

## Hexavalent chromium reduction and energy recovery by using dual-chambered microbial fuel cell

Praveena Gangadharan and Indumathi M. Nambi

### ABSTRACT

Microbial fuel cell (MFC) technology is utilized to treat hexavalent chromium (Cr(VI)) from wastewater and to generate electricity simultaneously. The Cr(VI) is bioelectrochemically reduced to non-toxic Cr(III) form in the presence of an organic electron donor in a dual-chambered MFC. The Cr(VI) as catholyte and artificial wastewater inoculated with anaerobic sludge as anolyte, Cr(VI) at 100 mg/L was completely removed within 48 h (initial pH value 2.0). The total amount of Cr recovered was 99.87% by the precipitation of Cr(III) on the surface of the cathode. In addition to that 78.4% of total organic carbon reduction was achieved at the anode chamber within 13 days of operation. Furthermore, the maximum power density of 767.01 mW/m<sup>2</sup> (2.08 mA/m<sup>2</sup>) was achieved by MFCs at ambient conditions. The present work has successfully demonstrated the feasibility of using MFCs for simultaneous energy production from wastewater and reduction of toxic Cr(VI) to non-toxic Cr(III).

**Key words** | chromium, electricity generation, microbial fuel cell, wastewater treatment

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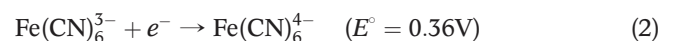
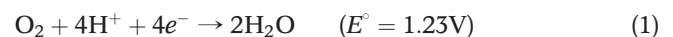
### INTRODUCTION

Hexavalent chromium (Cr(VI)) is widely used as an oxidizing agent in various industries, such as pharmaceutical, wood, electroplating, leather tanning, metallurgy, etc. (Jadhav & Hocheng 2012). The removal of Cr(VI) from wastewaters is significant due to their high toxicity and tendency to accumulate in living organisms. Several treatment techniques, such as chemical precipitation, coagulation, flocculation, ion exchange, membrane filtration and bio-sorption, have been applied to treat chromium from wastewater (Sharma *et al.* 2008). However, these treatment techniques have inherent disadvantages such as high energy requirements, excessive chemical consumption, generation of a large quantity of secondary pollutants and toxic waste sludge (San & Donmez 2012). Therefore, it is necessary to investigate a cost-effective and sustainable treatment technology to treat Cr(VI). If this technology can be coupled simultaneously with recovery of energy, industries could benefit greatly.

Microbial fuel cell (MFC) technology has emerged in recent years as a promising technology for wastewater treatment along with energy production. MFCs consist of anode and cathode chambers separated by a proton exchange membrane (PEM). Microorganisms oxidize the substrate

and produce electrons and protons in the anode chamber. The electrons will pass through an external circuit to the cathode and protons will migrate through the PEM to the cathode, where they combine with an electron acceptor to form water (Logan *et al.* 2006).

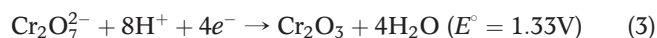
Previously, MFCs had been developed to generate electricity from domestic (Puig *et al.* 2011), food processing (Cercado-Quezada *et al.* 2010) and paper mill (Velasquez-Orta *et al.* 2011) wastewater. The role of the cathode chamber in electricity generation is to form a pathway for electrons and protons. In existing MFCs, oxygen (Zhao *et al.* 2006) and ferricyanide (Wei *et al.* 2012) are commonly used as electron acceptors. The standard half-cell reactions and potentials (acidic condition) for oxygen and ferricyanide at 25 °C are reported in Equations (1) and (2):



The drawbacks of using such electron acceptors are high energy consumption and toxic end-product generation. To

minimize these drawbacks and maximize the power generation, an alternate electron acceptor is required for MFCs.

