Feasibility Study of Disposed LCD Monitor and Carbon Cloth Electrodes for Synchronized Removal/Recovery of Cr^{6+} by Microbial Fuel Cells

Praveena Gangadharan and Indumathi M Nambi

Abstract—**This study compares the use of Liquid Crystal coated Polaroid Glass Electrode (LCPGE) material collected from the disposed computer monitor and carbon cloth as electrodes in microbial fuel cell (MFC) for the simultaneous reduction/recovery of hexavalent chromium (Cr^{6+}) from wastewater. The Cr^{6+} is bioelectrochemically reduced to the non-toxic Cr^{3+} form in the cathode chamber of a two-chambered MFC. At the cathode LCPGE interface, 100% of Cr^{6+} reduction was achieved within 48 h of operation. Similarly, using carbon cloth as cathode, 100 mg/L of Cr^{6+} was completely removed within 24 h (initial pH 2.0). In both the electrodes, the chromium was recovered as highly stable and non-toxic chromium oxide (Cr_2O_3). The recovered Cr_2O_3 was characterized by ATR-FTIR analysis. A maximum power density of 10 mW/m^2 and 700.11 mW/m^2 was achieved for the LCPGE and carbon cloth electrodes, respectively at ambient conditions. Moreover, 78% of organic carbon is mineralized at the anode chamber making this technology a more viable option for simultaneous chromium reduction and domestic wastewater treatment along with power production. Furthermore, the recovered Cr_2O_3 can be used as a raw material for various applications.**

Index Terms—**Carbon cloth, hexavalent chromium, e-waste, microbial fuel cell (MFC).**

I. INTRODUCTION

During a past few decades, many industries like pharmaceutical, wood, electroplating, leather tanning and metallurgies are extensively used hexavalent chromium (Cr^{6+}) as an oxidizing agent due to its high reduction potential [1]. However, Cr^{6+} is a well-known pollutant, and their discharge is critically concerned due to i) non-biodegradable nature; ii) undergo various transformation and forms toxic carcinogenic compounds; iii) bioaccumulative [2]. Therefore, United State Environmental Protection Agency (USEPA) and the European Union regulated the discharge of Cr^{6+} and total Cr to the surface water by 0.05 mg/L and 2 mg/L, respectively [3]. The possible treatment strategy adopted for the removal of Cr^{6+} from the water bodies/industrial wastewater is chemically or electrochemically reduce into non-toxic Cr^{3+}. The conventional treatment technologies for the removal of chromium from the industrial effluents are chemical precipitation, coagulation-flocculation, Ion exchange, ultrafiltration, reverse osmosis, adsorption, and electrochemical techniques. Certainly, these treatment techniques display good efficiency in treatment aspects, however, they have some inherent limitations like chemical addition, large sludge production, high energy requirement, and secondary toxic waste generation [3].

Recently, Microbial Fuel Cells (MFCs) have received a lot of attention as it is a sustainable technology for energy production via wastewater treatment. An MFC consists of anode and cathode chamber, separated internally and externally by a proton exchange membrane (PEM) and an external resistance, respectively [4]. Microorganisms oxidize the organic matter at the anode chamber, results in the generation of electrons and protons. The electrons and protons drifts through respective PEM and external resistance to the cathode chamber, where they accepted by an electron acceptor (catholyte). Generally, potassium ferricyanide and aerated oxygen are used as catholyte in MFCs due to high reduction potential and low overpotential. However, the usage of conventional catholyte is restricted for large scale application due to the toxicity of ferricyanide and large activation loss of oxygen. Recently, a few studies were successfully demonstrated Cr^{6+} as catholyte in two–chambered MFC (t-MFC) due to its high reduction potential [5]. In fact, the standard half-cell potential (25°C) of Cr^{6+} displays moderately higher value than that of the half-cell potential of oxygen as shown in the Eqn. 1 and Eqn.2.

