ISSN (Print) : 0974-6846
ISSN (Online) : 0974-5645
Indian Journal of Science and Technology, *Vol 10(13), 10.17485/ijst/2017/v10i13/111203, April 2017*

Simultaneous Electricity Generation and Heavy Metals Reduction from Distillery Effluent by Microbial Fuel Cell

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Abstract

Objectives: Raw distillery effluent put to use as substrate for electricity generation in MFC and effectiveness in treatment including heavy metals reduction using MFC are the focus of the study. **Methods/Statistical Analysis**: Dual chamber fuel cells were fabricated using Poly (methyl methacrylate) sheet as a single unit, graphite rods are used as electrodes. Microporous PVC separators are used for salt bridge to distinct the anode and cathode chambers so as comparing with the conventional 'H' type dual chamber reactor the distance between the electrodes are reduced. The fuel cells were operated in batch mode at room temperature. **Findings**: The Microbial Fuel Cell is a bio-electrochemical device draws electricity from the microorganism that utilizes the organic matter from the wastewater, different wastewater could be employed as a substrate. Distillery effluent consist of high chemical oxygen demand, it effectuated electricity generation for 73 days. The fuel cells produced a maximum voltage of 206 mV that derived a maximum current density 123.50 mA/m^2 and power density of 25194.8 mW/m^2. Electricity generation and effluent treatment depends on the ability of the microorganism to convert the organic matter of the substrate. The COD removal 68.7% was obtained from the fuel cell it is effective than the conventional treatment techniques without pretreatment or dilution of the effluent. The MFC treatment also assisted the removal of Nitrate 76.6%, Phosphate 79.4%, Sulphate 70.8%. The overall performance of the fuel cell determined by the Columbic Efficiency rendered by the process was 47.12%. Elemental analysis of treated effluent exhibited considerable reduction of heavy metals present in the distillery effluent. **Application/Improvements:** This study shows that the treatment of raw distillery effluent is effective with MFC technique. It also signifies the potential of heavy metal reduction with MFC by simultaneous electricity generation.

Keywords: COD, Distillery Effluent, Electricity, Heavy metals, MFC, Treatment

1. Introduction

Increase in population and standard of living demands need of more energy in the modern world. Conventional use of fossil fuel for energy are leading to the depletion

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of non renewable sources and increase in pollution. Scientists are in search of sustainable energy from renewable sources which are more demanding alternative source of sustainable green energy, substituting fossil fuel energy became an important prerequisite for the economic development of a country[1]. High energy need is in high priority for the human kind for the growth of population and depletion of clean renewable energy. Distillery effluent that are high in chemical oxygen demand due to the high organic content in it. Distillery industry produce 12-15 liters of spent wash per liter of alcohol production[2]. Untreated disposal of effluent can cause considerable stress on the water courses leading to widespread damage to aquatic life. High COD, Nitrogen and Phosphate content contribute to eutrophication in the water bodies[3]. Colorants present in the effluent that intensify the effect by limiting the permeability of sunlight, which leads to inhibition of the photosynthetic activity and in turn decreased dissolved oxygen levels[4]. Land disposal was practiced as a main treatment, due to it's high nitrogen, phosphorus and organic content[5]. Different methods used for the distillery effluent treatment which are Anaerobic treatment, Continuous Stirred Tank Reactor, Anaerobic Suspended Growth Reactor, Upflow Anaerobic Sludge Blanket (UASB) Reactor, Anaerobic Sequencing Batch Reactor, Anaerobic Baffled Reactor, Anaerobic Fluidised Bed Reactor, Upflow Sludge Blanket Filter (USBF) Reactor, Anaerobic Membrane Bioreactors (AMBR), Kubota Submerged Anaerobic Membrane Bioreactor (KSAMBR), Ozonation, Oxidation, Floculation and Coagulation, Adsorption, Membrane treatment etc.[6]. Distillery waste has to diluted to bring down the COD to 50,000 mg/L before for anaerobic treatment[7]. Dilution lead to more need of using water to dilute, without dilution the use of water could reduced. Microbial Fuel Cell is a technique in which energy is generated during the process of wastewater treatment under anaerobic condition. Substrate is regarded as one of the most important factor affecting the electricity generation[8]. MFC emanates as an alternative technique that coincides electricity generation and wastewater treatment[9]. In this context this study is an attempt for the distillery effluent treatment without dilution and to find the reliability of MFC in electricity generation and wastewater treatment from it.