A pollutant with high reduction potential can be used as an alternate electron acceptor, enhance the benefits of MFCs by reducing it to a non-toxic form. Toxic Cr(VI) has a high reduction potential under acidic conditions and can be replaced by conventional electron acceptors. The reduction potential of Cr(VI) at 25 °C is considerably more than oxygen, as indicated in Equation (3):



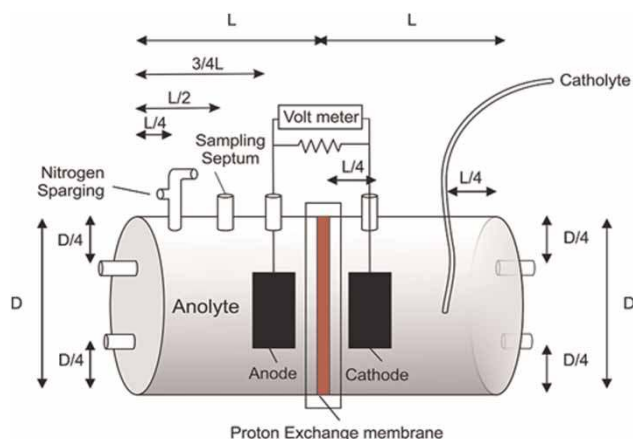
Recently, Li *et al.* (2008) utilized cathode chamber of the MFCs for treating Cr(VI) from electroplating wastewater. This confirms the feasibility of MFCs for sustainable heavy metal treatment.

The present study focused on the feasibility of using MFC technology to treat Cr(VI) from wastewater along with energy recovery. The substrate degradation rate at the anode chamber and Cr(VI) reduction at the cathode chamber was investigated simultaneously in batch mode. The reactor was also run at fed batch mode to study total chromium reduction at the cathode chamber along with energy recovery.

## MATERIALS AND METHODS

### MFC construction

The experiment set-up is shown in Figure 1. A two-chambered reactor (each with 8 cm diameter and 10 cm length; 500 mL capacity and 250 mL working volume) was made



**Figure 1** | Schematic of two-chambered MFC ('D' and 'L' represent the diameter and length of the reactor).

with Plexiglas acrylic tube. The chambers were arranged directly adjacent to each other with a PEM (Nafion 117; Sigma Aldrich; projected surface area of 50.24 cm<sup>2</sup>) held between the two sides with an O ring and rubber gaskets, reducing the electrode spacing and increasing the performance of the MFC (Ditzig *et al.* 2007). PEM was subsequently pretreated in 30% H<sub>2</sub>O<sub>2</sub>, deionized water, 0.5 M H<sub>2</sub>SO<sub>4</sub> and deionized water for 1 h each (Li *et al.* 2008).

The anode and cathode were made up of non-wet proof plain carbon cloth (5 × 5 cm; Synergic India Pvt. Ltd, India) and connected externally by copper wire. The electrodes were placed at a distance of 5 cm on either side of the PEM, soaked in deionized water for 24 h and dried in the oven at 100 °C for 15 min. The anode and cathode chambers were continuously purged with nitrogen to maintain an anaerobic condition in both chambers.

### Inoculation

The anaerobic sludge was collected from the anaerobic digester of the sewage treatment plant, Nesapakkam, Chennai, India. The sludge was washed with 0.85% NaCl (w/v) solution and subjected to heat shock pretreatment (100 °C, 2 h) to suppress the activity of methanogens (Venkata-Mohan *et al.* 2008). Sodium acetate (1 g/L) was used as the carbon source in the anode chamber (pH value 7.0). For inoculation, 50 mL of anaerobic sludge was added to 200 mL of synthetic wastewater containing macro-nutrients as NH<sub>4</sub>Cl, 125 mg/L; NaHCO<sub>3</sub>, 125 mg/L; MgSO<sub>4</sub> · 7H<sub>2</sub>O, 51 mg/L; CaCl<sub>2</sub> · 2H<sub>2</sub>O, 300 mg/L; FeSO<sub>4</sub> · 7H<sub>2</sub>O, 6.25 mg/L and 1.25 mg/L trace metal solution as reported in Lovely & Philips 1988. The catholyte was prepared by mixing an appropriate quantity of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>; 99%; Sigma Aldrich) with deionized water. Similarly, phosphate buffer solution (PBS: pH 7.0) was prepared by the addition of KH<sub>2</sub>PO<sub>4</sub> (13.60 g/L) and NaOH (2.33 g/L). NaCl (11.70 g/L) was added to increase the conductivity of the catholyte. The pH value of the influent solution was adjusted with H<sub>2</sub>SO<sub>4</sub> (0.1 M) and NaOH (0.1 M).

