

# Removal of metals (chromium and copper) and power generation through sediment microbial fuel cell



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## ABSTRACT

A sediment microbial fuel cell (SMFC) is a type of microbial fuel cell (MFC) that has recently attracted significantly attentions due to its unique property of removing organic and inorganic compounds from sediments. In this study, different parameters were optimized for the performance of SMFC. The chromium and copper were detected in the sediment samples. The experiments were carried out in a dual-chamber SMFC under ranges of pH, 1-7 temperature 0-80°C and external resistance 10-100 Ω. At pH 2, temperature 37°C and 10 Ω external resistance the removal of chromium and copper were about 96% and power generation was 400-450 mV/m<sup>2</sup>. The removal of chromium, copper from sediments and power generation were high at acidic pH, temperature on 37°C and at lower external resistance. The results indicated that the SMFC system could be applied as a long term and effective tool for the removal of chromium and copper contaminated sediments and supply power for commercial devices.

## 1. Introduction

Sediments are important components of aquatic environment. Sediments play an important role in determining the quality of lakes, rivers and oceans as they can acts as either a source or sink for pollutants especially heavy metals (Sajana et al. 2013). The heavy metals release from different anthropogenic sources and accumulate into sediments (Ahmad et al. 2015). These anthropogenic sources include Mining, tannery, jewelry, chemical, metallurgical, electrical and electronics large scale industries in industrial nations, and also arts and crafts in developing countries (Rafatullah et al. 2009; Ahmad et al. 2013). The accumulation of heavy metals into sediments depends upon the physical and chemical adsorption mechanisms, the nature of the sediment matrix and the properties of the adsorbed compounds. Once the input pollution is controlled, sediment as a secondary source of pollution can release the accumulated pollutants to overlying waters (Pekey and Doğan 2013). If heavy metals accumulated

in sediments more than threshold standard guidelines then they are be more dangerous for human health and also for aquatic ecosystem. To date, traditional sediment remediation methods include ozonation, dredging, in-situ treatment and ex-situ treatment (Fu et al. 2013). These traditional methods are either expensive or not environmentally friendly, so it is crucial to find a cost-effective and environmentally friendly way to solve the contaminated sediments problems.

Sediment microbial fuel cells (SMFCs) technology is considered an environmentally friendly and promising approach for removal of heavy metals with ability of power production (Logan 2006). Recently, some studies have shown that SMFCs can alter the properties and enhance the removal of heavy metals from sediment (Hong et al. 2010). SMFCs remove heavy metals from sediment by placing anode into sediments to create anoxic conditions and cathode in overlying water. The anode and cathode made up of carbon rods with copper wiring. Exoelectrogenic (the microbes which transfer the electrons to electrodes) bacteria degrade heavy metals present in the sediments and

generating electrons and protons. The degradation of heavy metals depend upon the oxidation states of metals and mainly on the voltage potential of electrodes. Electrons reduce the anode and are transferred to the cathode through an external circuit. Protons move from sediment to the cathode side and combine with oxygen and electrons on cathode to produce water (Reimers et al. 2006). So this study was aimed to investigate SMFCs heavy metals removal abilities, power production by SMFC sand optimization of SMFCs external factors.

## 2. Materials and methods

### 2.1. Sediment sampling

The sediments were collected from the bottom (approximately 10 cm down from the sediment–water interface) of identified points in Penang, Malaysia using a Ponar type grab sampler (86475 Gene Lassere BLVD, USA). All samples including surface water were placed into clean polycarbonate jars with no headspace gas (i.e. air) and transported to the laboratory in a cooler box with ice packs. All sediments were passed through a < 2 mm sieve (ASTEAE-11, USA) to remove plant debris, macrofauna, and other large terrestrial leaves and then homogenized by mixing with a stainless steel spatula prior to use.

### 2.2. Sequential extraction

For sequential extraction 250 mg fine sediments were taken and add 5 mL of H<sub>2</sub>SO<sub>4</sub>, 2 mL of HNO<sub>3</sub> and 1 mL of HF in teflon tubes. For releasing the heavy metals of sediment the teflon tubes were put into microwave digester (Microwave 3000 Anton Paar, USA) for 2 hours at 500 revolutions per minute. The heavy metals were analyzed in mg/l (parts per million) by using inductively coupled plasma mass spectrometry (PCB model 480E09, Germany) (Xu et al. 2015). The total detected amounts of heavy metals in mg/l were taken as percentage.

