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Contaminants Removal from Real Refinery Wastewater Associated with Energy Generation in Microbial Fuel Cell

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ABSTRACT

Microbial fuel cells (MFCs) pertain to a kind of modern technology for the direct conversion of chemical energy in organic matter from wastewaters into electricity during the oxidation of organic substrates. A system of continuous MFC was constructed for the treatment of real petroleum refinery wastewater (PRW). The treatment of real PRW, operational performance of the MFC system, biodegradation of furfural, and energy output were investigated in this study. The MFC was inoculated by mixed anaerobic bacteria, with *Bacillus* sp. as the dominant type, and continuously operated for 30 days. The biodegradation of furfural and phenol, which are the most prevalent toxicants in refinery wastewater, was investigated. The MFC system reached maximum energy outputs of 552.25 mW/m^3 and 235 mV. In the anodic chamber, the maximum removal of furfural and phenol was higher than 99%, with biodegradation of organic content reaching up to 95%. This study demonstrated the viability of a continuous-flow MFC system as a green technology for the treatment of furfural-rich real refinery effluents while generating electricity.

Keywords: microbial fuel cell, phenol, furfural, power generation, COD, petroleum refinery wastewater.

INTRODUCTION

Environmental issues related to energy and wastes are major issues that should be addressed. Improper waste management causes irreparable damage to the environment. Meanwhile, we still rely heavily on non-renewable resources for energy. The high demand for energy prompted the movement for energy production from renewable sources. To date, a growing worldwide interest focuses on the development of wastewater treatment technologies (Uygur and Kargi, 2004; Włodarczy and Włodarczy, 2017).

Two environmental concerns, namely, waste and energy, can be handled simultaneously by microbial fuel cells (MFCs) (Ortiz-Martínez et al., 2015, Patil et al., 2021; Kugarajah and Dharmalingam, 2021; Bhagat et al., 2022; Choudhurt et al., 2022). MFCs have caught increasing attention and have revealed promising results in numerous applications, including bioremediation (Rosenbaum et al., 2014), biosensors (ElMekawy et al., 2018), and wastewater treatment (Yakar et al., 2018), as a novel alternative source of renewable energy in remote areas (Castro et al., 2014) and desalination (Zhang et al., 2018). MFCs can offer solutions to the problems of clean water and sustainable energy demands. MFCs have been developed as eco-friendly alternatives for the generation of electricity by oxidization of organic matters by microorganisms. In the anodic chamber, bacteria oxidize organic matters (which serve as fuel) and release protons, electrons, and CO_2. The released protons in the anodic section migrate to the cathodic chamber through the separator between the two chambers, whereas the electrons move toward the cathode through an external circuit due to electrophilic attraction from the cathodic electrodes. Then, the protons and electrons subsequently react with oxygen (final electron acceptor), and the circuitry is completed by this reduction reaction (Aoudj et al., 2015; You, 2016).

Petroleum refineries use additional refining operations to improve certain product properties. Oils and their derivatives from petroleum production plants are attracting attention due to their widespread applications. Effluents from petroleum refineries pose the problems of decontamination and proper disposal due to the often toxic dissolved organics, such as oils, hydrocarbons, and phenols, and their chemical oxygen demand (COD) and BOD. Petroleum refinery wastewater (PRW) is one of the most affected sources of industrial wastewater pollution and a major cause of environmental problems, especially in the aquatic environment (Lan et al., 2009). Furfural is a furan-derived heterocyclic aldehyde. This liquid compound manifests an oily and pale yellow appearance that darkens during exposure to light and oxygen photochemical oxidation. Furfural is considered a refractory and toxic substance to numerous organisms, but it scarcely causes inhibited enzymatic metabolism in most microorganisms. Moreover, furfural removal can be achieved by taking advantage of the metabolic capability of certain bacteria (Farías et al., 2022). Phenols are environmental pollutants found in wide concentration ranges in wastewater from several industrial processes, such as leather, synthetic rubber, coking, plastic, ceramic, petrochemical, petroleum refineries, etc. (Song et al., 2014). At low concentrations, phenols are considered significant pollutants due to the harm that they cause on organisms and human health; several phenols have been categorized as hazardous pollutants (Huang et al., 2007). At concentrations of over 5.5 ppm, phenol can inhibit microbial activity in wastewaters (Neufeld et al., 1986).