### Analyses and calculations

Concentrations of Cr(VI) were measured at 540 nm by a UV spectrophotometer (UV-1800 PC, Shimadzu) after coloration with diphenylcarbazide. Total chromium was analyzed using atomic absorption spectrophotometry (AAS 700, PerkinElmer, Waltham, USA) after sampling at regular intervals. Degradation of substrate concentration was determined by monitoring the decrease in total organic carbon (TOC)

value. To determine the degradation efficiency, the samples were taken at regular intervals from the anode chamber and measured by TOC-TNM Analyzer (TOC-V CPH, Shimadzu). The samples were centrifuged at 6,000–7,000 rpm for 3 min (two to three times) to remove the biomass and the supernatant was taken for TOC analysis. The removal efficiency was calculated as represented by Equation (4):

$$\text{Removal efficiency (\%)} = \frac{(A - B)}{A} \times 100 \quad (4)$$

where,  $A$  is the initial TOC concentration in mg/L and  $B$  is the observed TOC concentration in mg/L.

Current ( $I$ ) and voltage ( $V$ ) were continuously monitored with a fixed resistance ( $R$ ) by a precise digital multimeter. Power was calculated according to Ohm's law ( $P = IV$ ). Power density and current density were calculated by dividing the power and current by anode surface area ( $m^2$ ). The polarization curves were recorded by varying the external resistances. The anodic, cathodic pH value and oxidation reduction potential (ORP) were measured against a saturated Ag/AgCl electrode using a multi-parameter probe (HQ40d, HACH). Biofilm growth on the anode and chromium precipitates on the cathode was examined using a scanning electron microscope (SEM, Quanta 200 Philips).

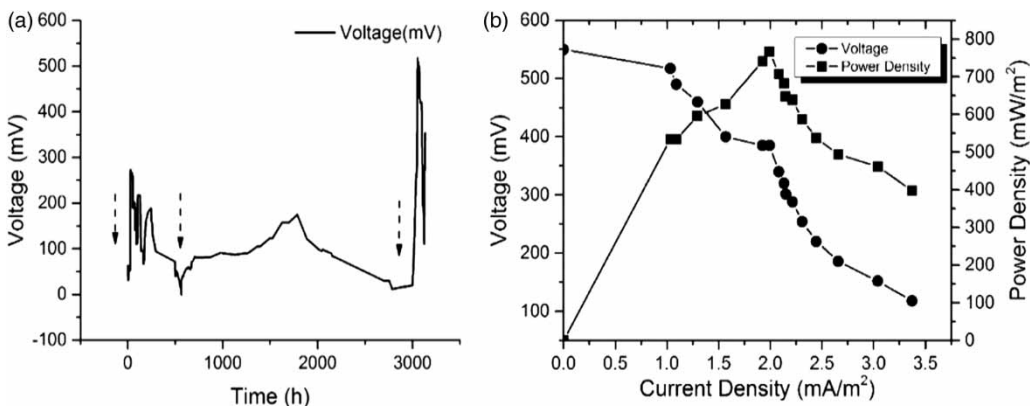
## RESULTS AND DISCUSSION

### Energy production of the MFC

During start-up, the anode chamber was fed with synthetic wastewater (1 g/L acetate) and the cathode

chamber with 50 mM of  $K_3Fe(CN)_6$  in 100 mM PBS. The initial pH value of the anode and cathode chambers was maintained at 7.0. After a stable power production was obtained (20 days), the cathode chamber  $K_3Fe(CN)_6$  solution was replaced with 100 mg/L of Cr(VI) and pH value 2.0 was maintained throughout the experiment. The anode chamber was running at fed batch mode with substrate concentration of 200 mg/L. Acetate was added periodically to maintain sufficient carbon sources in the anodic chamber. The output voltage was found to increase from 37.5 mV at 3 h to about 270 mV at 29 h ( $R$  1,000  $\Omega$ ).