### 2.3. SMFC assembly and operation

SMFCs were made of plexiglass. About 50 g of the sediment was added to two chambers SMFC with 50 L of the marine water as shown in Fig. 1. Three pieces of plain graphite plate connected in parallel with rubber-coated Cu wires were embedded within the sediment and used as anode. A piece of foam-bonded plain graphite felt was placed on the surface of the water and used as cathode. No additional electron donor was added to the SMFC. The anode and cathode were connected with a rubber-coated Cu wire. Each wire connection sites in the systems was protected by silica gel from corrosion. Voltage of the resistor was recorded using a multimeter data logger. After the voltage reached and maintained at the maximal value, the polarization curve was plotted by changing the external resistor. Control reactors (open-circuited SMFC) was tested in parallel with the closed-circuit SMFCs in natural temperature until three months (Sherafatmand and Ng 2015). The glucose about 1g/mL was added daily as external biodegradable source of carbon to overcome the evaporation of water and bacterial diet.

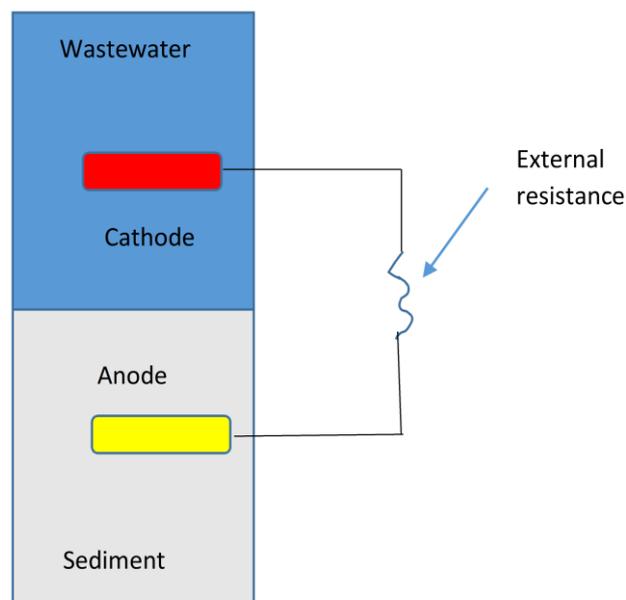


Fig. 1 SMFC assembly with two chambers

### 2.4. External factors

The SMFC performances were analyzed at range of 1-7 pH. The pH of sediment was adjusted to 1–7 with H<sub>2</sub>SO<sub>4</sub> (50%). The SMFCs were operated in temperature-controlled biochemical incubator in the range of 0-80°C and external resistances of 10-100 Ω were installed between the anode and cathode (Maanan et al. 2015).

## 3. Results and discussion

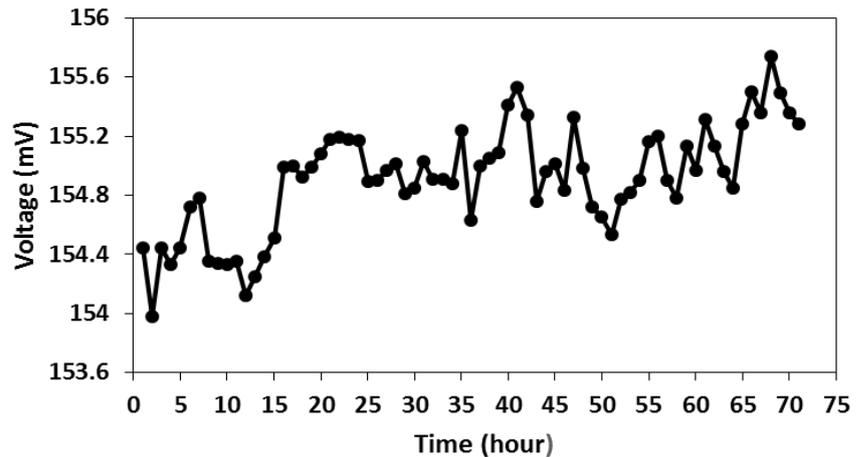
### 3.1. Physiochemical analysis of sediments

The values of various parameters like sediment color, temperature, pH, texture, water contents and carbon contents before the treatment of sediments samples are as shown in Table 1. The significances of these parameters are that these parameters determine the nature of sediments which can help for getting the optimal results from this study like maximum power generation.

