Microbial Fuel Cell with Carbon Composite Coated Flexible Electrode

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Abstract: Microbial fuel cell (MFC) has the ability to become a renewable energy resource by microbial transformation of wastes and organic pollutants in waste water using bioremediation approaches. In Pakistan, the concept of using MFC for wastewater treatment and Bio-electricity generation is remain limited due to various limitations. Electrode materials are important in design selection and operating costs of MFCs. To improve the feasibility of MFCs this study presents an easy way to synthesize effective electrode material in the form activated charcoal (AC) prepared from the local agricultural waste which is Date seeds. A lab scale H-type Double Chamber MFC with date seed activated charcoal was used for wastewater treatment and bio-electricity generation. The power density and conductivity with good biocompatibility was achieved by preparing electrode from date seed activated charcoal coated on flexible substrate. The maximum voltage of 520mV with maximum current density of 65.48mA/m² and maximum power density of 90030mW/m³ and yielded 86.42% efficiency against COD removal.

Keywords: Activated carbon, Bio-electricity, Carbon composite electrode, Microbial fuel cell, Date pits.

I. INTRODUCTION

Energy from different wastewater as a source of renewable energy is the trending issue that is currently being explored to lessen the dependence on the non-renewable resources. For bioelectricity generation, organic waste comprising lignocellulose biomass and low-strength wastewaters are the perfect substrate [1, 2]. An abundant low-strength wastewater and wide variety of organic compounds are present in municipal sewage that is subject by compounds that occur in food, comprising protein (40 to 60%), carbohydrates (25 to 50%), and fats and oils (10%). The high protein and fat concentrations in comparison with carbohydrates and the overall low substrate concentrations make municipal wastewater a poor candidate for production of liquid biofuels [3]. A real-time wastewater treatment and power generation using MFCs is a possible short-term application, in which by utilizing respiration of microbes, chemical energy converted into electrical energy [4]. Now, as an environmentally sustainable, economical, renewable energy source and wastewater treatment technology, MFC is gaining more attention from researchers[5]. Oftenly, MFC consist on two chamber, an anode chamber and cathode chamber. External resistance is applied in between both electrode to ease the flow of electrons from anode chamber toward the cathode chamber and an electrolytic medium in between both chambers to allow positive ions to diffuse toward the cathode [6]. The anode of MFC is exposed to electrogenic bacteria, where oxidation occur whereas, at cathode reduction occur. Industrial wastewater and greywater are the most abundant and inexpensive source of carbon, therefore MFC has great potential for bioremediation of industrial wastes, by recovering energy during effluent processing [4]. At the moment, however, the existing design is constrained by low power densities [7]. Furthermore, MFCs basically rely on the use of expensive electrode and a proton exchange membrane (PEM) between the cathode and anode. A variety of materials have been tested with varying results [8].

The electrode material used in MFC requires large surface area, chemical stability, strong bio-compatibility, and high electrical conductivity [9]. Electrode materials include challenges like clogging (especially with graphite fiber brush), high prices, large resistance, and fragility [10]. Some researchers alter electrode materials by heat treatment [11] and catalysts [12] for the improvement in electrode performance. However, these modifications add an extra cost in the construction of the MFC reactor [13].

Activated carbon is a carbonaceous material with a large internal surface area and vastly developed porous structure causing from the processing of raw materials under high temperature reactions. The activated carbon comprise of 87% to 97% carbon however it also contains other elements depending on the processing method used and raw material it is derived from. In this research, the production of activated carbon was carried out by using chemical activation method. In chemical activation, the carbonization and activation are accomplished in a single step by carrying out the thermal decomposition of the raw material impregnated with certain activating agents. Sulfuric acid was used as activating agent. After the impregnation step, the samples were carbonized in the furnace under inert atmosphere by varying the operating parameter such as carbonization temperature and carbonization time. Carbonization temperature was set as 700 °C with impregnation ratio of 3:1 and time duration of 3 hours to analyze the physical characteristics of activated carbon. After carbonization, the activated carbon completely removed. This stage was important because during impregnation the activating agent will penetrated into raw material particles and occupied substantial volumes. Once they were extracted by intense washing, a large amount of micro porosity was created. Date pits are not harmful for environment and they are produced in large quantity in world, inexpensive, easily available and also used as

raw material for the manufacturing of activated carbon.