The efficiencies of phosphorus, ammonia nitrogen, and COD removal in wastewaters are significantly affected by high phenol concentrations (Uygur et al., 2004). Majumder et al. (2014) treated refinery wastewater and generated electrical current using an air-cathode MFC in a batch mode of four cycles. The maximum power density of 50 mW/m^2 was obtained, and the COD removal efficiency as a function of time reached 30%. Guo et al. (2016) investigated the influences of granule graphite and granule-activated carbon as packing materials on electricity generation and the treatment performance of MFCs using PRW as the substrate. The maximum power density was 330.4 mW/m^3, and the treatment efficiency was 84% ± 3%. Srikanth et al. (2016) treated refinery wastewater using MFCs in a batch-mode operation. The batch-mode operation revealed a high power density of 225 ± 1.4 mW/m^2 and good substrate degradation (81 ± 1.8%) but required a long hydraulic retention time. As a result, a significantly low degradation rate of the substrates was observed. Mohanakrishna et al. (2018) applied voltage for a short period in a single-chamber MFC to improve the treatment of PRW. The maximum efficiency (89%) detected at the applied voltage of 500 mV was nearly 50% higher than that of the control system (59%), which implied the effectiveness of auxiliary voltage in the treatment of PRW. Mohanakrishna et al. (2020) added labneh whey as a co-substrate to improve the bio-electrochemical treatment of PRW in a dual-chamber MFC. The results showed a moderate removal efficiency (63.1%) for COD. Abu-Reesh et al. (2022) investigated the performance of MFCs in the treatment of PRW using dual- and single-chambers MFC reactors with various configurations. For dual-chamber MFC in the continuous mode of operation, the removal efficiencies for COD in the treatment of PRW reached 84.4%, and the bioenergy generation in terms of volumetric power density and current density reached 328.26 mW/m^3 and 79.2 mA/m^2, respectively.

Thus, from these studies, various techniques are used for the treatment of the samples of PRW. Nevertheless, not one reached a stable removal efficiency higher than 95%. On the other hand, furfural and phenol are very toxic substances in PRW, and they have not been studied as a single constituent in the mixture of toxicants in PRW. Therefore, this research investigated the biodegradation of furfural and phenol in real PRW using a mixed culture of bacteria, with *Bacillus* sp. as the dominant species, as biocatalyst in a dual-chamber MFC.

EXPERIMENTAL AND METHODS

Real-field PRW (RPRW)

Fresh RPRW samples were collected from Al-Dura Oil Refinery in Baghdad city, Iraq. The refinery processes produce about 20,400 m^3/day wastewater. For the wastewater used in this study, the average initial concentrations of COD, furfural, total suspended solid, total petroleum hydrocarbon (TPH), phosphate (PO_4^{-2}), and sulfate (SO_4^{-2}) were 1180 ± 50, 10 ± 0.78, 68 ± 9, 350 ± 30, 7.1 ± 0.8, and 43 ± 9 mg/l, respectively, with pH in the range of 6.82–7.47.

Biocatalyst

A fresh sample of activated sludge was collected from the outlet of the biological treatment units at AL-Rustumia wastewater treatment plant (WWTP), Baghdad. The sample was used as the source of active bacteria for the proposed MFC system, without prior adaptation to the target levels of furfural in the RPRW. Before use, the biocatalyst was first stored in a closed container under strict anaerobic conditions for approximately one month to induce the increased ability of facultative microorganisms for oxidizing organic content in the absence of oxygen. Then, the metabolic pathway was switched to anaerobic function. During this period, the biocatalyst morphology changed significantly from a brown and fluffy appearance to a black and dense texture. Qualitative analysis of bacterial species and scanning electron microscopy (SEM) were performed to monitor microbial growth. Facultative bacteria were targeted in this study. The analysis of the collected activated sludge indicated *Bacillus* sp. as the most dominant type in the mixed culture.