$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \qquad (E \simeq 1.23\ V) \quad (1)$$

$$Cr_2O_7^{2-} + 8H^+ + 6e^- \leftrightarrow Cr_2O_3 + 4\ H_2O \qquad (E \simeq 1.33\ V) \quad (2)$$

The potential implication of Cr as catholyte is its high reduction potential improves the power output from the t-MFC, and simultaneously reduces to nontoxic Cr^{3+} by accepting the electrons from the anode chamber [6]. Additionally, the electrodes play an important role for the overall performance of MFC. Selection of suitable anode and cathode material is critically concerned as they can influence the bacterial adhesion as well as power generation, respectively [7]. Carbon based material such as carbon cloth, carbon paper, carbon felt and graphite brush are widely used electrodes in MFCs [8]. However, they are quite expensive which further increases the cost of overall wastewater treatment [9]. Therefore, in this present study, disposed computer monitor, Liquid Crystal Polaroid Glass Electrode (LCPGE) is used as electrode material for the

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removal/recovery of chromium from the wastewater. The advantage of using LCPGE is highly conductive due to the presence of liquid crystals. Additionally, LCPGE surface contains various functional group such as NH_2, C≡N, C=O and O-C and/or C-O-C, which exhibits excellent electrochemical response for bacterial adhesion as well as metal reduction in the anode and cathode chamber, respectively [10]. In this study, the performance of LCPGE electrode is compared with carbon cloth (CC) electrode in a separate t-MFC for the removal/recovery of chromium from the wastewater.

II. MATERIAL AND METHODS

A. MFC Construction

Two identical MFCs (MFC_{CC} and MFC_{LCPGE}) were fabricated by two pyrex glass bottle of equal volume with a capacity of 250 mL, separated by proton exchange membrane (PEM) (Nafion 117; Sigma-Aldrich) [10]. PEM was pretreated with 30% H_2O_2, 0.5 M H_2SO_4, and deionized water for 1 h [5]. In MFC_{CC}, non-wet proof plain carbon cloth (CC) (10.5 cm^2; Synergic India Pvt. Ltd. India) was used as anode and cathode. Alternatively, MFC_{LCPGE} was employed with LCPGE electrode as anode and cathode. The anode and the cathode were placed at a distance of 5 cm, and are connected externally by a copper wire. Nitrogen was continuously supplied to the anode and cathode chamber to maintain anaerobic condition, and the bottles were air tighten by Teflon covered caps.

B. Formation of LCPGE Electrode

LCPGE was formed from a disposed computer monitor, collected from Department of Civil Engineering, computing facility, IIT Madras, India. LCPGE (10.5 cm^2) was carefully stored in an airtight container after removing the outer glass layer. Subsequently, LCPGE was pretreated by isopropanol, 0.1 N HCl, and deionized water. Afterward, LCPGE was subjected to oven dry at 50 ℃ for 15 minutes) [10].

C. Inoculation

Anaerobic sludge was used as inoculum, and are collected from anaerobic digester of the sewage treatment plant, Nesapakkam, Chennai, India. The sludge was washed several times with 0.85% of NaCl (w/v) solution, and the methanogenic activity was suppressed by applying heat shock treatment (100 ℃, 2 h) [5]. The synthetic wastewater was prepared by mixing an appropriate quantity of macronutrients of NH_4Cl, 125 mg/L; $NaHCO_3$, 125 mg/L; $MgSO_4.7H_20$, 51 mg/L; $CaCl_2.2H_2O$, 300 mg/L; $FeSO_4.7H_2O$, 6.25 mg/L, and 1.25 mL/L of micronutrients [11]. The anolyte was prepared by adding 50 mL of anaerobic sludge with 150 mL of synthetic wastewater. Acetate of 1g/L was used as a source of organic carbon in the anolyte. The catholyte was prepared by potassium dichromate (K_2Cr_2O7; 99%; Sigma-Aldrich), phosphate buffer solution (KH_2PO_4, 13.60 g/L; NaOH, 2.33 g/L), and NaCl (11.70 g/L). pH of the catholyte was maintained by the addition of H_2SO4 (0.1 M) and NaOH (0.1 M).