According to the official records of the Pakistan Agricultural and Research Council, the total annual production of dates in Pakistan is about 0.54 million tons with the contribution of Sindh coming to 0.28 million tons, Baluchistan 0.175 million tons, Khyber Pakhtunkhwa 0.05 million tons and Punjab 0.039 million tones [14]. Date palm trees are spread over 98,000 hectares across Pakistan making it the fifth largest date producer in the world at 0.7million metric tons, with most orchards found in Baluchistan. However, Sindh leads in production. Sindh is the largest dates producing province of Pakistan. It produced around

350,000 tons of dates every year", which accounted for around 52% of the total dates produced each year". These dates are produced on an area of around 279,855 hectares in Sindh. Khairpur and Sukkur are the main districts having the highest production and the most suitable climate and soil conditions. Almost 80% to 85% dates are produce in these two districts. Besides these two main centers, there are a few more areas that produce around 15% of the total dates produced in Sindh [15]. To improve the feasibility of MFCs this study presents an easy way to synthesize effective electrode material in the form activated charcoal (AC) prepared from the local agricultural waste which is Date seeds. A lab scale H-type Double Chamber MFC with date seed activated charcoal electrode was used for wastewater treatment and bio-electricity generation. Instead of the conventional electrode for wastewater treatment and bio-electricity generation electrode was synthesized to decrease the cost of electrode.

II. MATERIALS & METHODS

A. Raw Material and Its Preparation

The dates were collected from Khairpur field, Sindh, Pakistan. Khairpur is situated at 27.53 north latitude and 68.77 east longitude. Seeds, which is our major biomass material were recovered from the dates which is washed several times with distilled water. After that the seeds were dried at temperature of 110oC, then the seeds were grinded using a jaw crusher. The date stones were inserted from the top, and the crusher grinded them in to different fine particles, the process was repeated two to three times. After grinding, to get desired size the crushed date seeds were sieved by using mechanical sieve shaker in which crushed stones were inserted from top and obtained a $1 - 10 \,\mu\text{m}$ size powder from bottom. Powder date stones of 35g were placed into an Oven at the temperature of 110°C for three hours. After drying, the powder was collected in a silica gel desiccator packets were added in an air tight container so that no moisture remains in the container.



Fig. 1: Date Pits Crushed and Sieve

B. Chemical Activation

Chemical activation process refers to making activated charcoal operational. In this case, carbonaceous material is treated primarily with a chemical agent, such as H2SO4 by simple impregnation under a controlled environment. Besides, Chemical activation, carbonization and temperature rate are important factors for obtaining ACs with specific characteristics. Since, for chemical activation process sulfuric acid with concentration of 70% was prepared (14.5 ml of distilled water and 35.5 ml of concentrated H2SO4). During this process room temperature maintenance is necessary, because if temperature is not maintained the volume of solution decreases, due to high temperature vapors of H2SO4 evaporates rapidly.

C. Pyrolysis

Pyrolysis of impregnated dates stones was conducted in a muffle furnace. The samples were loaded into crucible and then placed in muffle furnace. The experiment was conducted in a batch process where activated charcoal was a main product. The experiments were conducted at low heating range from 5 to 10oC so that slow pyrolysis is performed. The furnace took about 2 to 2.3 hours to reach the desired temperature. The carbonization times was measured from the moment the furnace reached the desired temperature. After 3 hours a sample was withdrawn from the furnace and allowed to cool.

