



Hexavalent Chromium

Reduction in a Biocathodic Microbial Electrolysis Cell

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1. ABSTRACT

In the present study, we have assessed the possibility to remove Cr(VI) in a biocathodic chamber of a dual-chamber (2C) Microbial Electrolysis Cell (MEC) with cathode as the sole electron donor. The cathode was first put into the anodic compartment of a 2C-Microbial Fuel Cell (2C-MFC) inoculated with sludge from an anaerobic digester. After the acclimation period, the electrode was transferred into the cathodic chamber to work at -300 mV (vs. Standard Hydrogen Electrode - SHE) as the biocathode in a Cr(VI)-reducing MEC with 1000 $\mu\text{g Cr(VI)/L}$. The acclimation phase in the 2C-MFC allowed to shorten time for the electroactive-biofilm growth, and to increase the efficiency of the Cr(VI)-reducing MEC. The bioelectrochemical system ensured higher removal efficiency than the pure chemical, biological, and electrochemical processes.

2. MATERIALS AND METHODS

Biocathode production

2C-MFC set up:

- Two pirex-glass bottles separated by Cation Exchange Membrane (CEM), with 1100 mL total volume (**Figure 1**).
- Graphite cylinders (length: 6 cm, diameter: 1 cm, surface area: 18.85 cm^2) locked on stainless steel wires used as the electrodes.
- Cathodic chamber filled with sterile M9 minimal medium (autoclaved twice at 120 °C for 30 min).

Inoculum (at the anode): sludge from an anaerobic digester (20% final volume) and acetate (0.1 g L^{-1}) to provide sufficient carbon substrate for bacterial growth. During 30 days of **anode acclimation**, acetate was periodically added when the voltage dropped below 0.01 V. At the end of the period, the bioelectroactive anode was used as the biocathode in a Cr(VI)-reducing MEC.

Cr(VI)-reducing MEC

The **Cr(VI)-reducing MEC set up:** as for the 2C-MFC, but CEM was replaced by Nafion (Proton Exchange Membrane, PEM).

Cathodic solution: M9 minimal medium (1X), KHCO_3 (2 g L^{-1}), Cr(VI) (1000 $\mu\text{g L}^{-1}$).

Anodic solution: the same as for the cathodic 2C-MFC.

At the **biocathode**, a **potential** of -500 mV against Ag/AgCl reference electrode (i.e., -300 mV vs. SHE) was set. Three Cr(VI)-reducing MEC worked in parallel for 6 days.

Monitoring:

- Voltage at an external resistance (1 k Ω) was continuously recorded using a Picolog 1012 logging system.
- Cr(VI) dissolved concentration was analyzed at the beginning, during the experiment, and at the end of the tests by spectrophotometric method.
- Current density was calculated as current intensity (by Ohm's law: $I = (\Delta V / \Omega)$) flowing through the electrode area (18.85 cm^2).

Alongside tests of Cr(VI) removal, an abiotic control and an open circuit were also operated in parallel, in order to assess the electrochemical removal component.



Figure 1

Figure 1
2C-MFC used in this study



Figure 2

Figure 2
Cr(VI)-reducing MEC, abiotic control and open circuit control. Behind on the left, the potentiostat and the data acquisition system.

3. RESULTS

A. Current density trends in the MFC

Current density in the MFC ranged between 0.5 and 230 mA m^{-2} . A relationship between substrate availability and current production was observed, as rapid increase in the circulating current was recorded at acetate additions carried out when current density dropped below 1 mA m^{-2} (**Figure 3**).

