Journal of Hazardous Materials 355 (2018) 197–205

Contents lists available at ScienceDirect

Journal of Hazardous Materials

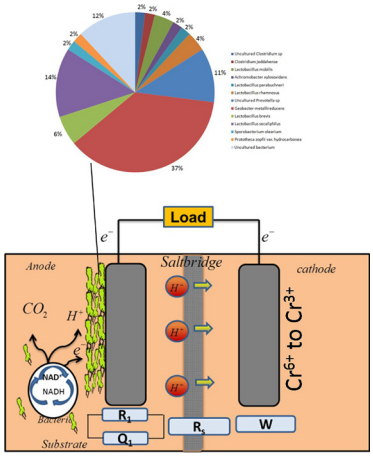
journal homepage: www.elsevier.com/locate/jhazmat

Environmentally available biowastes as substrate in microbial fuel cell for efficient chromium reduction

M. Sindhuja[a,b], S. Harinipriya[a,*], Amarnath C. Bala[c], Arvind Kumar Ray[c]

[a] Electrochemical Systems Lab, SRM Research Institute, SRM Institute of Science and Technology, Kattankulathur, 603203, India
[b] Department of Physics and Nanotechnology, SRM Institute of Science and Technology, Kattankulathur, 603203, India
[c] Aquatic Animal Health and Environment Division, Central Institute of Brackish water Aquaculture-CIBA (ICAR), Chennai, Tamilnadu, India

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Cr(VI) reduction
16s rRNA
Geobacter metallireducens
Power generation
Microbial fuel cell
Tannery effluent

ABSTRACT

Dual chambered microbial fuel cells with Potassium dichromate (22 g/L, MFC-1) and tannery effluent waste water containing 26 mg/L (MFC-2), 5 mg/L (MFC-3) of Cr(VI) as catholyte, sweet lime waste inoculated by cowdung as anolyte and graphite electrodes were used to reduce toxic Cr(VI) to Cr(III) with simultaneous power generation. Cr (VI) in the cathode chamber reduced to Cr_2O_3 within 24 h. Complete reduction of Cr(VI) from tannery effluents by microbial fuel cell is noticed within 10 days. The 16 s rRNA sequencing studies demonstrated presence of Geobacter Metallireducens in mixed culture bacteria in anaerobic anode. The power density of the device is 396.7 mW/m^{2}on day1which is 7.2 times higher than literature data of 55.5 mW/m^2. The processes involved on the biofilm/electrolyte interface and graphite/electrolyte interface is studied by Electrochemical Impedance Spectroscopy. Electrochemical studies demonstrated the active growth of biofilm on anode which reduces charge transfer resistance from day 1 to day 25. The concentration of Cr(VI) reduced in the present studies are approximately 1000 times higher than those reported in the literature.

* Corresponding author.
E-mail address: harisesha@yahoo.co.in (S. Harinipriya).

https://doi.org/10.1016/j.jhazmat.2018.05.030
Received 25 November 2017; Received in revised form 4 May 2018; Accepted 15 May 2018

1. Introduction

Industrial processes such as electroplating, leather tanning, dye/pigment manufacturing, mining, photographic materials and fungicide production releases toxic Cr(VI) rich effluent [1]. Cr(VI) due to its toxicity, mutagenic and carcinogenic activity can cause severe threat to the environment and humanity [2]. Removal of Cr(VI) is carried out via several techniques such as ion-exchange, bioadsorption, membrane filtration and electrodialysis [1,3]. Conversely, these techniques have various limitations *viz a viz* high energy requirement, excessive chemical consumption, generation of a large quantity of secondary pollutants and toxic waste sludge [4,5]. Consequently a simple and cost effective method becomes inevitable to treat toxic Cr(VI). It is observed by several researchers that Microbial Fuel Cells (MFCs) can reduce heavy metals as well as generate electricity simultaneously utilizing microbial culture growth [6]. MFCs is an emerging technique to treat wastewater, industrial effluents with heavy metal contamination such as Cr(VI) as well as convert organic wastes into electricity using microorganisms concurrently [7–10]. A wide range of aerobic as well as anaerobic microorganisms such as Pseudomonas dechromaticans, Escherichia coli, Desulfovibrio vulgaris, Shewanella Oneidensis, Aeronomas dechromatica, Enterobacter cloacae and Geobacter Mettallireducens have been employed to reduce Cr^{6+} to Cr^{3+} [11,12,13]. Among these, Geobacter Metallireducens is an excellent candidate for Cr(VI) bioremediation due to its metabolic diversity, sequenced genome and adaptation to laboratory conditions [14].

