Increasing bioanode performance by thermal, chemical, and electrochemical oxidation treatment of carbon electrodes

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Abstract
In this work carbon cloth electrodes were modified by thermal, chemical, and electrochemical oxidation to enhance oxygenated surface groups and modify the electrode texture to improve the electron transfer and bacterial adhesion in order to increase bioanode performance in bioelectrochemical systems (BESs). Bioanodes were formed from domestic wastewater amended with acetate under potentiostatic control. The physical, chemical, and electrochemical electrode characteristics were compared. The bioanode performance was followed by current production, charge generated, biofilm quantity, substrate consumption, and potentiostatic electrochemical impedance spectroscopy. The electrode characterization showed that all oxidation treatments were effective for exposing surface groups and modifying electrode porosity and electrode surface area. A comparative analysis of bioanode performance revealed the thermal oxidized electrode as the most suitable treatment to form bioanodes. The maximal current density observed with untreated electrode was 0.152 ± 0.026 mA; the current increase was 78% (0.272 ± 0.006 mA) and 28% (0.195 ± 0.042 mA) for thermal and electrochemically oxidized electrodes respectively. The characteristics of un-colonized electrodes were correlated with the bioanode performance, and the impact of biotic and abiotic factors was analyzed.

Keywords
Bioanodes; bioelectrochemical systems; microbial fuel cell; carbon electrodes; oxidation treatment.

INTRODUCTION

Electrode materials have an important role in the performance and cost of bioelectrochemical systems (BESs). Carbon materials are the most widely used anodes due to their chemical stability, conductivity, and biocompatibility; they traditionally include graphite rod, graphite fiber brush, carbon cloth, carbon paper, carbon felt, reticulated vitreous carbon, and activated carbon. To achieve better performance of BESs, different modifications have been tested on the electrode surfaces. In some instances these modifications have helped increase the biocompatibility of the anode, increase the surface area, and decrease the resistance of the charge transfer between the biofilm and the electrode. Secondly, it has been widely accepted that the bacteria adhesion depends on the surface charge and other physicochemical properties of the anode [Zhou *et al*. 2011].

MATERIALS AND METHODS

Oxidation treatments, electrodes characterization, and bioanode construction

Carbon cloth electrodes (2 cm x 2 cm) were oxidized by chemical (CO), electrochemical (EO), and thermal (TO) methods. CO was achieved in HNO_3 diluted solution under reflux at 80 °C over 1 h. EO was performed by electrode anodization at +1.6 V (*vs.* Ag/AgCl) in a phosphate buffer solution 0.5 M amended with NaCl 10 mM. TO was performed in a muffle furnace at 636 °C for 0.5h.

Physical-chemical characterization of electrodes was focused on the surface area and porosity using a Micrometrics ASA P 2000; surface groups were investigated by FTIR in a Thermo Scientific

Nicolet 6700; electrode surface images and elemental analysis percentage were achieved by FEI Quanta 200 and Helios NanoLab 600 ultrahigh resolution microscopes. Electroanalytical techniques were performed in the phosphate buffer solution using a BioLogic VSP potentiostat/galvanostat. Electrochemical impedance spectroscopy was performed to determine the ohmic and polarization resistances (Rp), and capacitance. Cyclic voltammetry was also achieved to detect redox processes on the anodes.

Electroactive biofilm was developed on the carbon cloth electrodes at +0.1 V (*vs.* Ag/AgCl). Domestic wastewater amended with sodium acetate 20 mM was used as inoculum and substrate source. Conventional three-electrode electrochemical cells (120 mL) were placed in a water bath at 25 °C, and biofilm performance was followed for 5 days from inoculation.

Monitoring and analytical techniques

Each modified and control electrode was tested in duplicate. Substrate was measured as CODs with the APHA standard method; volatile solids and pH were also monitored. The biofilm formation was determined by extracting and quantifying soluble protein from the biomass by the Bradford method. Current generation was monitored by chronoamperometry, and experimental charge was calculated as the integral of current over the time. Biofilm structure and composition were observed with SEM.