Analytical methods and electrochemical measurements

Samples were collected and analyzed on a daily basis for the total dissolved solids (TDS), dissolved oxygen, COD, electrical conductivity (EC), and pH. Furfural and phenol concentrations in aqueous samples were determined by ultraviolet/visible spectrophotometer (model: UVD-3000, LABOMED, USA) at 278 and 270 nm, respectively. The cell voltage was monitored to determine power generation and the performance of the MFC. The potentials between the edges of the fixed external resistance (100 Ω) were measured using a data logger and a portable handheld digital multimeter for double-checking. Once the voltage outputs of each reactor were stabilized, the electrochemical performance of the systems was analyzed in term of polarization and power density.

MFC INSTALLATION AND OPERATION

MFCs consist of two electrodes, namely, a negative anodic electrode and a positive cathodic electrode, which are separated by a semi-permeable membrane such as a cation-exchange polymer-based membrane. A rectangular dual-chamber MFC was constructed from Perspex material. As shown in Figure 1, the anode and cathode chambers were of the same shape and had 1 L capacity. The chambers were separated by a cation exchange membrane (type: CMI-7000, Membrane International INC., NJ, USA). An uncoated graphite plates was used as the cathode and another identical graphite plate as the anode. The electrodes were connected to each other by wires with a fixed resistance of 100 Ω. This circuit was eventually connected to a digital multimeter and used for the central monitoring of electrical parameters. The system consisted of holding and neutralization tanks prior to the MFC to adjust the fuel feed pH (if required) and TDS, furfural, COD, and EC. The MFC was fed at a flow rate of (0.55

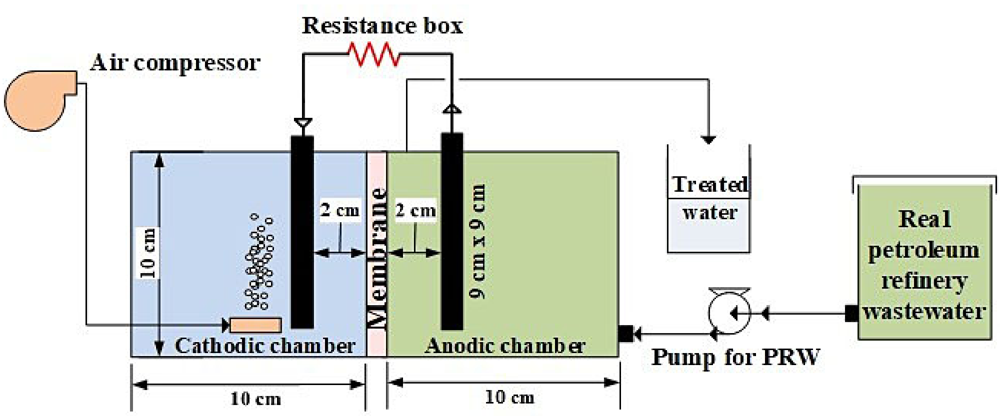

Figure 1. Schematic for MFC

ml/min) from the holding tank through a peristaltic pump (Variable Speed Pump 3386, USA). For further measurements, the treated wastewater was collected in a final collection tank. The anode compartment was maintained under anaerobic conditions by flushing the wastewater with nitrogen gas prior to operation. By contrast, the cathodic compartment was filled with phosphate buffer solution as a catholyte and maintained under fully saturated aerobic conditions.

