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BIOELECTROCHEMICAL SYSTEM FOR REMOVING HEXAVALENT CHROMIUM FROM WATERS

G. Beretta*, D. Calloni*, A. Mastorgio*, E. Sezenna*, and S. Saponaro*
* Politecnico di Milano DICA Environmental section, Piazza Leonardo da Vinci 32, Milano 20133, (*Italy*)

Abstract **- BES include a set of technologies that exploit the ability of certain microorganisms to use electrodes as the electrons acceptors/donors and to catalyze redox reactions in order to promote a flow of electrons. 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 (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 2000 µg Cr(VI)/L. The acclimation phase in the 2C-MFC allowed to shorten the 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 process.

Index Terms **– Biocathode, Bioelectrochemical system, Hexavalent chromium reduction.**

I. Introduction

Groundwater is the environmental matrix most frequently affected by anthropogenic hexavalent chromium contamination. Due to its cancerogenicity, Cr(VI) has to be removed, hopefully using environmental-friendly and economically sustainable remediation technologies (e.g. Bioremediation techniques). The aim of bioremediation is to enhance the removal and transformation of pollutants by microorganisms through the addition of: nutrients and/or final electron acceptors (biostimulation), selected bacterial strains or consortia that are able to degrade contaminants (bioaugmentation), or chemicals that increase the contaminant bioavailability.

To overcome the limits of currently applied bioremediation technologies (substances to be injected, production of side metabolites, etc.), an alternative strategy is the use of BioElectrochemical Systems (BES) to stimulate bioreduction of Cr(VI), without affecting the natural groundwater conditions. BES are biological reactors where an electrode (anode) works as the final electron acceptor for the oxidation of organic compounds; then electrons pass through the circuit and reach the cathode, which acts as the electron donor for the reduction of metals and/or chlorinated compounds. In BES for the removal of metals, cathode is used as an electron donor to reduce metallic ions present as oxidized species. Tandukar and colleagues (2009) observed for the first time biological chromium reduction at the cathode of a Microbial Fuel Cell (MFC) [1]. Huang and colleagues tested a MEC (Microbial Electrolysis Cell) with the biocathode polarized at -300 mV (vs. Standard Hydrogen Electrode - SHE), which was able to efficiently reduce Cr(VI) [2]. Unlike previous works, the aim of this study was to evaluate the possibility to remove Cr(VI) in a biocathodic chamber of a dual-chamber (2C) MEC with cathode as the sole electron donor.

II. Materials and Methods

A. Biocathode production

A dual-chamber H-shaped reactor, made of 2 pirex-glass bottles separated by Cation Exchange Membrane (CEM), with 1100 mL total volume was used in this study. Graphite cylinders (length: 6 cm, diameter: 1 cm, geometric area: 18.85 cm^2) locked on stainless steel wires were used as the electrodes. The cathodic chamber was filled with sterile M9 minimal medium (autoclaved twice at 120 °C for 30 min). The anodic chamber was also filled with sludge from an anaerobic digester (20% final volume) and glucose (2 g L^{-1}) to provide sufficient carbon substrate for bacterial growth. Then the anodic chamber was flushed for 15 min with sterile-filtered N_2 to establish anaerobic conditions. During 50 days of anode acclimation, glucose concentration has been periodically replaced when the voltage has dropped below 0.01 V. For the whole test, the voltage across an external resistance (1000 Ω) was

continuously recorded using a Picolog 1012 logging system. At the end of the period, this bioelectroactive anode was used as the biocathode in a Cr(VI)-reducing MEC [3].

B. Cr(VI)-reducing MEC set up and operation

The Cr(VI)-reducing MEC set up was the same as for the 2C-MFC used for the biocathode production. The cathodic solution was composed of M9 minimal medium, $KHCO_3$ (1 g L^{-1}) as the sole carbon source, and hexavalent chromium (2000 µg L^{-1}). The anodic chamber, instead, was the same as for the cathodic chamber of the 2C-MFC, with the addition of $KHCO_3$ (1 g L^{-1}) to balance charges between the two compartments. At the biocathode a potential of -500 mV against Ag/AgCl reference electrode (i.e., -300 mV vs. SHE) was imposed [4]. The Cr(VI)-reducing MEC was operated for two cycles of 9 days each, 20 days one from the other. Hexavalent chromium dissolved concentration was analyzed at the beginning, during the experiment, and at the end of each cycle by spectrophotometric method. During the entire duration of two cycles, the current intensity was monitored by a potentiostat connected to a personal computer. Alongside tests of removal, an abiotic control and an open circuit were also operated in parallel, in order to assess the electrochemical removal component from the biological one.

III. Results

A. Current trends in the MFC

Current density in the MFC ranged between 0.53 and 38.2 mA m^{-2}. A relationship between substrate availability and current production was observed, as rapid increase in the circulating current was recorded after glucose addition, carried out when the current density has dropped below 1 mA m^{-2}.

B. Current trends in the MEC and the abiotic control

Current density in Cr(VI)-reducing MEC ranged between 20 and 60 mA m^{-2} in the first cycle, and increased up to 70 mA m^{-2} in the second cycle. In the abiotic control, the current density was below 10 mA m^{-2}.

C. Reduction of Cr(VI) in the MEC

A decrease in Cr(VI) concentration was observed at the end of the tests (Fig.1). In the Cr(VI)-reducing MEC and in the open circuit system, an increase in Cr(VI) removal efficiency was observed during the second cycle compared to the first cycle. This increased Cr(VI) removal efficiency was ascribed to the selection of a bacterial community containing electro-active and Cr(VI) reducing/resistant bacteria. However, the MEC system ensured higher removal efficiency (65%) than the pure chemical process (49%).

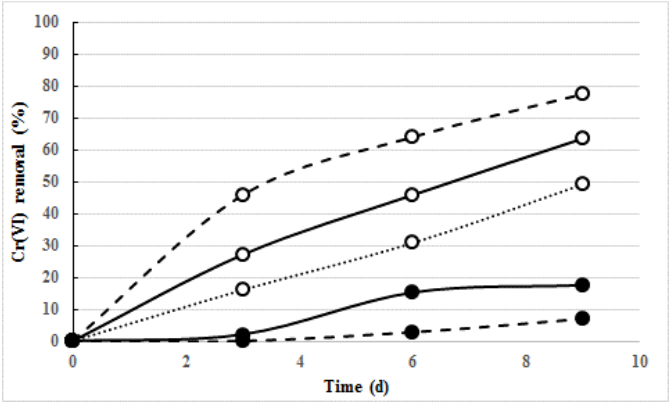

Fig. 1 Cr(VI) removal efficiency: open circuit system (broken line), Cr(VI)-reducing MEC (solid line), and abiotic control (pointed line). First cycle (black dots), second cycle (white dots).

IV. Conclusion

The acclimation phase in the MFC allowed to shorten the 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 generating current; higher current values were measured in the Cr(VI)-reducing MEC than in the abiotic control.

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 to remove this and other contaminants from polluted aquifers.

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