RESULTS AND DISCUSSION

Electrode characterization

The physical-chemical and electrochemical characterization of untreated and oxidized electrodes is summarized in Table 1. Considering the Rp as a measure of the ability of the electrode to transfer electrons, and inversely proportional to the capacitance, which is a property of the material to retain charge, the TO and CO electrodes were identified as the most appropriate to form bioanodes.

Table 1.Characterization of untreated and oxidized carbon cloth electrodes in phosphate buffer solution.

	Untreated UE	Thermal TO	Electrochemical EO	Chemical CO
Surface area (m^2/g)	1.112	10.892	1.592	1.868
Area in pores/Surface area	0.208	0.326	0.620	0.205
O% content	3.86	5.23	6.52	5.22
C% content	80.97	76.35	73.30	75.75
Polarization resistance Rp (Ω)	1741	831	1279	2019
Capacitance (F)	1.81E-4	9.06E-4	2.20E-4	0.48E-4

The electrode surface area was greatly increased with the TO treatment. This electrode had a better performance in terms of its high production of current (see Figure 1). The high surface area probably promoted bacteria-electrode contact, in addition to the electron transfer achieved by mediators. Electron transfer very probably was enhanced by the lower Rp of the TO electrode. The porosity texture can also promote biofilm anchoring; thus the EO electrode was marked as the most suitable to form bioanodes.

As a result of the electrode treatments, the oxygen content in the carbon cloth electrodes increased, regardless of the oxidation method. This suggests the formation of oxygenated surface groups like carboxyl, keto, hydroxyl, and quinone, which are reported to be involved in electron transfer at carbon electrodes [Leon y Leon, 1994]. The occurrence of surface groups was investigated by FTIR. Bands observed around 1500 cm^{-1} were related to C=O stretching.

Biofilm performance

The performance in current production was in the order TO > EO > UE > CO and was similar for the experimental charge generated (Figure 1); this charge indicates the total electron transfer at the interface of the electrode. The variations among the current and the charge observed were investigated considering the biofilm as a catalyst on the electrode; thus the biofilm quantity and microbial diversity were explored by SEM.

Differences in the start-up time were observed between the oxidized electrodes. The start-up time was slightly lower for bioanode using the CO (6.5 ± 0.0 h) than the other electrodes.

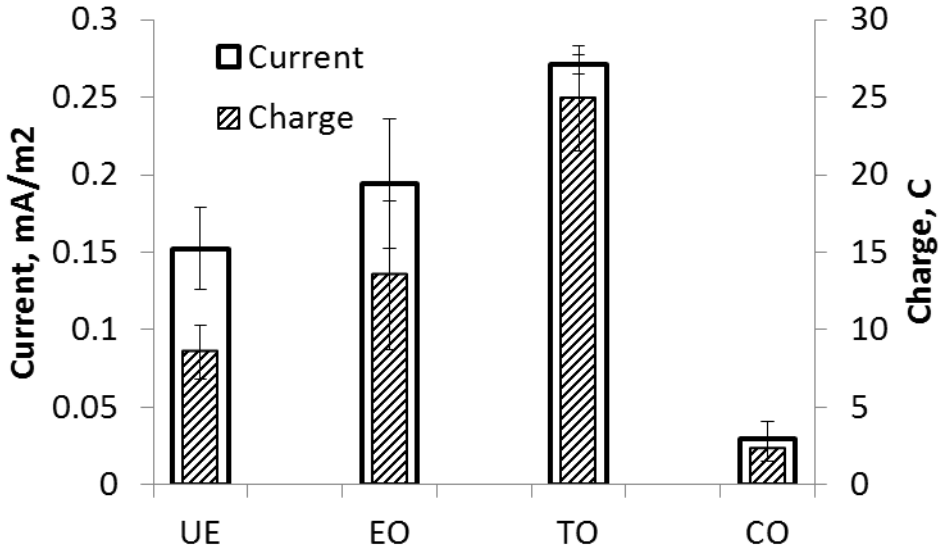

Figure 1.Current and experimental charge produced by bioanodes formed on untreated carbon cloth electrode (UE), electrochemically oxidized electrode (EO), thermally oxidized electrode (TO), and chemically oxidized electrode (CO). Standard deviation bars correspond to duplicates.