When the anolyte concentration was increased to 600 mg/L and catholyte concentration to 300 mg/L ( $R$  10,000  $\Omega$ ), the voltage production increased rapidly to 517 mV at 3,034 h (Figure 2(a)), which could be attributed to the high-carbon source at the anodic chamber. Polarization studies were also carried out when the anolyte concentration was 600 mg/L (pH value 7.0) and the catholyte concentration 300 mg/L (pH value 2.0). A polarization curve (Figure 2(b)) was obtained to characterize the performance of the MFC at different external resistances ( $\Omega$ ). The external resistance was varied from 7,000 to 100,000  $\Omega$  after reaching a stable voltage production. The maximum power density observed was 767.01  $mW/m^2$  (2.08  $mA/m^2$ ) at 38,000  $\Omega$ . With increasing external resistance, the electrode potential (or MFC voltage) decreases from its equilibrium state due to the flow of current. At an external resistance of 38,000  $\Omega$  and power density of 767.01  $mW/m^2$ , the maximum voltage that can be obtained from the cell is 385 mV (refer to Figure 2(b)). This is the limiting value of voltage for the specific concentration of electrolytes.



**Figure 2** | (a) Electricity production using potassium dichromate as electron acceptor. Arrow marks indicate the addition of a carbon source at the anode chamber, (b) polarization curve.

### Effects of pH on removal efficiency of Cr(VI) ion

Three pH conditions were carefully chosen in the cathode chamber to understand the effect of pH value on the removal of Cr(VI) from synthetic wastewater (Figure 3). The initial concentration of Cr(VI) was 100 mg/L. The pH value of the synthetic wastewater was maintained at 2.0, 7.0 and 9.0 by adding 0.1 M NaOH and 0.1 M H<sub>2</sub>SO<sub>4</sub>.

The reduction of Cr(VI) was not observed at pH values of 7.0 and 9.0. However, at pH value 2.0, 98% of Cr(VI) was removed at 24 h and was completely removed after 48 h with increasing the solution pH from 2.0 to 2.75 and finally

equalized to 3.75 after the complete removal of Cr(VI) (data not shown). The increase in solution pH may be related to the consumption of protons in the reduction of Cr(VI) to Cr(III) as reported in Equation (3).

It was inferred that at low pH values the protons take part in the Cr(VI) reduction, which eventually increases the reduction potential of the reaction. To confirm this, the ORP of Cr(VI) in aqueous solution was monitored along with the pH value. It was observed that the ORP of the cathode chamber was increased by decreasing the pH value (Figure 3). At pH value 2.0, the ORP was 540 mV, which subsequently decreased to 270 mV at pH 7.0 and 139 mV at pH 9.0. These results verify that the removal rate and the reduction efficiency of Cr(VI) was strongly dependent upon the pH value and ORP.

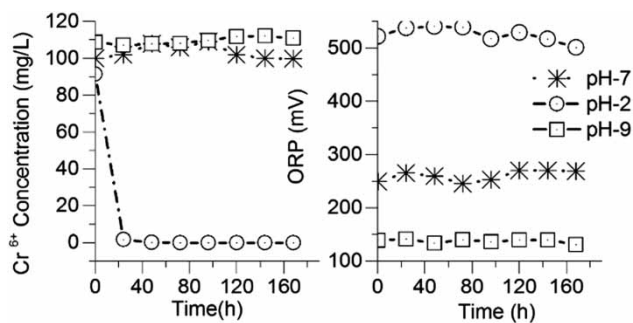


Figure 3 | Cathodic reduction of Cr(VI) and ORP at pH values 2.0, 7.0 and 9.0.

### Substrate degradation

During start-up, the initial TOC concentration at the anode chamber was 200 mg/L. The degradation of organic matter was observed within a few days. After the start-up, the batch studies were carried out at an acetate concentration of 300 mg/L. TOC was reduced to 63.3% in 6 days. When the acetate concentration was increased to 600 mg/L, 78.4% reduction was achieved in 13 days (Figure 4(a) and 4(b)).

