Journal of Water Process Engineering 11 (2016) 39–45

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Short communcation

Reduction of chromium(VI) with energy recovery using microbial fuel cell technology

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ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form 10 March 2016
Accepted 11 March 2016
Available online 24 March 2016

Keywords:
Modified microbial fuel cell
Chromium reduction
Catholyte
Anaerobic

ABSTRACT

A simple microbial fuel cell (MFC) method for the reduction of hexavalent chromium (Cr^{6+}) at an abiotic cathode by using an exoelectrogenic biofilm on the biotic anode, has been established. Two different Cr^{6+}-containing effluents were synthetically prepared in the laboratory (4 and 8 mg l^{-1}). The chromium effluents were used as catholyte and anaerobic microorganisms as anodic biocatalyst. 4 mg l^{-1} of Cr^{6+} was reduced 95% while, 8 mg l^{-1} reduced 86% during 456 h reaction in the MFC systems investigated. The MFC system with 4 mg l^{-1} of chromium exhibited a maximum power density of 89 ± 3 mW m^{-2} and a maximum voltage of 931 mV. A power density of 69.5 ± 2.1 mW m^{-2} and voltage of 700 mV was obtained by 8 mg l^{-1} chromium containing MFC cell. This work verifies the possibility of current production and simultaneous cathodic Cr^{6+} reduction. The novelty and significance of this system is that it uses an uncomplicated and economical salt bridge which replaces costly membranes like Nafion and an abiotic cathode.

1. Introduction

Hexavalent chromium is one of the most hazardous metal ions which is released into the environment by industries such as, electroplating, leather tanning, mining and metal finishing. As a widely known mutagen, teratogen and carcinogen, Cr^{6+} has high water solubility and mobility. In contrast, Cr^{3+} is less soluble in water, less mobile and less harmful. Discharge and accumulation of Cr^{6+} in the environment causes a serious threat to humans and other forms of life [25]. The most common method for removing Cr^{6+} from aqueous effluents is reduction of Cr^{6+} to Cr^{3+} followed by chemical precipitation as $Cr(OH)_3$. However, this conventional treatment for Cr^{6+} wastewater may be either consume energy to run or generate pollutants that have to be treated or later cause environmental problems [26].

Microbial fuel cells is an emerging method for converting chemical energy in organic wastes into electricity using the micro-organisms and also the advantage of performing a coupled mechanism of treating the waste waters containing pollutants. This treatment process uses microbiologically catalyzed reduction of Cr^{6+} to Cr^{3+}, which has gained wide attention recently [6,7,9]. A wide range of aerobic as well as anaerobic microorganisms have been used to reduce Cr^{6+} to Cr^{3+}. A large number of microorganisms such as, *Pseudomonas dechromaticans*, *Escherichia coli*, *Desulfovibrio vulgaris*, *Shewanella oneidensis*, *Aeronomas dechromatica*, and *Enterobacter cloacae*, can reduce hexavalent chromium [4,3].

This study attempts to reduce Cr^{6+} contaminated waste water in a MFC using a highly economical salt bridge and an abiotic cathode. An abiotic cathode was chosen in this study. Conventional MFC consists of an anode, cathode and an ion exchange membrane, most predominantly a Proton Exchange Membrane (PEM). This PEM might be either Nafion, Ultrex, etc. These membranes are extremely costly. Novelty and simplicity of this study is that it, alternatively uses a salt bridge as a proton exchange membrane, to conduct cations (H^+) through it. The usage of salt bridge makes the MFC an economically viable option when compared with the other studies [28,13,29].

2. Experimental

2.1. Lab scale MFC set-up

A two compartment microbial fuel cell as shown in Fig. 1 was constructed, with a tubular junction of 25 mm diameter, connecting the compartments contained the salt bridge at a height of 80 mm above the base. The salt bridge was formed by dissolving 1% KCl salt in 5% agar. The net working volumes for the anode and cathode