RESULTS AND DISCUSSIONS

Organic content removal

As shown in Figure 2, the MFC system was continuously operated for 30 days with real petroleum wastewater, and the operation comprised three phases: a slow COD removal rate for the first 5 days, a gradually increasing phase for 10 days, and a steady-state condition within 90 ± 4.7% COD removal in the last 15 days of operation. The maximum removal efficiency of 95.7% on the 27th day indicated the high activity and enrichment of microorganisms in the anodic chamber.

The significantly high removal of COD indicated an almost excellent organic content removal, which was higher than the previously reported values for the treatment of COD (68%) using MFCs fed with synthetic furfural wastewater in a 30 h batch mode, as reported by Luo et al. (2010) and the 71% COD removal in a continuous inflow cyclic biological reactor containing stirring media previously reported by Moussavi et al. (2016).

Furfural biodegradation

Furfural is considered one of the main pollutants in petroleum wastewater (Anbia and Mohammadi, 2009). Consequently, the biodegradability and elimination of this component must be monitored. Figure 3 shows the profile of furfural removal efficiency during the 30-day continuous MFC operation. The profile showed the significant removal of furfural with a high maximum removal efficiency of 99.05% in the MFC. Nevertheless, the profile of furfural removal in the MFC consisted of two consequent phases (Fig. 3). The first phase revealed significant fluctuation in the first 18 days, and the second phase, which was observed after nearly 23 days, revealed a steady-state condition over the remaining period of continuous operation. These promising results promote the application of MFCs without any requirement for the pretreatment of real PRW to remove furfural. These findings are better than those reported by Zheng et al. (2015), who isolated an aerobic bacterial strain DS3 from an activated sludge of WWTP after enrichment. Strain DS3 showed 31.2% degradation for furfural under optimum conditions: 35 °C, pH 8.0, 10% inoculum, and 150 rpm. Furthermore, strain DS3 tolerated a high furfural concentration. Farías et al. (2022) also examined the furfural degradation ability of a mixture of *Brevundimonas* sp., *Bacillus licheniformis,* and *Microbacterium* sp., and the results verified the absence of exponential bacterial growth within 72 h and the very low removal efficiency.