Table 1 Physiochemical characteristics of sediment samples

Parameters	Untreated sediments
Color	Dark black
Temperature	25-29°C
pH	6.0-7.0
Sand(% ,w/w)	11.7 ±8.0
Silt (% ,w/w)	86.9±70.2
Clay (% ,w/w)	3.9 ±2.6
Water contents (% ,w/w)	44.9 ±1.40
Carbon contents (% ,w/w)	1.7 ±0.3

**Fig. 2** The trend of power generation by SMFC using glucose as carbon source



**3.2. Heavy metals removal and power production**

By using sequential extraction technique and analysis by inductively coupled plasma mass spectrometry the chromium (Cr) and copper (Cu) were detected. The concentration of these heavy metals was higher in sediments than sediment Canadian guidelines (Hübner et al. 2009). To see the relationship between power density and heavy metals removal the power generation curve of SMFC was noted as shown in Fig.2. The trend of power production was increased with time because initially bacteria need to take some time for adjustment with environment.

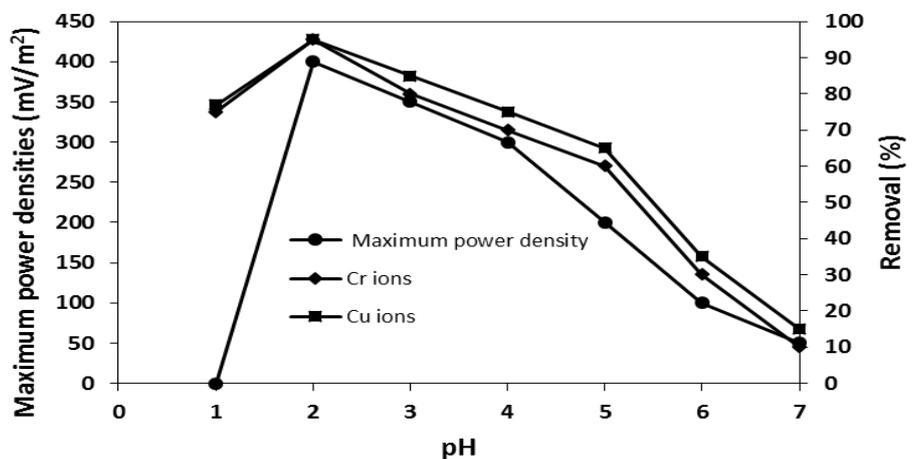
**3.3. Effect of pH, temperature and external resistance on SMFCs performance**

To determine the effect of pH, the power density and the removal of Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions were examined using natural sediments range from 1.0 to 7.0. Fig.3 illustrates that Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions removal increases from 10% to 96.3%, as the pH decreases from 7 to 2 and green deposit could be evidently observed on the surface of cathode. The initial concentrations of Cr<sup>6+</sup> and Cu<sup>2+</sup> ions in the sediments were 60 mg/kg and 70 mg/kg, respectively. However, the removal was not further increased at lower pH (pH 1). This was attributed to the H<sup>+</sup> in cathode chamber diffused to anode

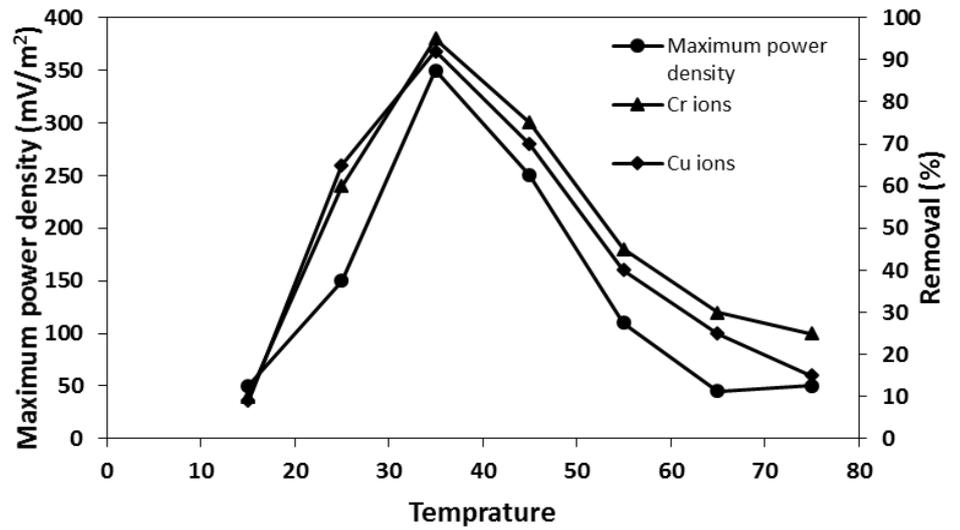
chamber at pH 1, leading to a decrease in pH of anodic medium from 6.9 to 1.9 over the course of experiment. The low pH of anodic medium deactivated the microorganism and reduced the performance of SMFC (Sajana et al. 2014). The highest removal 96.3% (10 mg/kg) of total Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions was achieved at pH 2, while removal decreasing about 10% at pH 7 and to 0 at pH 1. The maximum power density was increased as pH decreased from 7 to 1. This revealed that low pH played a positive effect on power generation. The summary of pH profile was that the maximum removal of Cr<sup>6+</sup> and Cu<sup>2+</sup> ions and power density were at pH 2.0 about 96.3% and 400 mV/m<sup>2</sup> respectively due to acidophilic nature of bacteria. At pH 7.0 the removal of Cr<sup>6+</sup> and Cu<sup>2+</sup> ions and power density were low about 10% and 50 mV/m<sup>2</sup> because the metabolism rates of bacteria were inhibited due to high concentration of OH<sup>-</sup> ions.