It is imperative from the literature that performance of dual chambered MFCs is severely affected by the electron acceptor in the cathode chamber [15,16]. Cr(VI) possess higher standard redox potential (1.33V vs SHE) in comparison with other potential electron acceptors such as oxygen and hexacyanoferrate (1.23 V and 0.36 V respectively vs SHE) and hence Cr(VI) is also a favorable electricity generator [17,18]. Following redox reaction at cathode facilitates reduction of toxic Cr(VI) as

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad E^o = 1.33\,V \qquad (1)$$

Numerous studies in the literature [1–19] reported treatment of Cr (VI) by MFCs using abiotic cathodes at acidic pH and biotic cathodes at neutral pH. Using narrow band semiconductor such as graphite plate as a cathode, Zhao et al. [20] obtained 92.8% Cr(VI) removal with maximum power density of 108 mW/m^2 in 10 h. Thus from the literature it is clear that the abiotic cathode based Cr(VI) reduction produced higher power density, current density and Cr(VI) reduction percentage in comparison with biotic cathodes. The advantages of abiotic over biotic cathode are (i) abiotic cathode does not require buffer medium in the catholyte and this in turn reflects in easy handling of the system as well as cost of MFCs (ii) abiotic cathodes can handle higher concentrations of Cr^{6+}solutions while biotic cathode leads to shock and death of microorganisms (iii) formation of chemical scales due to P, Na and Ca are eliminated in abiotic cathodes [10]. The major objectives of the present study (as depicted in Fig. 1) are (i) reduction of saturated concentration of Cr(VI) and tannery effluent containing Cr(VI) contaminants (26 mg/L and 5 mg/L) in abiotic chamber to non-toxic Cr(III) at neutral pH employing simple and cost effective lab scale MFCs, (ii) investigation as the first attempt to reduce Cr(VI) employing saturated concentration of $K_2Cr_2O_7$ (MFC-1) as well as tannery effluents (MFC-2 and MFC-3) in abiotic cathode with simultaneous power generation, (iii) to achieve utilization of easily available sweet lime waste as electron donor in anode, abiotic cathode and low cost salt bridge as proton exchange membrane that makes the fabrication of MFCs highly feasible and cost effective,

(iv) usage of agar-agar (KCl) salt bridge in the MFCs as an economically viable option when compared to other studies [1,5,8,16,18,20,21], (v) 16S rDNA sequencing studies to identify the bacterium causing efficient Cr(VI) reduction, (vi) Electrochemical Impedance Spectroscopy(EIS) to confirm Cr(VI) reduction process at graphite/electrolyte interface and demonstrating the technique using Cr(VI) contaminated wastewater collected from tanning industries.

2. Materials and methods

2.1. MFC Construction

The lab scale dual chambered MFCs were constructed with plastic boxes separated by salt bridge. The working volume of each chamber is 300 ml. Graphite rod is used as electrodes. The salt bridge is formed by dissolving 7% KCl in 20% Agar. The anodic chamber of the MFCs is maintained in anaerobic condition which promotes microorganism growth. The cathode chamber of MFCs is also sealed to avoid oxygen acting as electron acceptor instead of Cr (VI).

2.2. Tannery effluent sample collection

The study area is located in the Tannery Industrial Zone at Chromepet, Chennai, Tamilnadu, India. Its coordinates are 12°95′N latitude and 80°14′E longitude towards Chennai. It hosts several tannery clusters company pvt. Ltd. that executes chrome tanning of leather. The sample collected was black in colour. Two samples were collected (i) near the effluent outlet around 10 m from the industry and (ii) around 100 m from the industry. The area within this distance is chosen to estimate the dilution of the heavy metals due to utility drainage water mixing by the city corporation. Parameters such as pH, electrical conductivity (EC), total suspended solids (TSS), total dissolved solids (TDS), total solids (TS), biological oxygen demand in 5 days at 20 °C (BOD_5) and chemical oxygen demand (COD) were measured for both the samples (cf. Supporting Information S1).

2.3. Inoculation and operation

The sweet lime waste is used in anode chamber. 1 g of Cow dung* is added to anode chamber as innoculum for bacterial growth. The cathode chamber is filled with (i) 300 ml of $K_2Cr_2O_7$ solution (MFC-1) (ii) tannery effluent with 26 mg/L of Cr(VI) content (MFC-2) and (iii) tannery effluent with 5 mg/L of Cr(VI) content (MFC-3) as catholyte respectively. The phosphate buffer solution is added to both chambers to maintain at pH 7. In anodic chamber, microorganisms consume glucose and generate electrons and protons**.

2.4. Material characterization

The reduced Cr(III) is centrifuged and dried at 60 °C for an hour. The recovered Cr(III) nanoparticles from catholyte and Cr(III) deposited on the surface of cathode is examined by various analytical and spectroscopic techniques. The crystal size and the crystallographic planes of the Cr(III) deposited and precipitated on cathode are determined using XRD (pananalytical X-ray diffractometer, Netherlands). The functional group present on the recovered Cr(III) is identified by FTIR (ALPHA FTIR Spectrometer). The presence of Cr(III) in catholyte solution is further determined by UV–vis and UV-DRS (Analytikjena,Germany). As the amount of Cr(VI) is in ppm in the case of tannery effluent (MFC-2 and MFC-3) the absence of Cr(VI) after MFC treatment is confirmed by UV–vis spectroscopy.

* Foot note: Cow dung is collected from a single source (cow) at potheri, Kattankulathur. The feeding constituents of the cow are grass, cotton seeds, hay, husk, rice washed water. The cow dung is obtained fresh and utilized within 10 min.

** The electrons are transferred from anode to cathode chamber through external circuit and protons transfer through salt bridge. The reduction process of Cr(VI) takes place in cathode chamber as long as protons and electrons are available.