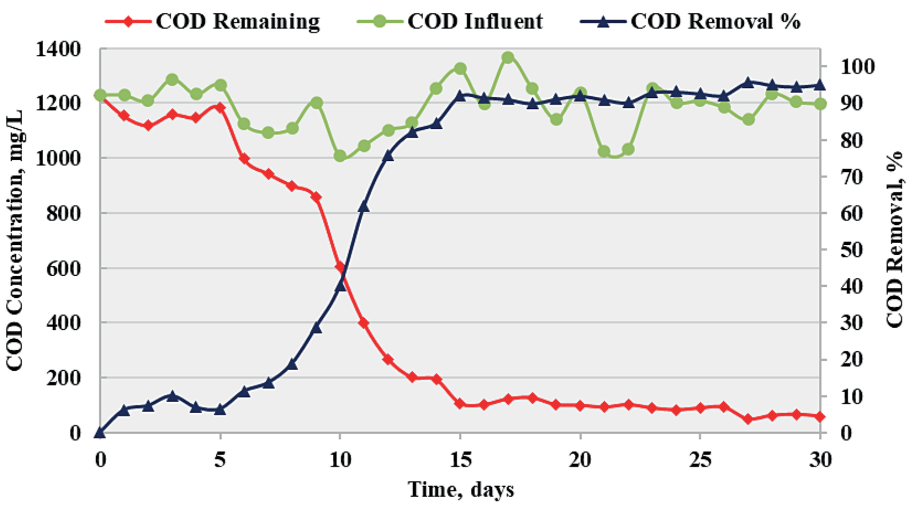

Figure 2. Profile of organic content removal efficiency

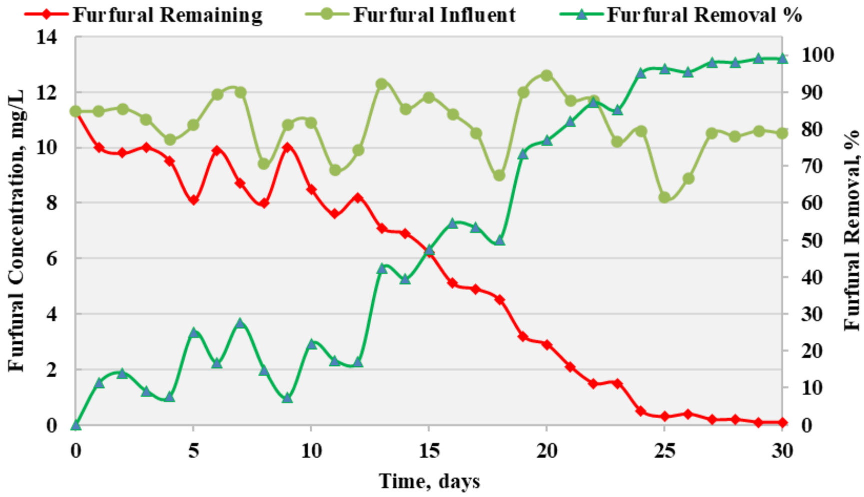

Figure 3. Profile of furfural removal efficiency

Phenol biodegradation

Figure 4 shows the biodegradation of phenol by the mixed bacterial culture as a function of time. The bacteria degraded more phenol within the given time compared with furfural in spite of the higher average of phenol concentration (240.2 ppm). The profile of phenol removal in the MFC also consisted of two successive phases. The first phase revealed substantial variation in the first 10 days. Afterward, a steady state appeared in the second phase after several days. The profile showed the significant removal of phenol with a high removal efficiency of 99% in the last ten days. The results of this study revealed that the MFC can improve phenol degradation compared with other techniques dominated by normal anaerobic metabolism. Morris and Jin (2007) attributed this improvement to the transfer of electrons to the terminal electron acceptor of oxygen in the cathodic chamber rather than to the electrons acceptors, such as metals and sulfate, in the anaerobic anodic section, causing indirect aerobic degradation.

Energy profile

As mentioned above, the MFC's electrical energy was monitored strictly using an electrical data logger and measured directly with a digital multimeter during the entire period of continuous operation. Energy generation was analyzed and calculated as power densities normalized to the effective anodic volume (Fig. 5).

The first day of system operation with real wastewater 1 mW/m^3 generated electrical energy. The power densities still increased the following days until a steady-state condition,