2. Materials and Methods

2.1 Substrate

Distillery effluent sample was collected from the effluent treatment plant of Sakthi Sugars Ltd., Appakoodal, Erode District, Tamil Nadu, India. Samples were stored at 4°C,

Table 1. Physicochemical characteristics of distillery effluent used for this study

SL.No	Parameters	Values
1.	Color	Reddish Brown
2.	Odour	Fruity Smell
3.	pH	4.0
4.	Conductivity (ms)	20.5
5.	Turbidity (NTU)	6500

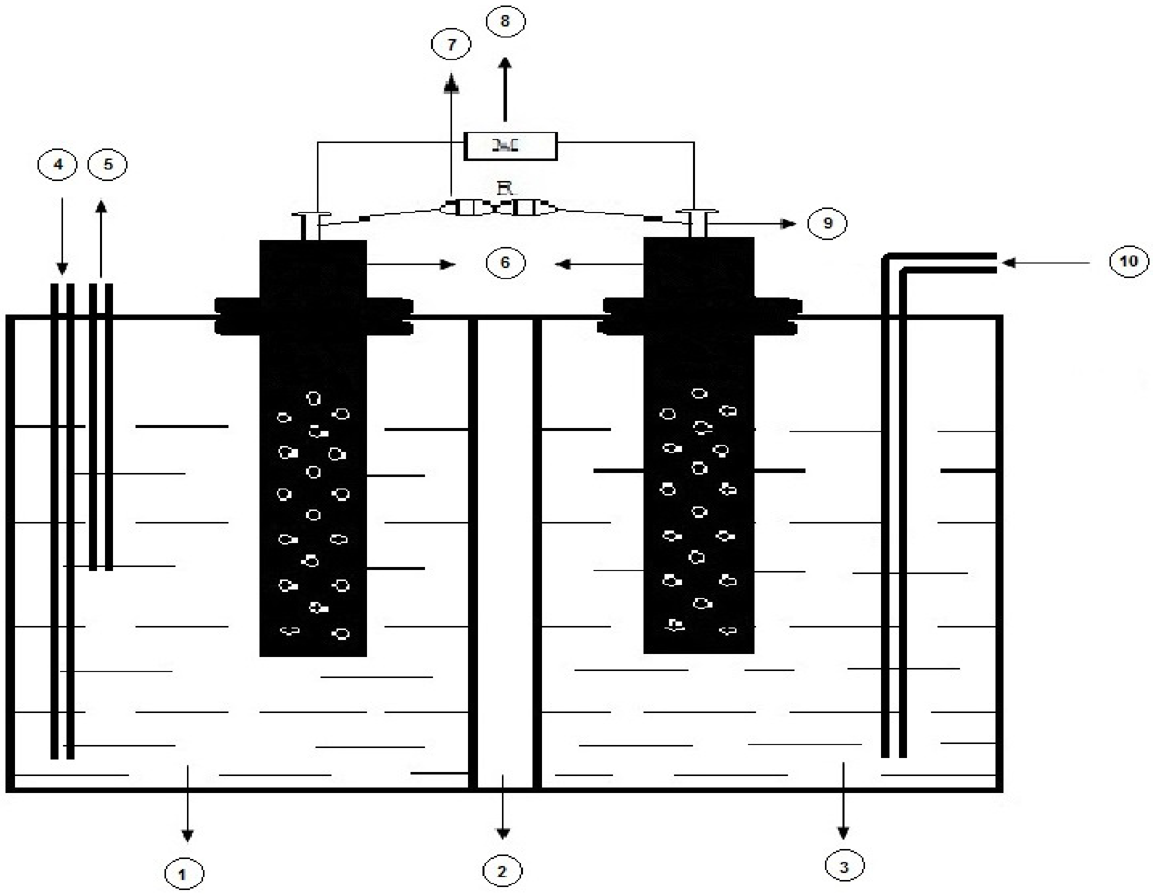
Table 1 Continued

6.	Alkalinity (mg/L)	495.3
7.	Acidity (mg/L)	58.24
8.	Total Hardness (mg/L)	2064
9.	Total Suspended Solids (mg/L)	14,236
10.	Total Dissolved Solids (mg/L)	79,120
11.	Total Solids (mg/L)	93,356
12.	Chemical Oxygen Demand (mg/L)	1, 53, 846
13.	Chloride (mg/L)	2729
14.	Nitrate (mg/L)	999
15.	Phosphate (mg/L)	39
16.	Sulphate (mg/L)	254

sample collection and analysis was performed according to the standard methods[10]. The characteristics of distillery effluent are given in Table 1.

2.2 Fuel Cell Fabrication and Assembly

The MFC reactor was fabricated using Poly (methyl methacrylate) of 8 mm thickness as a single cell unit. Microporous PVC separators was used as a support to pour the salt bridge. The preparation of salt bridge was done as per reported by[11]. The total volume of the reactor was 2600 mL fabriciated as a single unit with a anodic and cathodic chamber having working volume of 1250 mL each and volume of the salt bridge portion was 100 mL. The reactor is designed to overcome the distance between the anode and cathode from the conventional H type reactor, so that the distance between the electrodes can be reduced. Figure 1 shows the schematic representation of the fabricated reactor designed for this study. Earlier report stated that graphite electrode was best for the MFC[9]. Hence in this study graphite rod having surface area of 166.81 cm^2 was used. Electrodes are soaked in deionised water for a day before using it in the MFC. In order to increase the surface area for the microorganism interaction small pores were made on the electrodes. The electrodes were connected using copper wire through a resistor, reactor lid sealed using silicon paste for maintaining anaerobic condtion. Anode and cathode chambers were provided with inlet and outlet. A digital multimeter (Magtech Ltd., New Delhi, India) was connected to the circuit to measure the potential difference of the cell.