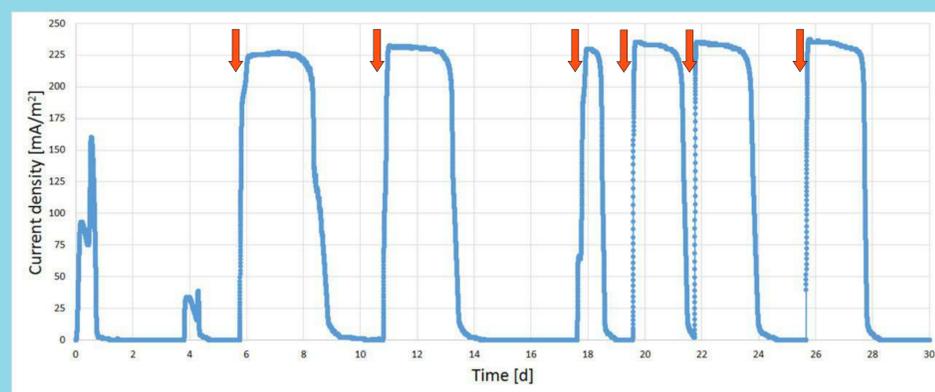


Figure 3. Current density during the anode acclimation phase in 2C-MFC. The red arrows indicate the addition of acetate (0.1 g L^{-1}).

B. Reduction of Cr(VI) in the MEC

A decrease in Cr(VI) concentration was observed at the end of the tests (**Figure 4**). In the Cr(VI)-reducing MEC the maximum Cr(VI) removal efficiency was observed (93%). In the same time, in the biotic open circuit system the chromium removal efficiency was around 78%. In the abiotic control open circuit, no significant changes were observed. Instead, the polarized abiotic control showed a rapidly decrease in the chromium concentration; this trend stopped at 35% of the initial concentration. In the latter case, the purely electrochemical reduction of Cr(VI) led to the precipitation of Cr(III) in solid form on the electrode; consequently the electrode was passivated, preventing further reduction of the dissolved Cr(VI). The higher Cr(VI) removal efficiency in the MEC system, was ascribed to the selection of a bacterial community containing electro-active and Cr(VI) reducing/resistant bacteria.

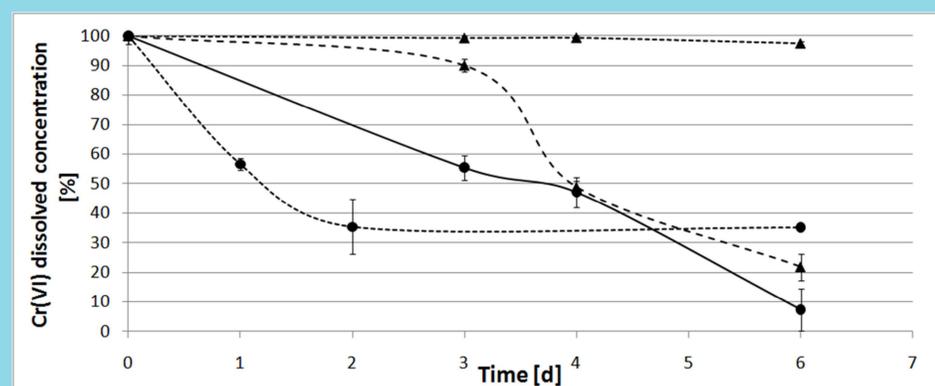


Figure 4. Cr(VI) concentration trend: open circuit system (broken line), Cr(VI)-reducing MEC (solid line), and abiotic control (pointed line). Systems controlled by potentiostat (black circles), systems without imposed potential (black triangles).

ACKNOWLEDGMENT

This work has been supported by Fondazione Cariplo in the framework of the project BEVERAGE - BioElectrochemical Remediation of Groundwater plumes (2015-0195).

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4. CONCLUSIONS

The acclimation phase in the MFC allowed to shorten time for the electroactive biofilm to deposit on the electrode, and to increase the efficiency of the Cr(VI)-reducing MEC. The bioelectroactive film was essential for high performance chromium removal; higher chromium removal efficiency values were measured in the Cr(VI)-reducing MEC compared to electrochemical or biological processes. Although BESs require further laboratory testing and scale up, the use of bioelectrochemical systems for removing hexavalent chromium is a new, sustainable and promising approach for this and other contaminants in polluted aquifers.

Eleventh International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, April 8-12, 2018, Palm Springs, California