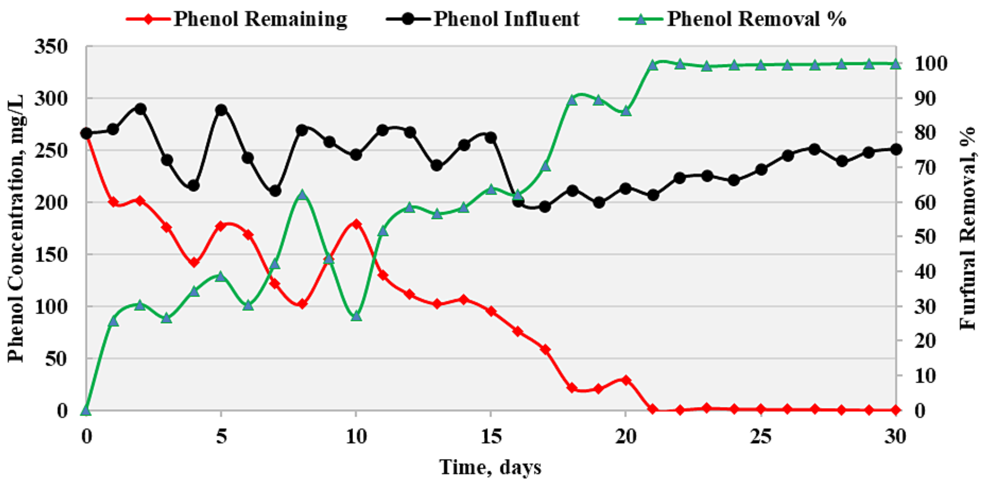

Figure 4. Profile of phenol removal efficiency

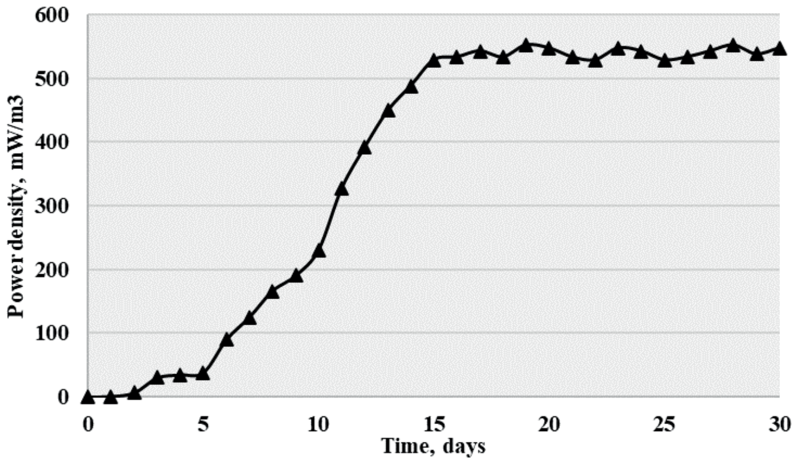

Figure 5. Profile of power density at external resistance of (100 Ω)

which corresponded to the steady state in the COD profile, was reached. Afterward, the power densities increased and reached the maximum value of 552 mW/m^3. This value is higher than the maximum power density of 103 mW/m^3 observed by Luo et al. (2010) in the ferricyanide-cathode MFC fed with furfural as a sole pollutant in the refinery wastewater.

Electrochemical property

The MFC electrochemical properties, such as overvoltage, can be compared through the polarization curve method (current versus voltage) using various resistances during the operation of MFCs (Moon et al., 2005). Figure 6 shows the results of the experimental polarization curves. The optimum current density was 340.74 mA/m^2, whereby the power density, which was obtained at 75 Ω external resistance, was 70.53 mW/m^2 in the stable operation period. This reasonably low internal resistance value provided an effective conventional MFC design including all electrical connections.

The results of experimental polarization curves were compared with the findings obtained and reported by Huang et al. (2021), and the comparison revealed the higher internal resistances of different materials for electrode, such as graphite felt and carbon brush; these results proved the efficiency of the present design.

Biofilm formation

SEM images were used to specify the rate of biofilm formation on the electrode in the anode chamber. SEM images were recorded on a ZEISS MODEL (Sigma VP EDS and mapping: Oxford