1. Anode Chamber
2. Salt bridge/Membrane
3. Cathode Chamber
4. Anode Chamber Inlet
5. Anode Chamber Outlet
6. Electrodes (Anode and Cathode)
7. Resistor
8. Multimeter/ Ammeter/Datalogger
9. Electrode Terminals
10. Inlet to purge Oxygen to Cathode Chamber

Figure 1. Schematic representation of MFC used for the study.

2.3 Operational Condition for MFC

Raw distillery effluent of 1000 mL having a chemical oxygen demand of 1,53,846 mg/L and acidic pH (4.0) was used as substrate in anodic chamber. The experiments were carried out under anaerobic condition and operated at room temperature. Cathodic chamber was purged with oxygen using aquarium aerator (Shenzhen, China) at a rate of one liter per minute by controlling through air flow meter (Mahavir, SN 31, Coimbatore, India). The uniform suspension of the substrate was ensured by using

(Superfit Equipments, Mumbai, India) magnetic stirrer. The MFC was operated in batch mode and continued up to a period of 73 days.

2.4 Electrical measurements

The potential difference measurements were done using a digital multimeter that was connected parallel to the external resistnace used. After obtaining a stable voltage for 3 minutes from the MFC average of the voltage was noted. An external resistance of 100 Ω was connected to the circuit of the MFC and the digital multimeter was connected in parallel. Current (I) was calculated using the relationship:

$$I = V/R \qquad \text{Eq (1)}$$

where, V is the voltage and R is the external resistance. Power (W) was calculated using the Equation:

$$P = I\,V \qquad \text{Eq (2)}$$

where, I and V represents current (A) and voltage (V). Power density (mW/m^2), current density (mA/m^2), volumetric power density (mW/m^3) and volumetric current density (mA/m^3) were calculated based on the procedures outlined by[12]. Columbic Efficiency was calcuted according to[13]:

