Simultaneous heavy metal reduction and voltage generation with synergy membrane-less microbial fuel cell

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Abstract. Metal contaminated wastewater effluent from industries has caused several environmental problems and public health due to its toxicity. Conventional heavy metal reduction processes are neither economical nor environmentally friendly. A synergy economical single chamber up-flow membrane-less microbial fuel cell (UFML-MFC) was fabricated to study the feasibility of heavy metal reduction and voltage generation. Cu (II) was used as electron acceptor to explore the mechanism of metal treatment in UFML-MFC. The performances of the UFML-MFC were investigated with 0 mg/L, 5 mg/L and 10 mg/L concentration of Cu (II) in terms of voltage output, chemical oxygen demand (COD) reduction and Cu (II) reduction efficiency and electrode spacing distance. UFML-MFC used carbon felt as anode and cathode material where anode region was filled with 0.2 cm of gravels at anode region. Overall performance deteriorated with increased initial concentration of Cu (II). Voltage generation decreased from 71 mV to 11.1 mV. COD reduction decreased from 56% to 36%. Moreover, the Cu (II) reduction efficiency was reduced from 87.56% to 36.98%. These results showed that the increased concentration of the Cu (II) could potentially reduce the microbial activities. However, UFML-MFC showed that the shorter distance of electrode spacing (anode and cathode) could enhanced the voltage output. These results showed the great ability of integrating UFML-MFC for heavy metal reduction.

1. Introduction
Heavy metals are commonly found in industrial wastewater resulting from electroplating, smelting, battery manufacturing and so on [1]. Steel production and mining industry are few of the common industries that contribute to the heavy metal pollutions in surface and groundwater. The most commonly encountered toxic heavy metals are arsenic, lead, mercury and Cu (II). Heavy metal pollution has caused a serious impact on the environment due to its high toxicity and also non-biodegradability. This problem not only affect the stability of the ecosystem but also has an adverse impact on the health of the human being. Heavy metal ions can be accumulated through food chain and is believed to be a risk for human beings even at trace level [1]. For instance, the discharge limit of 1 ppm of Cu (II) in the water could cause nausea and vomit. The pollution of surface water and groundwater by metal ions normally occurs in developing countries due to bad waste disposal systems and also unplanned industrialization [2], [3].
Over the years, various traditional methods have been tested and introduced in the industries to effectively remove the toxic heavy metal ions. Heavy metals that removed by various conventional methods such as chemical precipitation, solvent extraction, membrane filtration, ion exchange, electrochemical reduction, coagulation were proven to have some disadvantages [4]. However, these methods possess disadvantages include low reduction efficiency, high energy requirements, production of toxic sludge, sensitive operating conditions, among others [2], [3]. Among these processes, biological process is considered as an innovative technology and remedial strategy due to its cost effectiveness and eco-friendly nature [5], [6].

Microbial fuel cell (MFC) is a useful technology where it make used of the electrochemical active bacteria as a biocatalyst to decompose the substrate and caused the transfer of electrons from the oxidized substrate to the anode electrode [7]. The electron will then transfer from the anode to electrode and at the same time generating voltage from the process. The electron then leaves the cathode to the final electron acceptor and cause the reduction occurs. Furthermore, the biological treatment that utilize the usage of the bacteria and fungus has been proved to have high reduction efficiencies in removing the heavy metals from the wastewater [8]. On the other hand, single chamber microbial fuel cells have simple design and is proven to be more cost effective as it does not required an expensive separating membrane [9]. Apart from that, single chamber microbial fuel cells is consider to be cheaper than other design as it does not contain the cathodic chamber that requires extra expenditure for the cathodic side [10].

This study aims to determine the feasibility of a membrane-less MFC that can be used for heavy metal reduction. The heavy metal that is used is Cu (II), and the experiment is conducted by varying Cu (II) concentration, and how the distance between electrodes could affect the process of Cu (II) reduction.

2. Methodology and Experimental Setup

2.1 Configuration of UFML-MFC reactor

The UFML-MFC was constructed using cylindrical transparent acrylic with 32.5 cm height and 5.5 cm inner diameter as similar to previous described [11]. Holes are drill 2 cm from the bottom and 2 cm from the top in order to insert and extra cylindrical pipe with 1.5 cm diameter and 5 cm in length. The reactor consists of carbon felt as anode electrode with size of 1.0 cm width x 0.8 cm height x 3.5 cm length. The UFML-MFC reactor was designed to have 3 anodes in the anodic region where each having a different distance from the cathode electrode. 0.2 cm of gravels were filled up the anodic region to separate the anodic and cathodic compartment. The gravels responsible in immobilizing the microbes and also allow for the biofilm development.

Figure 1: Schematic diagram of UFML-MFC.
2.2 Inoculation of microbes on the gravels and electrode surface
The carbon felt that will be used as anode electrode were immersed in the activated sludge for inoculation. The carbon felt was cut into 3.0 cm length x 2.5 cm width x 2.0 cm height for the anode electrodes. The gravels were sieved through a sieve to ensure all the gravel have the same size where the size of each gravel used was approximately m 0.2 cm. The inoculation period will be 2 months to ensure the microbes are able to grow on the surface of the carbon felt and gravels to form a biofilm

2.3 Startup and operation of single chamber UFML-MFC
The wastewater containing activated sludge was collected from KCC Sdn Bhd wastewater treatment plant where the influent to the secondary tank is chosen. The medium was prepared using $C_2H_3NaO_2$ (2.35 g/L), $NH_4Cl$ (0.3 g/L), $K_2HPO_4$ (3.4 g/L), $KH_2PO_4$ (4.4 g/L) $MgCl_2.6H_2O$ (0.1 g/L) and $NaCl$ (0.116 g/L). Copper (II) nitrate trihydrate was used to dissociate and form Cu (II) ions in the synthetic wastewater. The synthetic wastewater without Cu (II) ions was added into the UFML-MFC to stabilize for one week. The effect of Cu (II) concentration on the performance of single chamber UFML-MFC were conducted at Cu (II) concentration of 0, 5 and 10 mg/L. The investigation on the effect of electrode spacing between anode and cathode was conducted with distance of 7.5, 15.0 and 22.5 cm.