D. Washing and Drying

Once the sample reach the room temperature the samples were washed several times with distilled water. Afterwards the samples were again dried in an oven at 110oC for 2 hours and the final samples were collected in an air tight silica gel desiccator packets



Fig. 2: Schematic Diagram for Making Activated Carbon

E. Preparation of Activated Carbon Composite Electrodes

The functionalized activated carbon washed by Distilled water with pH 7 to neutralize the pH. Vacuum filtration machine was used for properly washing and drying the activated carbon. After drying the activated carbon further vapors were evaporated by using oven 70oC. Binder solution of Carboxyl methyl cellulose 2% were prepared. Activated carbon and Binder were mixed properly and the slurry were keep in air tight bottle for complete agitation. The flexible mercerized cotton fabric of plain weave design with EPI × PPI 60×60 and warp x weft (Ne) 20×20 were used as a coated substrate. The slurry of activated carbon composite were coated on flexible substrate. The doctor blade technique was used for coating the activated carbon composite on the substrate. At first composite were pasted on the cotton cloth by using blade, as can be seen in fig. 3. The coated electrode were dried in oven at 65oC for thirty minutes and slowly increased up to 80oC, later then cure by using Iron. The gauge thickness meter was used to measure the thickness of activated carbon composite. Initially, the bare fabric thickness was measured and note down after coating the final coated electrode thickness was measured and the coated material surface was keep about 0.5 mm that was monitored by using cloth gauge thickness meter.

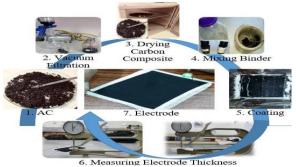


Fig. 3: Preparation of Activated Carbon Composite Electrode

F. H-Type Double Chamber Microbial Fuel Cell Construction

H-Type double chamber MFC were made using two plastic bottles of polyethylene terephthalate as chamber. Both chambers were joined by using an union joint with salt and agar solution contained in PVC pipe installed in the middle of the reactor as a proton exchange membrane[16]. Inlet and outlet valve were also fitted in the anode chamber. The anode chamber was properly maintained anaerobic by eliminating all the leaks and purging nitrogen before running the reactor. Real time data was saved in memory card by using Arduino board microcontroller assembled with Temperature, pH, and Voltage sensors. The cathode chamber was kept aerobic by installing an aquarium air pump to provide oxygen/air. The anode chamber was used to treat Greywater whereas cathode chamber was filled with DI water.

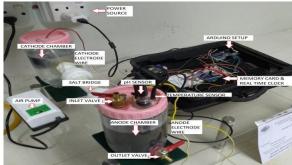


Fig. 4: H-Type DCMFC.

G. MFC construction, operation and tests

The Greywater sample was collected without any treatment from the domestic region near Mehran University of Engineering and Technology. The activated carbon coated flexible electrode was installed among the center of the anode and cathode chamber. The reactor was kept at room temperature and anaerobic conditions was maintained by purging nitrogen before running the reactor. All the required parameters like pH, temperature, and voltage was saved in the SD card modular and reactor was being continuously monitor with the help of data acquisition model. The saved data in the memory card was later on connected to the SD card support device. The reactor was monitored up to the decrease in voltage. The greywater organic substrate removal efficiency by activated carbon electrode was measured as Chemical oxygen demand (COD). COD analysis was performed by the closed reflux colorimetric method. The power generation was calculated by Maximum Voltage, current density, and power density. Maximum voltage measure in between two ends of anode and cathode electrodes under the applied external resistance. By using ohm law current was measured whereas, Current density was measured by current production per unit surface are of electrode. Power density calculated by power produced per unit total volume of reactor.