$$CE = M0\int t_b Idt/(Fb\ Van\ \Delta COD) \qquad \text{Eq (3)}$$

The total Coulombs obtained is determined by integrating the current over time, so that the Coulombic Efficiency (CE) for an MFC run in batch mode,CE evaluated over a period of time *tb*, where M represents molecular weight of oxygen, F represents Faraday's constant, b = 4(number of electrons exchanged per mole of oxygen), Van in the volume of substrate in the anode compartment, and ΔCOD change in Chemical Oxygen Demand (COD) over time 't_b'.

2.5 Analysis

Selected parameters of inorganic and organic substances were analyzed according to standard method[10]. pH values were determined by Susima pH Meter (India) and conductivity was measured by conductivity meter, (ELICO-180, India). The performance of the MFC was evaluated by organic and inorganic contents removal as well as electricity generation. Morphology of the biofilm formed on the surface of the anode electrode was examined using the

SEM (Quanta-200, Czech Republic)[14]. Elemental analysis of wastewater before and after treatment were carried out using ICP-MS (Nex Ion 300, Perkin Elmer, USA) after triple acid digestion.

3. Results and Discussion

3.1 Power Generation

Power generation of the MFC was evaluated in terms of Current density, Power density, Volumetric Current density and Volumetric Power density. The current generated in the MFC is directly proportional to the assimilable organic contaminants in the sample[15] and suggested that higher the COD value of the sample higher will be the power produced. Inorder to find the efficiency of MFC distillery effluent has been taken as such as a substrate in the anodic chamber. The experiments were carried upto 73 days, the results obtained were presented in the Figure 2 as closed circuit voltage. It shows that MFC generated a stable potential around 200 mV ± 7 mV for 29 days. A maximum voltage of 206 mV was obtained on the 30th day. During the initial days MFC showed poor electricity generation, could be the reason for the microorganism to get acclimatize in the system to form the biofilm. Once the microorganism get acclimatized the voltage started to increase from 19.4 to 200 mV. The decrease in voltage trend was noted from 48th day onwards to 73rd day and the decrease in the voltage would be due to the reduced availability of nutrients. Maximum current density 123.50 mA/m^2 and maximum power density of 25194.8 mW/m^2 obtained is higher than the 28.2 mW/m^2 reported by[16]. MFC produced a maximum volumetric current density of 0.00206 mA/m^3 and Maximum volumetric power density of 0.42436 mW/m^3 are as depicted in the Figure 3.