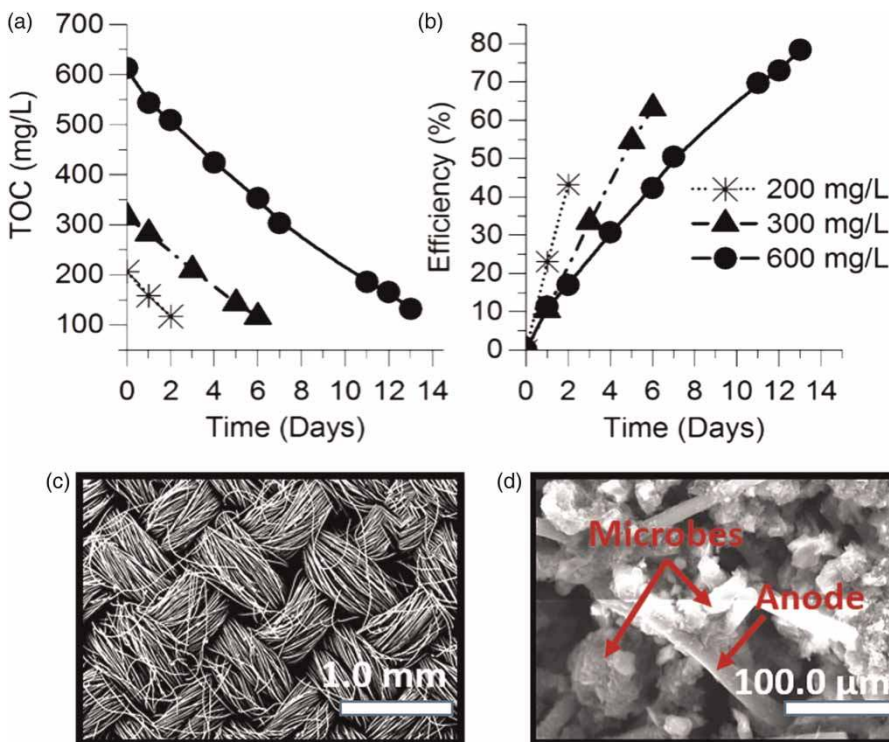


Figure 4 | (a) Temporal changes in substrate concentration, (b) substrate degradation efficiency, (c) SEM image of plain carbon cloth, (d) SEM image of bacteria attached to the surface of the anode after 30 days.

SEM images (Figure 4(c) and 4(d)) of biofilm growth on the anode surface and TOC degradation indicates effective functioning of microorganisms to utilize the carbon source as electron donor. The positive charge of the anode attracts electrochemically the microorganisms (with surface negative charge) to the surface of the anode. This may be the reason for gradual improvement in the voltage output along with substrate degradation.

### Cathodic reduction of Cr(VI)

The MFC was run at different initial Cr(VI) concentrations and the initial pH value of the catholyte was maintained at 2.0. The reaction time required for the complete removal of 300 mg/L, 150 mg/L and 75 mg/L was 1,350 min, 750 min and 180 min, respectively (Figure 5(a)).