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http://dx.doi.org/10.1016/j.jwpe.2016.03.006
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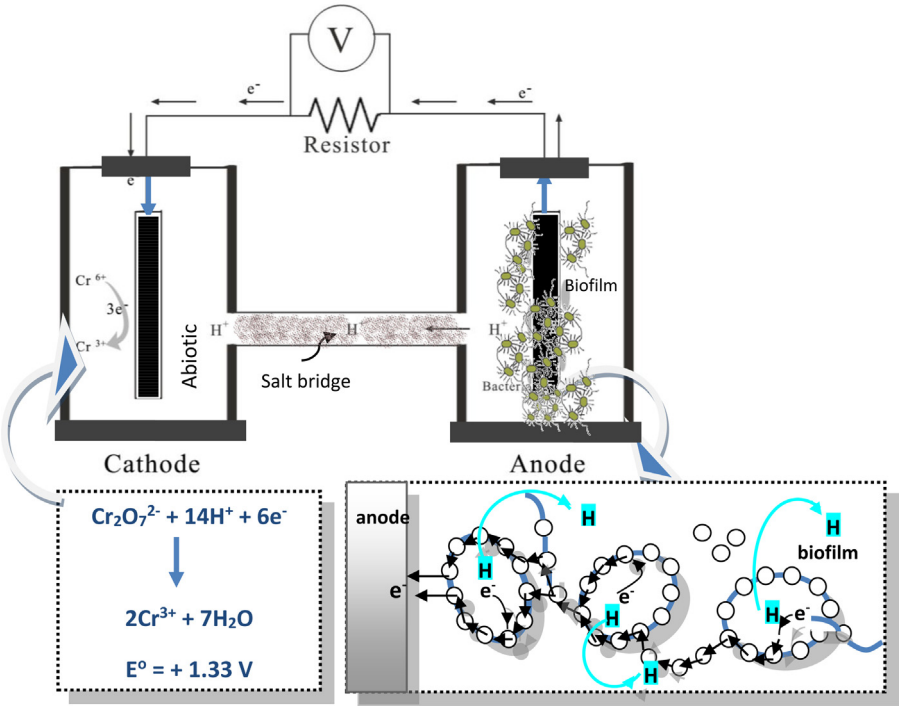

Fig. 1. Schematics of Cr(VI) reduction in the MFC.

chambers were 1.4 L. Thin graphite sheets of size (140 × 30 × 1) mm were used as electrodes for both the chambers. The electrodes in the two chambers were connected with a copper wire for electron (e^-) transfer. The exposed metal surfaces were sealed with non-conductive epoxy tapes. Dry electrodes were introduced into anode and cathode chambers. The whole anaerobic set up was autoclaved before assembling. The schematic representation of Cr^{6+} reduction in a MFC is shown in Fig. 1.

2.2. Principle

In the anode, electrons are generated from organic compounds are transferred to the cathode using microorganisms as "catalysts". In the cathode (abiotic/biotic), electrons are received by Cr(VI). When a resistor is connected externally to the system, electrical power is generated by the movement of electrons from the anode to the cathode. To balance the movement of electrons and close the electrical circuit protons are also delivered to the cathode through a proton or a cation exchange membrane [31].

2.3. Catholyte, anolyte and acclimatization

The cathodic Cr^{6+} solutions of 4 mg l^{-1} and 8 mg l^{-1} were prepared by dissolving $K_2Cr_2O_7$ in distilled water. Chromium concentration of 4 mg l^{-1} and 8 mg l^{-1} was chosen for this experiment based on chromium levels in tannery effluents reported [5,17,16]. The anode chamber was inoculated with waste water collected from the Adyar River, Chennai. This river has been contaminated with sewage outlets and industrial wastes of Chennai city over the past three decades [27].

The initial pH of the waste water was 6.21 ± 0.5. The initial COD of the waste water was 580 ± 102 mg l^{-1} and final COD after 456 h of MFC operation reduced by 41 ± 9%. The final pH after 456 h was 5.62 ± 0.3. The MFC was run in strictly anaerobic conditions for two cycles (i) 4 mg l^{-1} of Cr^{6+} in cathodic chamber and (ii) 8 mg l^{-1} of Cr^{6+} in a cathodic chamber. The acclimatization period of the microbes in the anodic chamber was 18 days, where every sixth day of operation, the anode chamber was replaced with growth media containing a medium (g l^{-1}) (KH_2PO_4: 4.4, K_2HPO_4: 3.4, NH_4Cl: 1.3, NaCl: 0.5, acetate: 1.0, $CaCl_2$: 0.0146, $NaHCO_3$: 1.0) 0.375 g yeast extract, 0.375 g peptone [29,8] and trace elements. The cathode chamber was filled with distilled water, during the acclimatization. The circuit by connecting a 10 Ω resistor parallel across the electrodes, and the cathode chamber is replaced with two varying concentrations of $K_2Cr_2O_7$ solution containing: 4 mg l^{-1} and 8 mg l^{-1} of Cr^{6+} for two separate cycles. The cathode chambers were maintained abiotic, in order to ensure Cr^{6+} reduction strictly through the electrons generated from anode chamber, instead of direct contact with any microbes.

2.4. Analytical techniques and calculations

The pH was recorded every day by using a Srico model 002 pH probe. The conductivity was measured by using a Digisun Electronics DI 9009 conductivity probe. COD was determined by open reflux method [1]. Samples from the cathode compartment were withdrawn every 24 h, and Cr^{6+} concentration was estimated using diphenylcarbazide method [1]. Total chromium in the cathode compartment was analyzed by using Varian Spectra AA 220 Atomic Absorption Spectrophotometer.

A digital multimeter was connected on both the electrodes, with positive end at the cathode and the negative end on the electrode in the anode chamber. The voltage readings were recorded every 24 h, and the current generated can be calculated using Ohm's law Eq. (1).

$$I = V/R \tag{1}$$

where V is the potential difference between two points which include a resistance R. I is the current flowing through the resistance. The power was calculated by using Eq. (2).

$$P = VI \tag{2}$$