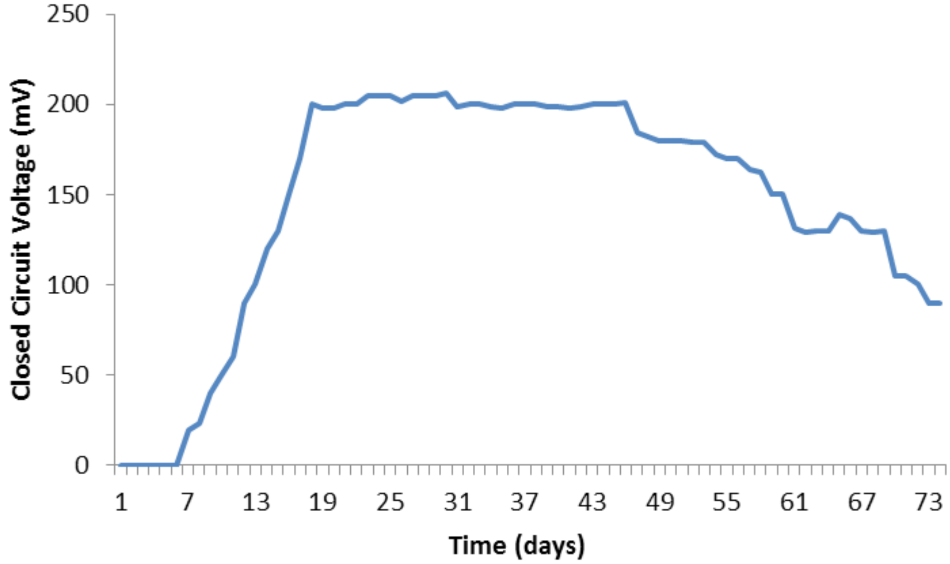
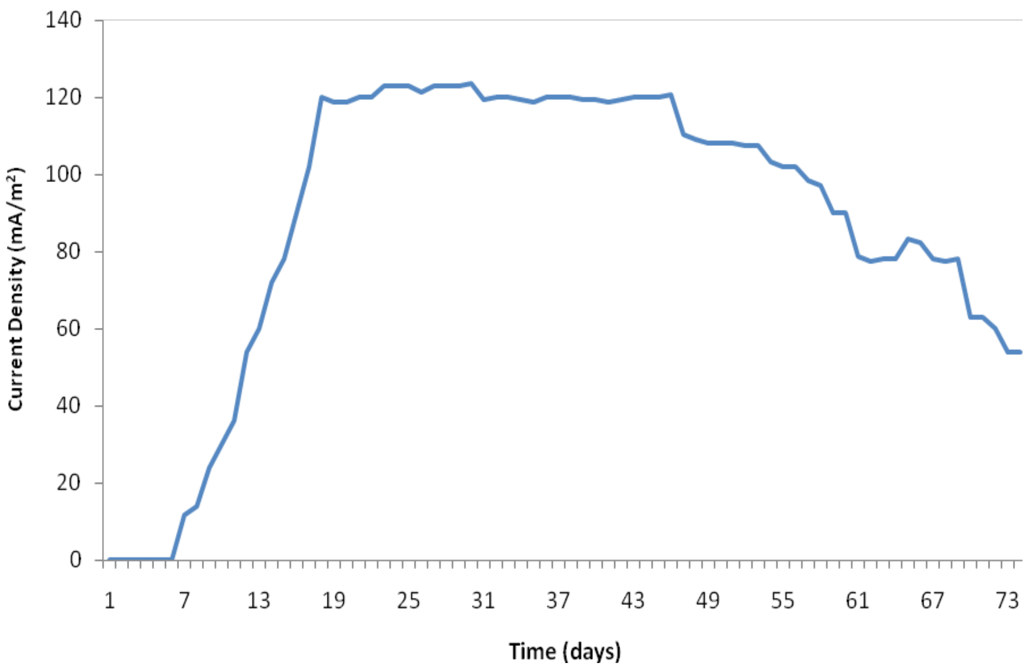
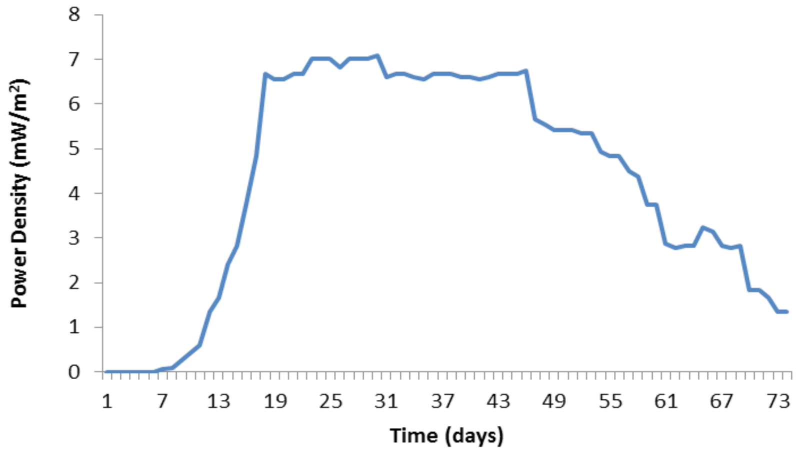