The functional surface groups created during the oxidation treatments contributed to increasing the current production as it was observed for the TO and EO electrodes; however, the CO electrode had the lowest current production even if the oxygen content in CO was higher than UE. Therefore, other factors were very probably involved in current production. The maximum current obtained in this work, 0.272 ± 0.006 mA (680 ± 15 mA/m^2), was in the range of the performance reported for potentiostatic controlled systems. Bioanode formation from a pure culture growing on multiwall nanotubes has been reported; current generation in this system was quite low, 9.7 mA/m^2 [Peng et al. 2010], while research with domestic wastewater and a number of different carbon type electrodes, reported a range of current from 7 to 1358 mA/cm^2 [Liu et al. 2011]. It is clear that the performance is highly dependent on the inoculum and the type of carbon electrode treatment. In the present work the current was increased by 78% with TO electrode. SEM micrographs showed different biofilm structures covering the carbon fibers. Mostly short and long bacilli covered the TO and EO electrodes, while coccus-shaped bacteria covered the UE and CO electrodes. These observations suggest that current variations between oxidized electrodes were possibly due to different electron transfer kinetics associated with different microorganisms.

Factors correlating with the bioanode performance

In order to determine the bioprocess parameters affecting current production, a correlation analysis was performed using current as the dependent variable and the volatile solids in inoculum, the protein content in biofilm, the initial COD, and the COD removal as independent variables. The highest coefficient obtained from the correlation matrix was for volatile solids, 0.768 significant at 0.05 level (Figure 2).

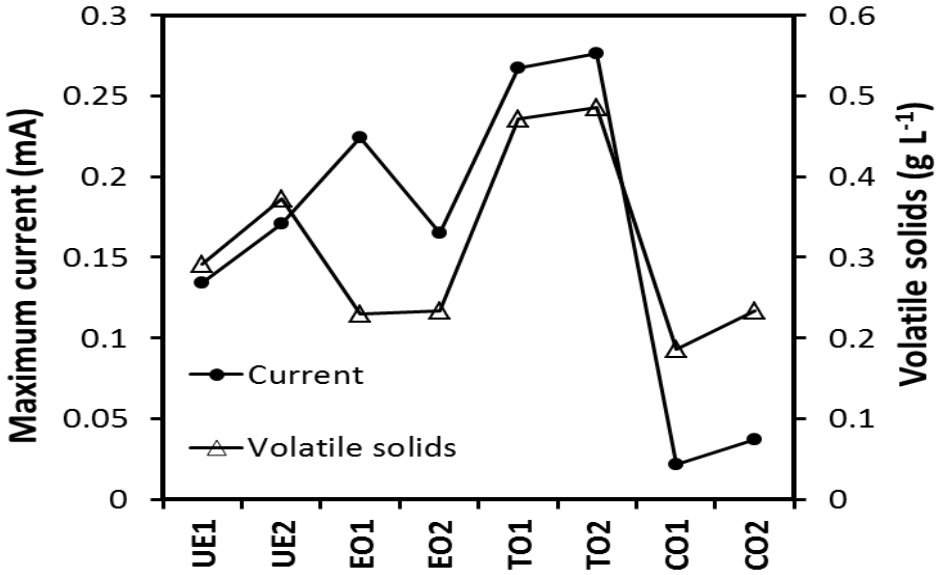

Figure 2. Maximum current production and volatile solids associated to bioanode formation.

The correlation coefficient between current production and COD consumed was not significant (0.395), indicating that mainly the planktonic microorganism consumed the COD rather than the biofilm attached on the electrode, which was confirmed by the Coulombic efficiencies (0.23 – 2.4%).

CONCLUSION

A critical factor to improving bioanode performance is biofilm formation on the electrode and the electron transfer at the interface. These phenomena can be controlled by the modification of electrode surfaces. In this work the thermal oxidation of carbon cloth showed to be the most effective method, increasing current production by 78%. The analysis of biotic and abiotic factors involved in bioanode formation revealed the volatile solids as a factor correlating directly to current production; moreover, electrode Rp, specific surface area, and textural surface had a high impact on biofilm formation; consequently, these parameters could be useful in predicting bioanode performance.

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