III. MEASUREMENTS AND ANALYSES

Cr^{6+} and total Cr was measured by UV spectrophotometer (UV-1800 PC, Shimadzu) at 540 nm and atomic absorption spectrophotometry (AAS 700, Perkin Elmer), respectively. The substrate degradation from the anode chamber was measured by TOC-TNM Analyzer (TOC-V CPH, Shimadzu) after sampling at regular intervals. The removal efficiency was calculated as represented by Eqn.3.

$$\text{Removal Efficiency (\%)} = \frac{(A-B\ )}{A} \times 100 \qquad (3)$$

where, A is the initial concentration in mg/L and B is the observed concentration in mg/L. Multichannel (4-channel) potentiostat (Bio-Logic, India) was employed to study polarization curve. The voltage (V) and current (I) were continuously monitored by data acquisition system (ADSENSORS Pvt. Ltd., India). Power (P) was calculated by $P=IV$. Current density and power density were calculated by dividing the power and current by cathode surface area (m^2). Recovered chromium was characterized by Attenuated Total Reflectance Fourier Transform Infrared Spectrum (ATR-FTIR- Spectrum 100; Perkin Elmer) from the spectral range of 400 to 4000 cm^{-1}.

IV. RESULT AND DISCUSSION

A. Wastewater Treatment

The substrate degradation was continuously monitored by performing total organic carbon (TOC) analysis. Initial substrate concentration of MFC_{CC} and MFC_{LCPGE} are 613 mg/L and 350 mg/L, respectively (Fig. 1). MFC_{CC} exhibits 78.4% of substrate degradation efficiency during 13 days of operation. Similarly, MFC_{LCPGE} shows 78.11% of removal efficiency within 4 days of operating time. Both the MFCs exhibits almost similar removal efficiency and can be attributed that the microbes are well acclimatized in the anode chamber of the MFC_{CC} and MFC_{LCPGE}. Moreover, the LCPGE electrodes are highly biocompatible, and therefore microorganisms can utilize the anode as their final electron acceptor [10].

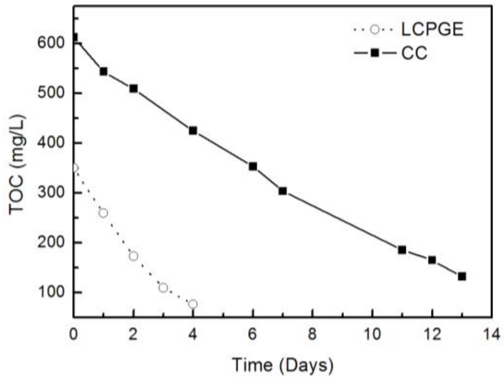

Fig. 1. Wastewater treatment at the anode chamber of MFC_{CC} and MFC_{LCPGE}.

B. Cathodic Reduction of Chromium

The MFC was operated with an initial Cr^{6+} concentration of 100 mg/L, and the pH of the catholyte was maintained at 2. The performance of MFC_{CC} and MFC_{LCPGE} for the reduction of chromium is shown in Fig. 2. The CC and the LCPGE electrodes exhibited more or less similar behavior with an initial rapid reduction in Cr^{6+} concentration followed by a static state. The rapid reduction of Cr^{6+} in the initial stage is probably due to the high reduction potential of Cr^{6+} (E ≃ 1.33 V) maintains sufficient electromotive force to drifts the electrons from the anode chamber.

Initially, the effluent color was orange-yellow, and as the experiment progresses, the color was changed to greenish-blue, indicating the complete reduction of Cr^{6+} into Cr^{3+}. While continuing the experiment, the nucleation of Cr^{3+} was formed on the surface of the electrode, results in the reduction of total chromium. Almost complete reduction of total chromium was achieved during 160 h of operation of the MFC employed with CC electrode. However, the MFC employed with LCPGE electrode achieve 77.2% of removal efficiency in total chromium during 160 h of operating time. This could be due to the limited availability of surface area for the electrochemical reaction to happen at the LCPGE surface.