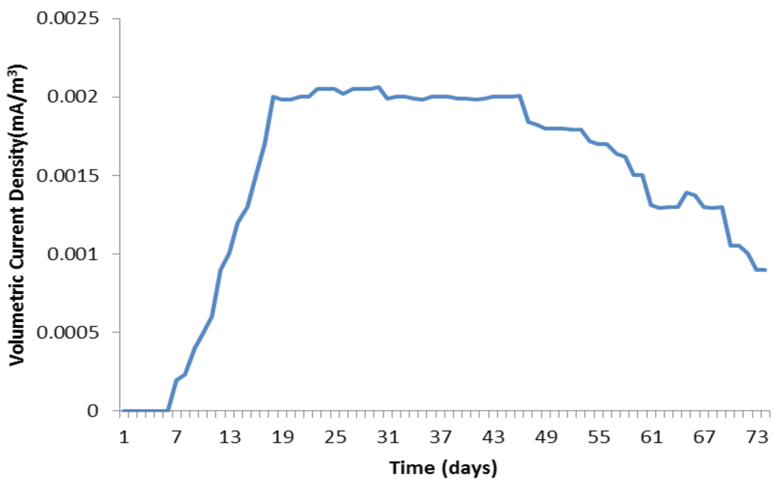
Figure 2. Closed circuit voltage obtained from MFC using distillery effluent as a substrate.



(a)



(b)



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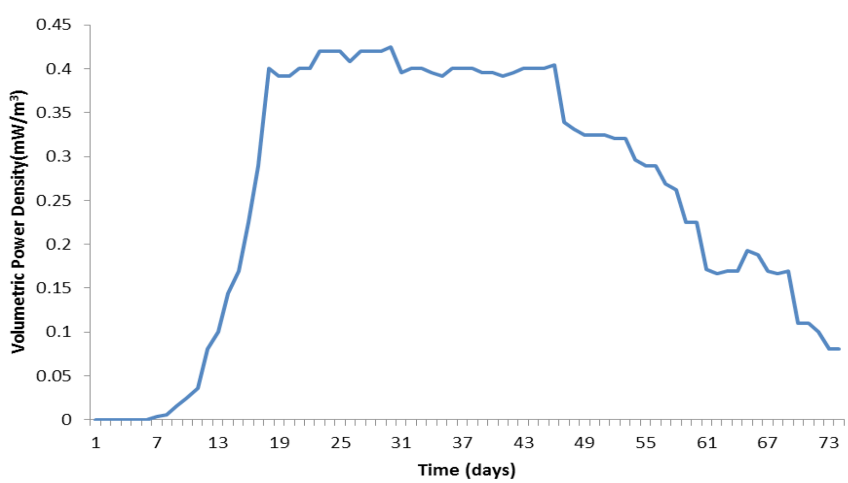

(d)

Figure 3. Power generation data in terms of (a) Current density, (b) Power Density, (c) Volumetric Current Density, (d) Volumetric Power Density.

3.2 COD Removal and Columbic Efficiency of the MFC

The efficiency of the MFC were determined by the COD removal and Columbic Efficiency (CE). COD is the major factor that influences the determination of the efficiency of the MFC. The ability of the microorganism to degrade the organic and inorganic matter drives COD removal, more complex or higher the COD of the substrate higher the time taken to degrade thus prolonged power generation takes place depends on the Microorganism. 68.7% COD removal and 47.12% Columbic Efficiency (CE) were achieved by the MFC. The percentage of reduction was shown in Table 2. The initial COD was 1,53,846 mg/L and after treatment by MFC was reduced to 48,076 mg/L. It was found that the COD reduction was 68.7% without dilution of raw distellery effluent . This COD reduction is higher than the most of the conventional methods adopted for the distillery effluent treatment which needs pretreatment, two stage process, dilution of the effluent or with lesser organic loading rate. Two-stage processes and hybrid reactors shows COD reduction of 54% in frist stage process[16]. It[17] employed sonication of distillery wastewater as a pre-treatment step to convert complex molecules into a more utilizable form reported 44% COD reduction. 56.7% COD removal using single chamber air cathode MFC[18]. Even though the earlier studies reported that removal efficiency is less than the present study further removal of COD from the effluent by the addition if new inoculum to MFC would increase the reduction of the remaining COD.