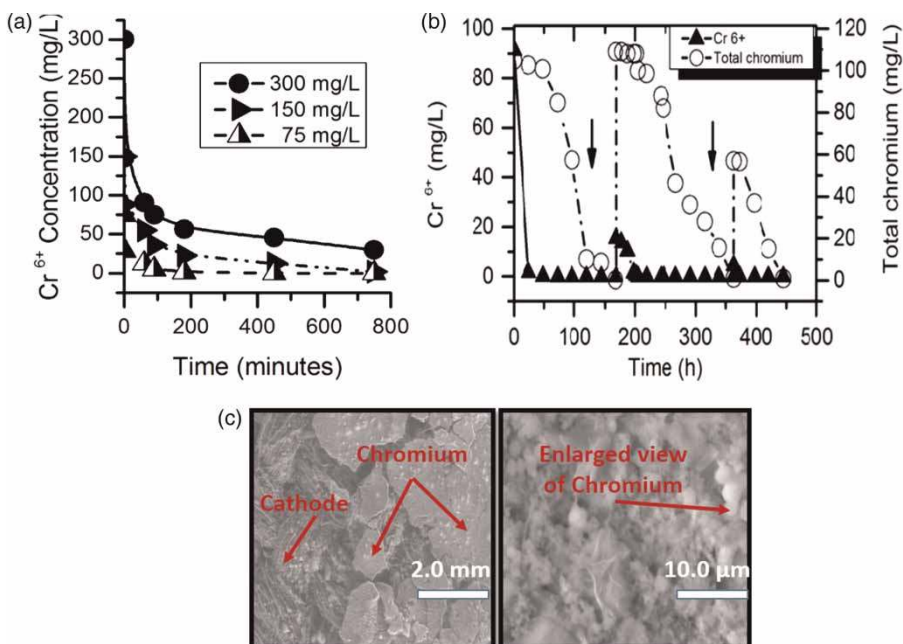
It was observed that a rapid reduction in Cr(VI) immediately after the addition of catholyte in the cathode chamber, followed by a steady state during the remaining time for all chromium concentrations (Figure 5(a)). The percentage reduction of Cr(VI) was about 50.67%, 41.33% and 61.53% for 300 mg/L, 150 mg/L and 75 mg/L, respectively. This rapid reduction was observed every time Cr(VI) was added (Figure 5(b)). The reason for this reduction is yet to be understood. This may be either due to low pH of the catholyte or large surface area of PEM for proton transfer or due to high substrate concentration (600 mg/L) at the anode

chamber, which promoted the biological activities of microbes which in turn speeded up the electron transfer for rapid Cr(VI) reduction.

### Cathodic reduction of chromium by fed batch mode

To study the reduction and recovery of chromium, the cathode chamber was run at fed batch mode (Figure 5(b)). In the first cycle (100 mg/L of Cr(VI); pH value 2.0; 1,000  $\Omega$ ) complete removal of Cr(VI) was observed in 48 h and 99.85% of total chromium was removed within 168 h. In the second cycle, a rapid reduction of Cr(VI) from 100 to 15.5 mg/L was noted immediately after the addition of feed. The same phenomenon was observed during Cr(VI) batch study and in the third cycle (50 to 4.57 mg/L). Initially, the color of the catholyte was orange yellow but as the reduction proceeded it changed to pale yellow and then to green. The green color of the solution indicated complete reduction of chromium from Cr(VI) state to Cr(III) state. Immediately after the reduction, the chromium started precipitating on the electrode surface. The reduction of total chromium was observed at this time. At the end of the experiment, a clear green deposit was observed on the cathode surface. SEM images clearly show deposits formed on the surface of the cathode (Figure 5(c)).

The mechanism of the cathodic removal of chromium involves two steps. First, the cathode easily gets protonated



**Figure 5** | (a) Cathodic reduction of Cr(VI) at different concentrations, (b) cathodic reduction of chromium by fed batch mode, (c) SEM images of Cr(III) on the surface of the cathode.

at low pH by surrounding the  $H^+$  ions, facilitating the approach of negatively charged  $HCrO_4^-$  species by electrostatic attraction, leading to the reduction of Cr(VI) to Cr(III). In the second step, it was observed that the Cr(III) formed was precipitated on the electrode surface as trivalent chromium oxides ( $Cr_2O_3$ ), thus reducing the total chromium in water to near zero concentrations.

## CONCLUSION

This work demonstrates that the MFC can be successfully used for removing Cr(VI) bearing water and organics in wastewater along with electricity production. The maximum power density achieved was  $767.01 \text{ mW/m}^2$  ( $2.08 \text{ mA/m}^2$ ). The reduction of Cr(VI) is strongly dependent on pH value, with acidic pH and high reduction potential making the reaction more favorable. At pH value 2.0, Cr(VI) was completely reduced within 48 h of reaction time and 99.85% of total chromium was recovered within 168 h. The study was based on primary research of MFC on treatment of Cr(VI) wastewater and power generation in MFCs. This work is the first of its kind where simultaneous treatment of chromium and domestic wastewater was achieved along with power production. It could be scaled up to treat wastewater from electroplating, tanneries and metallurgy industries.

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