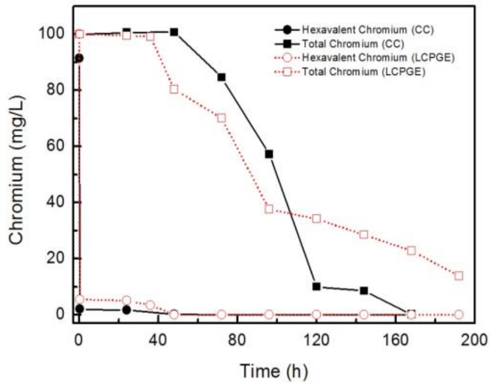

Fig. 2. Cathodic reduction of chromium in MFC$_{CC}$ and MFC$_{LCPGE}$

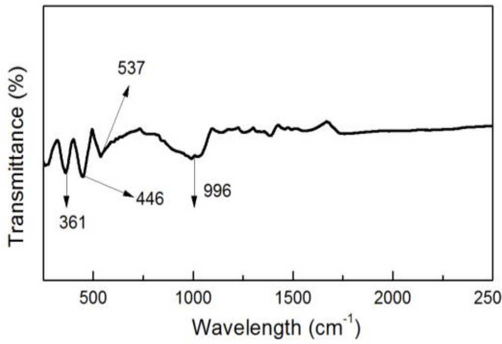

Fig. 3. ATR-FTIR spectra of recovered Cr_2O_3.

The nucleation of Cr^{3+} formed on the electrode surface was recovered and characterized for further studies. According to Eqn.2, the soluble Cr^{+6} is electrochemically reduced to insoluble chromium oxide (Cr_2O_3) precipitate. Both the MFCs exhibits a green color precipitates at the end of the experiment, and are oven dried at 200°C for further analysis (Fig. 3). The peaks observed at 446 cm^{-1}, 361 cm^{-1}and 537 cm^{-1} are attributed to Cr-O stretching, indicates the recovered Cr are in the form of Cr_2O_3 [12]. Additionally, a peak formed at 996 cm-^{1} was probably due to the presence of organic impurities.

C. Effect of pH

pH plays an important role in the reduction of Cr^{6+} at the cathode chamber. In the present study, the Cr^{6+} reduction was monitored by maintaining the initial catholyte pH of 2, 5, and 7. The experiment was performed with an initial Cr^{6+}concentration of 100 mg/L and the contact time of 24 h.

As depicted in the Fig. 4, the presence of H^{+} ions is highly influencing the reduction of Cr^{6+} at the cathode chamber of the MFC. MFC exhibits maximum removal efficiency at pH 2 irrespective of the electrode material. At pH 2, MFC employed with CC and LCPGE electrode material exhibits the Cr^{6+} removal efficiency of 99.89% and 91.67%, respectively. This is due to the presence of H+ ions for the reduction of Cr^{6+} to Cr^{3+}. According to the Eqn.2 the consumption of H^{+} ions accelerated the redox reactions in the forward direction, and therefore, the reduction was highly favored at pH 2. However, as the pH increases to 5, the availability of H^{+} ions was decreased, and therefore, the removal efficiency was decreased to 39.34% and 16.79%, for MFC$_{CC}$ and MFC$_{LCPGE}$, respectively. Furthermore, at pH 7, the removal efficiency was decreased to 9.33% and 4.78% for MFC$_{CC}$ and MFC$_{LCPGE}$, respectively. In all the experiment, CC exhibits superior removal efficiency, probably due to the large surface area and porous nature.