2.4 Analysis and calculations methods
The voltage across the external resistor were obtain every 10 minutes interval using data acquisition system. The power density and current density were calculated based on the voltage value obtained from the reactor. The Coulombic efficiency was determine and the purpose of determining it is to investigate the ratio of experimental Coulombs to the theoretical Coulombs transferred in the fuel cell. From the sample collected from the sampling point, those were used in analysis of final Cu (II) concentrations. Atomic adsorption spectroscopy (AAS) is used in measuring the concentration of Cu (II). Before using the atomic adsorption spectroscopy, the gas need to open and allow for the combustion. A standard solution of 0, 1.0, 1.5, 2.0 and 2.5 mg/L of Cu (II) concentration were used in constructing a standard calibration curve in the computer. After the calibration curve was done, each water sample were tested and the values of Cu (II) concentration were recorded in a paper.

3. Results and Discussion

3.1 Effect of different Cu (II) concentrations on UFML-MFC
Results showed that when the UFML-MFC was fed with Cu (II) from 0 to 10.0 mg/L, the voltage output declined from 71 to 11.1 mV (Figure 2A). This can be explain by a higher Cu (II) concentration can inhibit the activity of microbes on the surface of electrode [7]. However, based on Figure 2B the reduction of COD from day 0 to day 1 exhibit a highest reduction rate for Cu (II) concentration of 5 mg/L instead of 0 mg/L. This is due to the different initial COD concentration where the 5 mg/L batch contain a higher concentration of organic matters [12]. The initial state of UFML-MFC is able to reduce a higher amount of organic matters such as Cu (II) at the cathode area. Besides that, the overall COD reduction efficiency decreased from 56% to 36% when the Cu (II) concentrations increased from 0 mg/L to 10 mg/L. This shows inhibition that results in lower oxidation activity and lower amount of electron produced. Fortunately, this inhibition can be reversible by changing the fresh synthetic wastewater without Cu (II) in the solution [13].

When concentration of Cu (II) increased to 5.0 and 10.0 mg/L, the reduction efficiency deteriorated from 87.57% to 36.98% (Fig 2C). This can be explain by a higher Cu (II) concentration can inhibit the activity of microbes on the surface of electrode [7]. Hence, the reduction of Cu (II) decreased with higher initial Cu (II) concentration. Based on Figure 3B, the increased of the concentration of Cu (II) more than 5 mg/L could result in the reduce the performance in Cu (II) reduction and voltage output.
Figure 2: Effect of different Cu (II) concentrations on (A) voltage generation, (B) COD reduction and (C) Cu (II) reduction efficiency.
3.2 Effect of electrode distance on UFML-MFC performance

With the electrode distance at 5 mg/L batch of 22.5 cm, 15.0 cm, and 7.5 cm, the Cu (II) reduction efficiency was about 84.69%, 87.07%, and 87.56% respectively. Results showed that Cu (II) reduction efficiency was the highest at Section 3 with percentage of 87.57%. The reduction of Cu (II) increase from Section 1 to Section 3. The performance of voltage output (Figure 3A) and Cu (II) reduction (Figure 3B) revealed that a shorter distance results in higher Cu (II) reduction efficiency and higher voltage generation. A higher voltage due to shorter distance between electrodes can be explain by lower internal resistance. Hence, the voltage generation at 7.5 cm is the highest as compared to 15.0 cm and 22.5 cm. A higher voltage generation caused by a higher microbial activity in oxidizing substrates and producing more electron to be transfer to the cathode. Hence, higher reduction rate of Cu (II) can be achieved at the cathode area [14]. Based on Fig 3C, the COD concentration is the lowest at Section 3 as compared to Section 1 and Section 2. The COD reduction is decreased from 56% to 36% from Section 3 to Section 1. The reason is similar to Cu (II) reduction trend where shorter distance results in lower internal resistance that allow more ion to be diffuse into the cathode region for reduction [7]. The higher microbial activity results in higher voltage generation at a shorter distance (Figure 3A) and the low internal resistance due to short distance prove that the performance is the highest when the distance between electrodes is shorter. Furthermore, longer distance exceeded 7.5 cm could reduce the performance in Cu (II) reduction and voltage generation. Coulombic efficiency (CE) was analyzed for distance of 22.5, 15.0, and 7.5 cm. With distance of 7.5 cm, the Coulombic efficiency is 0.083% where the CE decrease to 0.0083% and 0.0067% at 15.0 cm and 7.5 cm respectively. The reduction of CE could be attributed to the higher internal resistance due to a longer distance between anode and the cathode [15].

![Voltage Output vs Time (Day) for different electrode distances](image)

![Cu (II) Concentration vs Time (Day) for different Sections](image)
4. Conclusion
In this study, the 0 mg/L of Cu (II) was used as a control for the experiment. In the event of different Cu (II) concentration, it is noted that 5 mg/L of Cu (II) is the ideal concentration for maximized performance of the reactor. When it is at 10 mg/L, the microbial activity decreases due to Cu (II) poisoning. This also affects the reduction of Cu (II) ions, as the batch with 10 mg/L of Cu (II) performs significantly worse than the other counterparts. As for the varying electrode distances, the experiment shows that performance of Cu (II) reduction is best when the electrodes are closer together. The result showed that the feasibility of reduction of heavy metals by using single chambered membrane-less microbial fuel cell.

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