III. RESULTS

A. Surface Morphology of Activated Carbon and activated carbon coated electrode.

Physical properties like Pore size, surface area and Density of Activated Charcoal is very important factor to characterize. Therefore, to study the effect of H2SO4 impregnated charcoal it was compared to its initial stage. For this Purpose, scanning electron microscope (SEM) was used, that images the sample by scanning it with high energy beam and pore size was measured using Image J software. These results help us to estimate the efficiency of Activated charcoal. Table 1. Physical Properties of Activated

Carbon.		
Sample	Initial Date Pits	H2SO4 Impregnated
		Charcoal
Surface Area	489.06 m ² /g	$700 \text{ m}^2/\text{g}$
Pore Size		0.11µm to 0.7µm
Pore Volume	$1.2 \text{ cm}^3/\text{g}$	0.44cm3/g
Density	0.8 g/ml	0.50g/ml

Surface morphology of activated carbon coated fabric analyzed by using compound microscope, also coated electrode captured by using scanning electron microscope (SEM). In fig 5 and 6 activated carbon is shown whereas, fig 7 and 8 Activated charcoal coated electrode is shown.

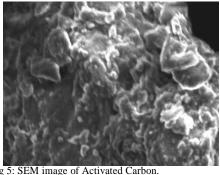


Fig 5: SEM image of Activated Carbon

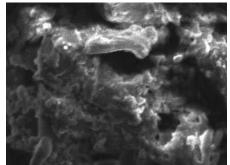


Fig 6: SEM image of Activated Carbon.

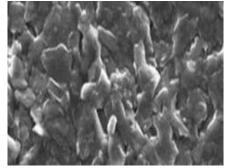


Fig 7: SEM image of Activated Carbon Coated Electrode

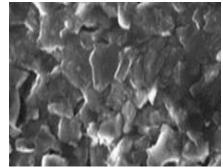


Fig 8: SEM image of Activated Carbon Coated Electrode

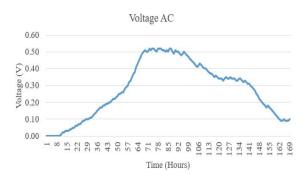
B. Performance of DCMFC & COD Removal Efficiency

The DCMFC performance was monitored with voltage observation with the time difference of 12 hours by using microcontroller having ability of auto data saving in memory card. The voltage generated by DCMFC can be observe from Graph 1, an initial voltage of 0.01V were recorded at 10th hour after startup of DCMFC and increased up to maximum

voltage 0.52 V recorded at 70th hour. The DCMFC generated the maximum voltage readings more than 0.50V about 24 hours continuously. The microbes present in activated sludge, they strategically position themselves on the activated carbon coated anode surface to form a biofilm. This biofilm which is made up of a complex extracellular proteins, sugars and microbes cells is rich with materials that can potentially transport electrons[17].



Fig 9: Biofilm Analysis using Compound Microscope



Graph 1: MFC Voltage generation.

As shown in graph, it can be note down that the maximum voltage limit more than 400mV generate in between duration of 64th hour to 110th hour having peak at 70th hour the maximum voltage of 520mV at AC coated electrode. The bio electricity recorded from the AC coated electrode as, maximum voltage 0.52V with maximum current density of 65.48mA/m2 and maximum power density of 90030mW/m3. Due to the various associated limits with its use as a power generation source it has been seen many researchers prefer the MFC for organic substrate removal and also recovery for heavy metals. The results showed that COD removal efficiency at AC coated Electrode was found 86.42%. The organic load was measured as Chemical oxygen demand (COD). COD analysis were measured at the beginning and end of each cycle of DCMFC.

IV. CONCLUSIONS

The aim of this research is to fabricate a MFC Electrode using inexpensive and local materials. The activated charcoal was successfully prepared from the date pits and electrode was synthesized from this date pits activated charcoal. The results shows that the DCMFC with activated carbon coated electrode generate 520mV whereas, the COD removal efficiency was 86.42%, and thus it has potential to contribute in the solution of the energy crisis in a developing country like the Pakistan. Results of the study confirmed that the MFC treated the wastewater and bring green energy.

V. RECOMMENDATIONS

This study would like to recommend that MFC is emerging technology in scientific world, that the materials and configuration of the MFC in the experiment be improved. Instead of using consumable resources for wastewater treatment, utilizing this MFC technology is much better as it decrease the pollution in the environment on the other hand also helps in the conservation of natural resources.

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