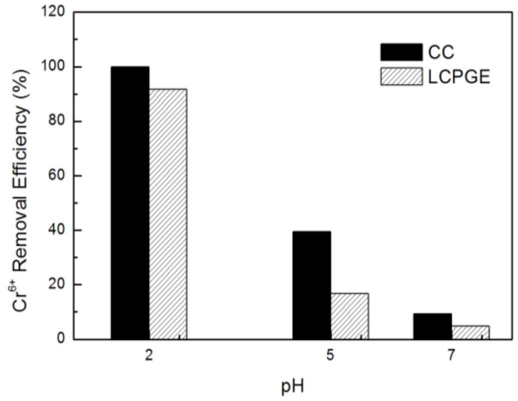

Fig. 4. Effect of pH on the reduction of chromium in MFC$_{CC}$ and MFC$_{LCPGE}$

D. Polarization Study

Polarization study was carried out to study the behavior of the voltage in response to the current production as shown in Fig. 5. The study was performed when both the MFCs are at steady state condition, and the catholyte pH was maintained at 2. The maximum power density of 700.11 mW/m^{2} and 10 mW/m2 achieved when the MFC operated with CC and LCPGE electrode material, respectively. Table I shows a comparative analysis of MFC$_{CC}$ and MFC$_{LCPGE.}$

MFC$_{LCPGE}$ exhibits more or less similar removal efficiency as compared to MFC$_{cc}$ for the reduction/ recovery of Cr$^{6+.}$ However, in the case of power generation, MFC$_{cc}$ exhibits superior performance than that of MFC$_{LCPGE}$. This could be due to the following reasons.

1) LCPGE electrodes are made up of transparent sheets in which one side is conductive, and the other side is covered with a thin plastic sheet. Consequently, the electrode surface area is limited due to minimum active sites at the electrode surface. Alternatively, the carbon cloth is highly porous, and therefore more surface area is available for the chemical reactions to happen on the cathode surface.

2) The resistance of the LCPGE electrode material is noticeably higher than that of the carbon cloth electrode material. The resistance of the LCPGE material is measured to be 147 ± 50 KΩ (measured by a precise multimeter), and for the CC is observed as 2 .1 ± 1.5 Ω. This could be the reason for low power output from the LCPGE electrode.

TABLE I: COMPARATIVE STUDY OF MFC_{CC} AND MFC_{LCPGE}

Anode	Cathode	Metal salt; Concentration (mg/L); pH	Catholyte removal efficiency; Time	Max. Power output
PCC (10.5 cm^2)	PCC (10.5 cm^2)	$K_2Cr_2O_7$; 100 ; pH 2	99.89%; 24 h	700.11 mW/m^2 (2.925 mA/m^2)
LCPGE (10.5 cm^2)	LCPGE (10.5 cm^2)	$K_2Cr_2O_7$; 100; pH 2	91.67%; 24 h	10 mW/m^2 (0.11 mA/m^2)

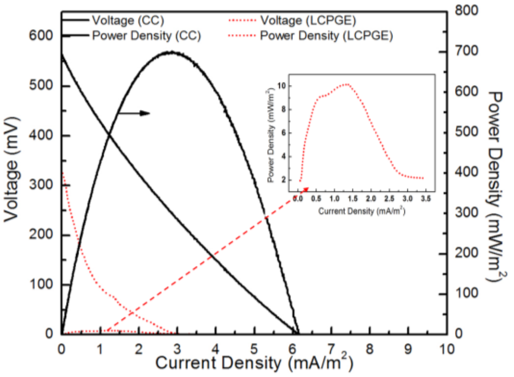

Fig. 5. Polarization curve.

V. CONCLUSION

The present study successfully demonstrated the novel LCPGE electrode material (discarded computer monitor) for the removal/ recovery Cr^{6+} from the wastewater in t-MFC. The LCPGE electrode material exhibits excellent performance for the removal/recovery of Cr^{6+} as compared with conventional CC electrode material. However, in the case of power production, CC exhibits superior performance than LCPGE electrode. If the primary goal is metal reduction/recovery, and the power generation is neglected, the LCPGE material is an ideal electrode material to scale-up MFC technology for various applications. The study insights to utilize MFC technology for metal reduction/recovery from various industries such as electroplating, tanneries, and metallurgy. The recovered Cr_2O_3 can be used as raw material for tanneries and electroplating industries.

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