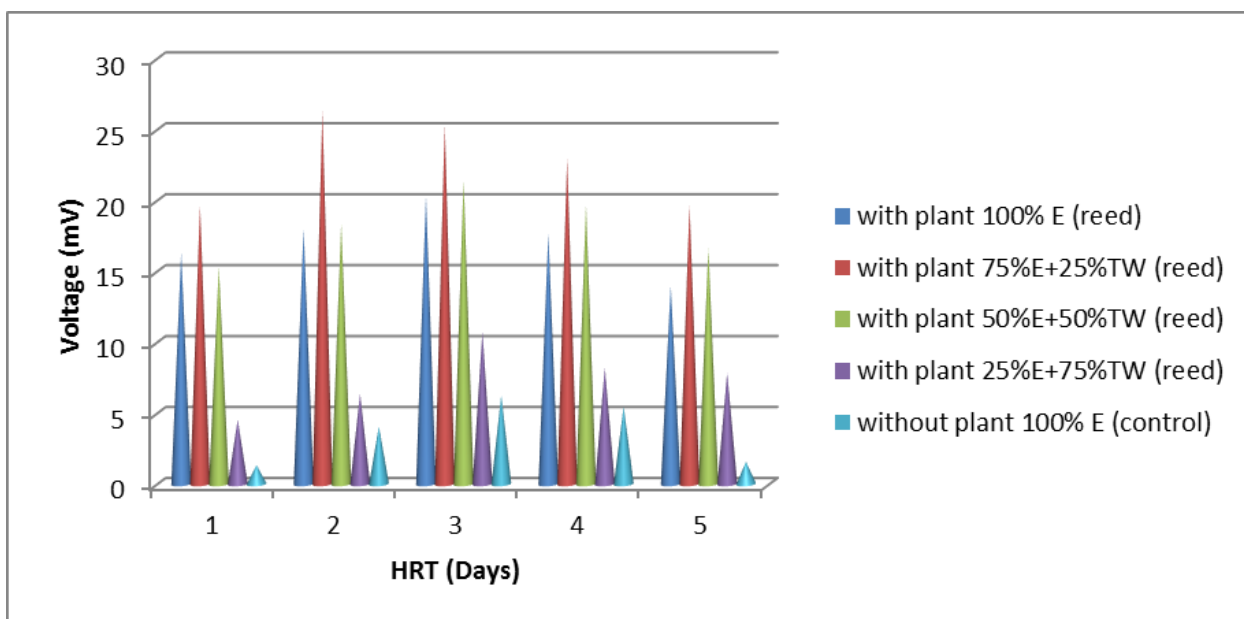


Fig 6: Voltage (mV)

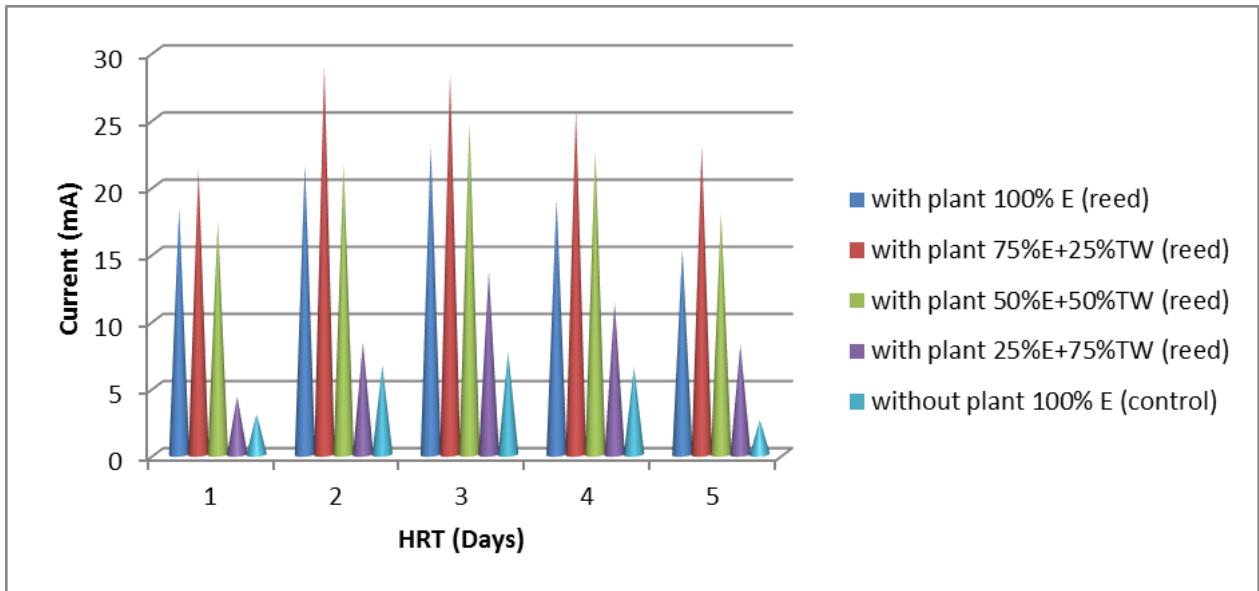


Fig 7: Current (mA)