Table 2. Physicochemical characteristics of distillery effluent after treatment

Sl.No	Parameters	Values	% of Reduction
1.	Color	Blackish Brown	
2.	pH	8.5	
3.	Conductivity (ms)	26.4	
4.	Alkalinity (mg/L)	905.1	
5.	Acidity (mg/L)	11.2	
6.	Total Hardness (mg/L)	380	70.0
7.	Total Suspended Solids (mg/L)	9,873	
8.	Total Dissolved Solids (mg/L)	22,940	71.0
9.	Total Solid (mg/L)	32,813	64.8
10.	Chemical Oxygen Demand (mg/L)	48076	68.5
11.	Dissolved Oxygen (mg/L)	109	73.0

Table 2 Continued

12.	Turbidity (NTU)	1750	55.8
13.	Chloride (mg/L)	1205.3	79.4
14.	Nitrate (mg/L)	233.06	76.6
15.	Phosphate (mg/L)	8.05	79.4
16.	Sulphate (mg/L)	74	70.8

3.3 Heavy Metal Removal

To study the removal efficiency of metals by the MFC the samples were analysed before and after treatment using ICP-MS. The results showed that Na, Mg, Al, K, Cr, Mn, Fe, Ni, Cu, Zn, trace amount of As, Se, Mo, Cd, Pd in distillery effluent presented in Table 3. After the 73 days, the elements showed a effective reduction of Na-57%, Mg-55%, Al-98%, K-38%, Cr-66%, Mn-95%, Fe-62%, Ni-81%, Cu-96%, Zn-97%, As-60%, Se-57%, Mo-47%, Cd-79%, Pd-98%. Interaction of microbes with the heavy metals lead to the reduction of heavy metals namely by bioabsorption process. Mechanism bind to the cell surface of microbes includes, vanderwaals force, electrostatic interaction, redox interaction and extracellular precipitation or combination of these procecess[19]. This study proves that MFC was effective for the removal of metals than the bacterial pretreatment and bioremediation by *Typha angustata* L. of post methenated distillery effluent[20]. Mixed consortia of bacteria and anaerobic digestion would have helped for the better reduction of complex metal from the wastewater.

Table 3. ICP-MS analysis of distillery effluent before treatment, after treatment and percentage of removal

Analyte	Before Treatment	After Treatment	Removal %
	(Conc PPb)	**(Conc PPb)**	
Na	72198.31	30339	57
Mg	27997	12358.03	55
Al	226.62	3.5	98
K	9400.4	5769	38

Table 3 Continued

Cr	19.8	6.57	66
Mn	608.19	28.42	95
Fe	2133.05	797.24	62
Ni	207.18	37.63	81
Cu	22.91	0.86	96
Zn	61.4	1.31	97
As	0.71	0.28	60
Se	0.49	0.21	57
Mo	1.74	0.92	47
Cd	0.39	0.08	79
Pb	2.7	0.04	98

3.4 Effluent Treatment Efficiency

The performance of MFC in removal of other parameters such as Total Hardness, Turbidity, Chloride, Phosphate, Nitrate and Sulphate were determined apart from COD. The physico chemical characteristics of the distillery effluent after treatment are shown in the Table 2. 81.5% of Total Hardness, 55.8% of Chloride, 79.4% of Phosphate, 76.6% of Nitrate and 70.8% of Sulphate, were removed during the process. According to[21] spentwash in India contains very high amounts of Sulphate as compared to spentwash in other countries and was reported that 52. 7% of Sulpahte removal achieved by UASB MFC system[22]. However this study shows the 70.8% removal of Sulphate higher than the reported studies.