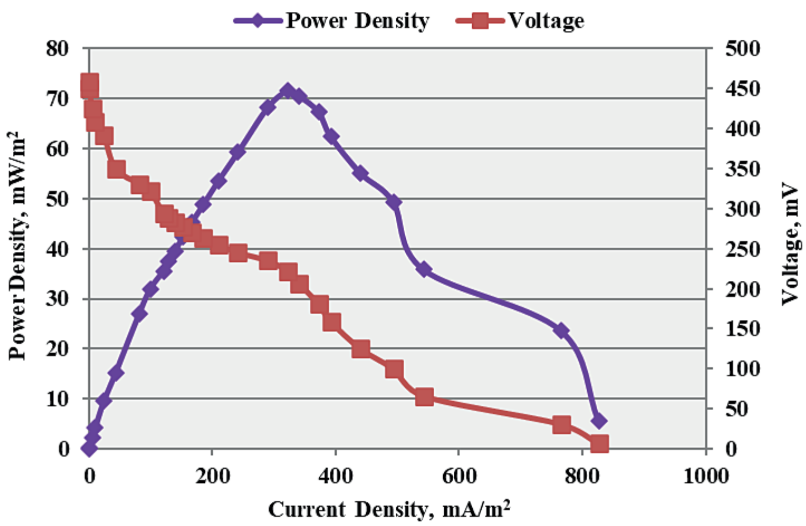

Figure 6. Polarization curves for a stable period of operation

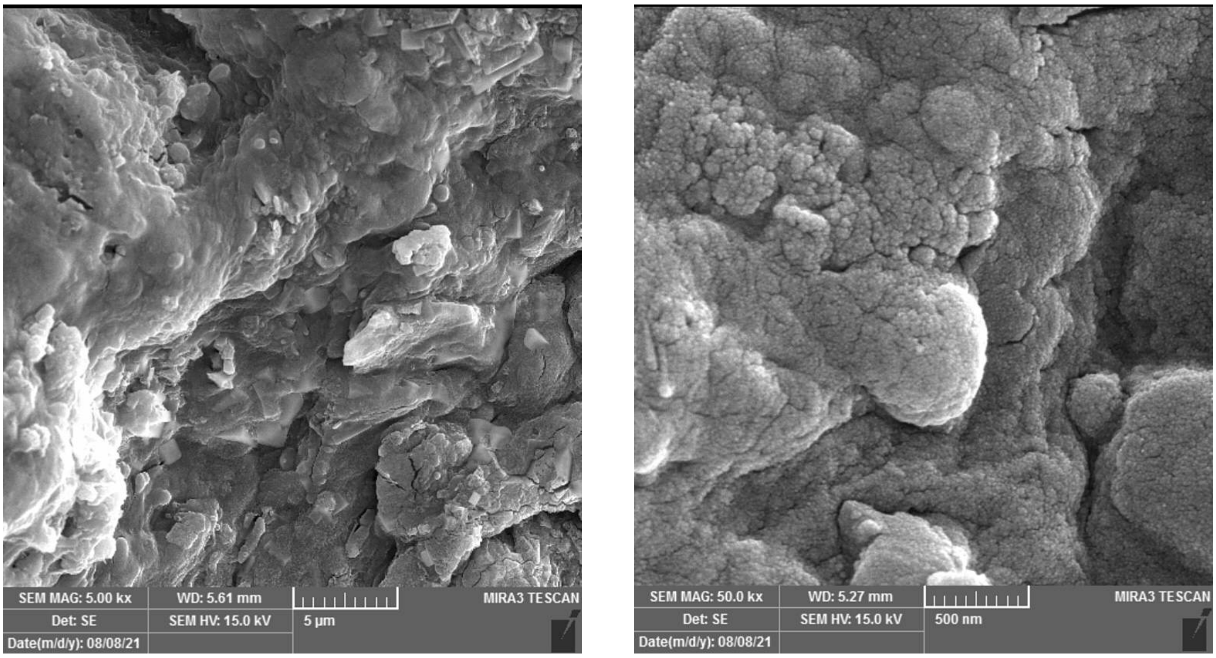

Figure 7. SEM images of the biofilm on the anodic electrode

instruments. UK) operating at 15 kV. Fig. 7 shows the SEM images of the biofilm within the MFC reactor before and after biofilm formation on the surface of the electrode inside the MFC reactor. The SEM images indicated that the biofilm formed on the surface of the electrode in the anode chamber played a substantial role in the biodegradation of COD, furfural, and phenol from real PRW. The number and size of bacterial cells after the biodegradation of RPRW also increased, indicating the growth and affinity of these microorganisms on these substrates.

CONCLUSION

This study investigated the biodegradation of furfural and phenol contained in RPRW as fuel for MFCs. The results of this study provide meaningful information for the utilization of RPRW as a useful source of MFCs. Mixed bacterial cells, with *Bacillus* sp. as the dominant microorganism in the culture, were inoculated into the MFC and used in the treatment of RPRW. Power generation, biodegradation of furfural and phenol, and COD removal were investigated. The MFC system attained maximum energy outputs of 235 mV and 552.25 mW/m^3. The maximum removal of furfural and phenol exceeded 99%, and the biodegradation of organic content was up to 95%.

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