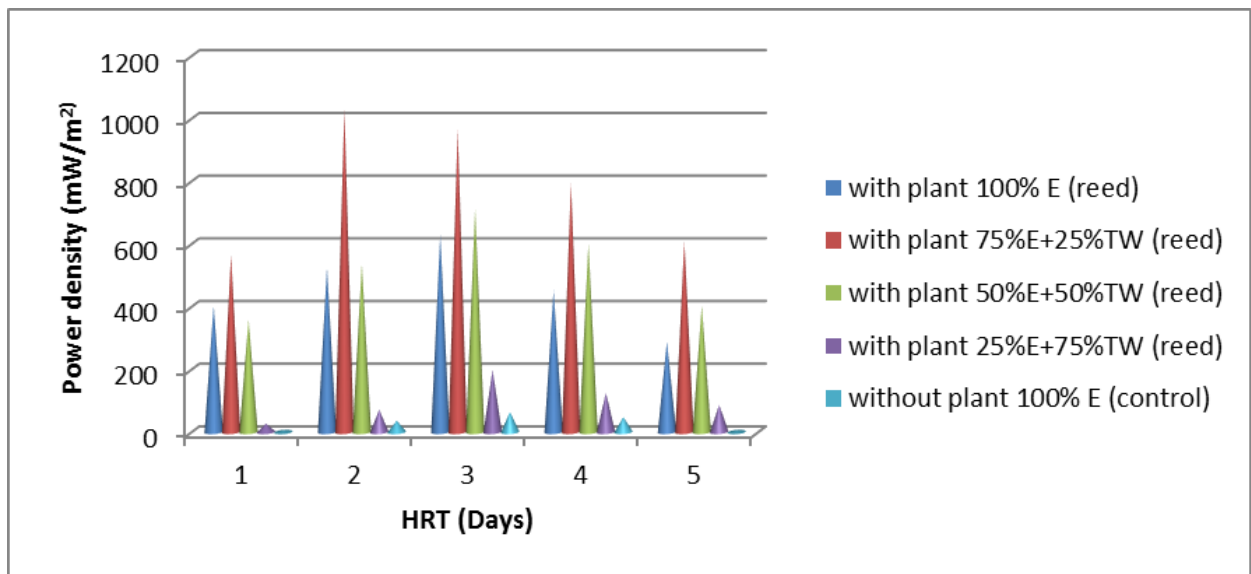


Fig 8: Power density (mW/m<sup>2</sup>)

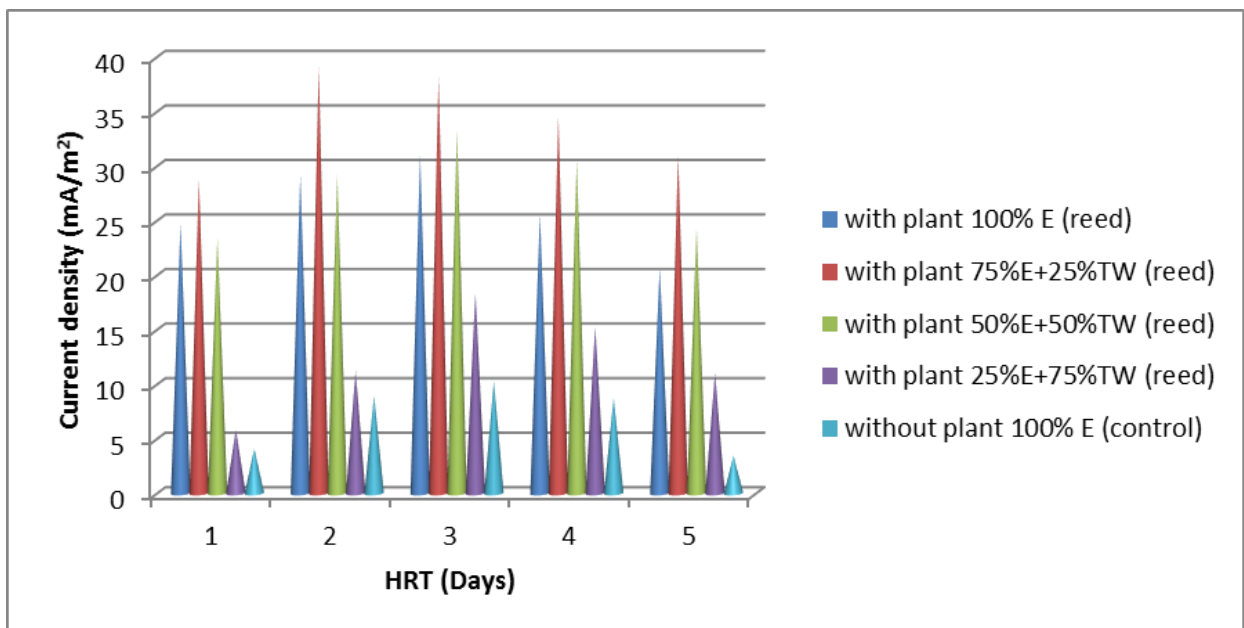


Fig 9: Current density (mA/m<sup>2</sup>)



#### 4. Conclusion

The present study clearly demonstrates that the addition of the MFC in the CW improved the treatment performance. The CW-MFCs tested in this study were suitable for long-term stable operation and showed strong adaptability to different water qualities. The cathode played an important role in electricity generation. It has been found that the individual advantages of CW and MFC technology improved to a large extent by combining of these two technologies.

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