3.5 Morphological Identification of Microorganisms

Electrochemically active bacteria in MFCs may be anaerobes or facultative anaerobes and the reaction in MFCs depend on the bacteria[23]. To identify the morphology of microbes on the anode surface biofilm was observed using Scanning Electron Microscope (SEM). Figure 4 shows the microbial attachment on the electrode, which promoted the power generation in the MFC.The biofilm was predominated by cocci shaped bacteria which might have contributed for power generation. It confirms that oxidation of substrate by the microorganism that helped in the generation of electricity and the treatment of wastewater.

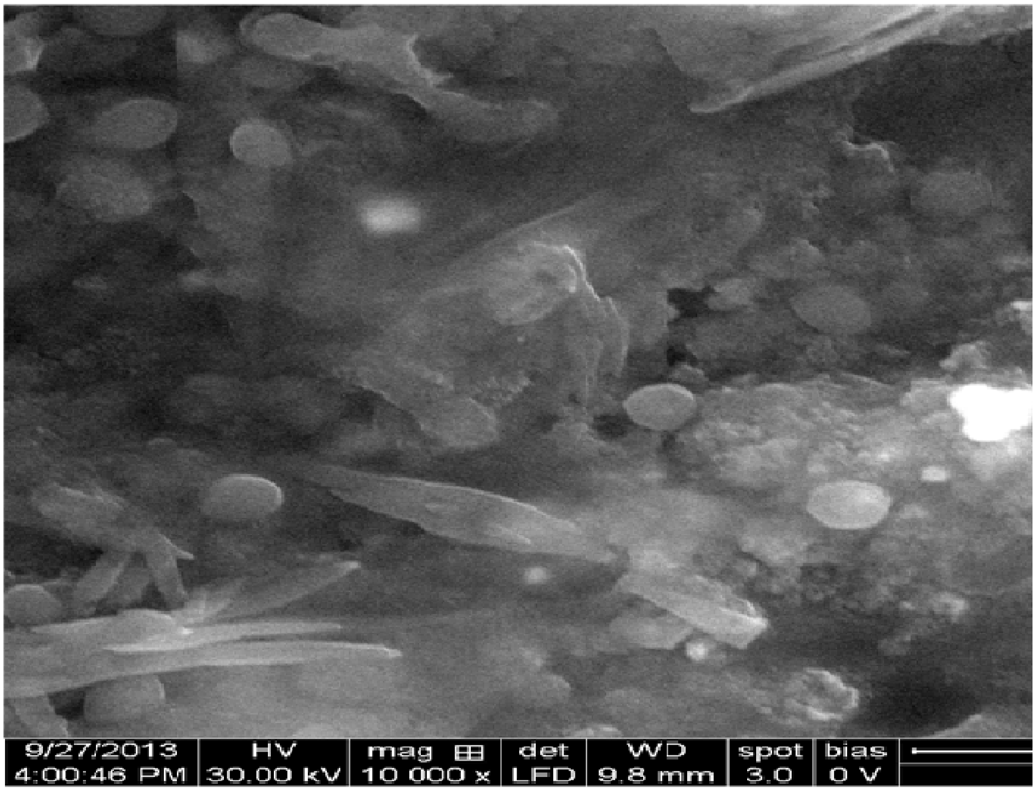

Figure 4. SEM image showing the microbial growth on the anode surface.

4. Conclusion

This study was an attempt to investigate the feasibility of MFC in production of energy from raw distillery effluent and its treatment. MFC generated a stable power for 73 days and maximum power observed on 29th day. It rendered 67.8% COD reduction with a Coloumbic Efficiency of 47.12% and also resulted in heavy metal removal. Morphological identification shows coci shaped bacteria supports in the effluent treatment and power production. The results convey that MFC is reliable technique for distillery effluent treatment and distillery effluent is a promising substrate for power production. Use of modified anode material, increase in surface area of the material would enhance the microbial interaction with the electrode thus more power generation and removal of pollutants can be attained.

5. Acknowledgment

Hanish Mohammed, C.H gratefully acknowledges the financial support in the form of MANF Research Fellowship provided by University Grants Commission, New Delhi, India.

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