A maximum Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions removal were higher at about 37°C. The power density was also high at 37°C but at high and low temperature the power density was very low. So the Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions removal rate were also very low as shown in Fig.4. However, this lower operating temperature proved that, the electrochemically active bacteria could remain active even at lower temperature (Jadhav and Ghangrekar 2009). Capability of SMFC converting substrate at lower temperature below 20°C has also been reported earlier (Pham et al. 2006).

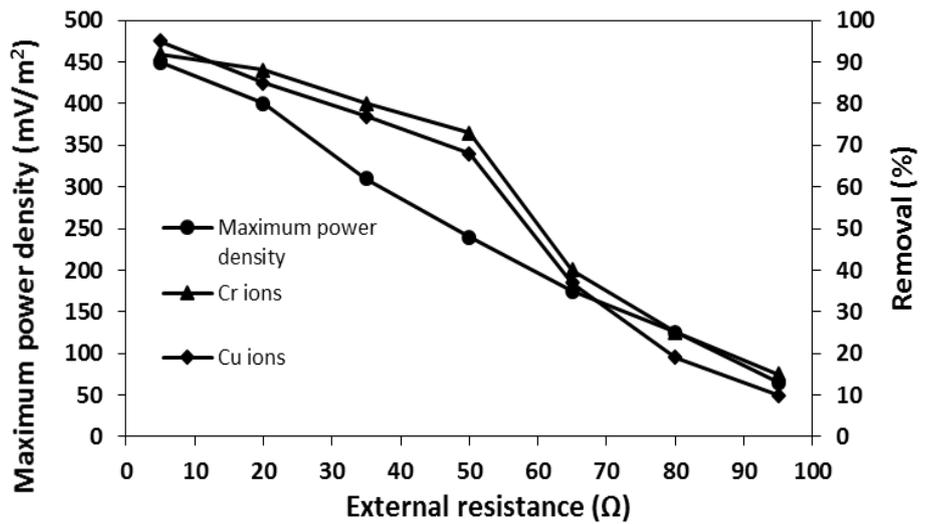
**Fig. 3** Effect of pH on the removal of Cr<sup>6+</sup> and Cu<sup>2+</sup> ions and maximum power density generation



**Fig. 4** Effect of temperature on the removal of Cr<sup>6+</sup> and Cu<sup>2+</sup> ions and maximum power density generation



**Fig. 5** Effect of external resistance on the removal of Cr<sup>6+</sup> and Cu<sup>2+</sup> ions and maximum power density generation



SMFCs were operated with an external resistance of 1-100 Ω. It was observed that during the experiments with and without aeration at cathode, the SMFCs showed higher Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions removal efficiency. At lower external resistance, the Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions removal efficiency was more, and with increase in external resistance it decreased, as reported earlier by Jadhav and Ghangrekar (2009). At lower external resistance the power density was higher because electrons move more easily through the circuit than at higher external resistance as shown in Fig.5.

#### 4. Conclusions

The effects of pH, external resistance, and operating temperature were evaluated on the performance of SMFCs. Treatment of sediments containing Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions and power production were carried out successfully in the

dual-chamber SMFCs. The pH value affected the power density, removal of Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions obviously. In addition, higher concentration of Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions could enhance the power density. The higher and lower temperature also effect the power density, Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions removal rate and were optimize at 37°C. The power density, Cr<sup>6+</sup> ions and Cu<sup>2+</sup> ions removal rate was also lower at higher external resistance and vice versa.

However, for the full scale application of SMFCs in the sediments, more experiments must be conducted on the factors affecting the performance of SMFCs such as temperature, pH, external resistance, distance between electrodes, anode to cathode surface area ratio and electrode materials. The energy efficiency of the SMFC system in power is still low, so there is need to study microbial consortia of SMFCs that will give more knowledge which microbial consortia mostly participate in power production.

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