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Production of hydrogen from domestic wastewater using a bioelectrochemically assisted microbial reactor (BEAMR)

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Abstract

Hydrogen production from domestic wastewater was examined using a plain carbon electrode or graphite-granule packed-bed bioelectrochemically assisted microbial reactors (BEAMRs) capable of continuous or intermittent hydrogen release. When graphite granules were added to the anode chamber (packed-bed mode) current density was increased when the domestic wastewater had a high initial chemical oxygen demand (COD > 360 mg/L), and produced a maximum Coulombic efficiency of 26% (applied voltage of 0.41 V) and a maximum hydrogen recovery of 42% (applied voltage of 0.5 V). The packed-bed system successfully treated the wastewater, with removal efficiencies of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and dissolved organic carbon (DOC) in the range of 87–100%. The final BOD of the treated wastewater was always reduced to less than 7.0 ± 0.2 mg/L. Overall hydrogen production based on COD removal was a maximum of 0.0125 mg-H_2/mg-COD (154 mL-H_2/g-COD versus a maximum possible conversion of 0.126 mg-H_2/mg-COD), with an energy requirement equivalent to 0.0116 mg-H_2/mg-COD, producing an 8% net yield of H_2. These results demonstrate that a wastewater treatment based on a BEAMR reactor is feasible, but improvements are needed in hydrogen recoveries and Coulombic efficiencies to increase the overall hydrogen yield.

Keywords: Hydrogen; Wastewater; Treatment; Electrochemical; Electrolysis; Bacteria

1. Introduction

In a microbial fuel cell (MFC), bacteria oxidize organic matter, producing protons and electrons. Protons diffuse through the electrolyte towards the cathode. The electrons travel around a circuit to the cathode, producing current. At the cathode, a species, such as oxygen, reacts with the electrons and protons to form a reduced compound, such as water. In a bioelectrochemically assisted microbial reactor (BEAMR), hydrogen is evolved at the cathode according to

$$2H^+ + 2e^- \rightarrow H_2 \quad (1)$$

by eliminating oxygen at the cathode, and adding a small voltage to the circuit [1,2]. The potential at pH = 7 that is required to produce hydrogen is theoretically −0.61 V (V_{Cat}; versus Ag/AgCl) [3]. The anode potential produced by the oxidation of the organic matter by the bacteria is approximately $V_{an} = -0.50$ V, so the minimum theoretical applied voltage is 0.11 V ($V_{app} = V_{an} - V_{Cat}$). In practice, the minimum applied voltage to produce hydrogen from the bioelectrolysis of acetate has been found to be more than ~ 0.25 V due to ohmic resistance and electrode overpotentials [1,2]. However, this is still substantially less than the 1.8–2.0 V needed for hydrogen production via water electrolysis (alkaline conditions; [4]).

The BEAMR and MFC systems share many similar characteristics, and therefore many findings for improving electricity generation in MFCs should be applicable for increasing hydrogen production in the BEAMR system. There are important differences between the systems, however, that can affect system performance relative to hydrogen recovery. First, in the

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BEAMR process, hydrogen can be lost due to its diffusion from the cathode chamber through the cation exchange membrane (CEM) into the anode chamber. Second, in the BEAMR process there is no potential for loss of substrate due to aerobic growth of bacteria due to oxygen diffusion into the anode chamber from the cathode chamber. This could allow higher Coulombic efficiencies (CEs) in the BEAMR than in the MFC, but it could also affect redox conditions in the anode chamber (and the development of the bacterial community), and therefore the performance of the system. The CE of a BEAMR, for example, can be as large as $92 \pm 6.3\%$ with acetate [2], while in MFCs the CEs range from 10% to 78% using mixed cultures and acetate [5,6]. Third, it cannot be predicted based on MFC tests what the minimum applied voltage will be for hydrogen generation in a BEAMR process for different substrates, or how current density might be affected by the applied voltage in these systems.

In this study, we examined hydrogen production using domestic wastewater as the fuel in the BEAMR process, and evaluated system performance in terms of hydrogen recovery, CE, and the effectiveness of treatment (BOD, COD, and DOC removal). The BEAMR process is new, and so far only acetate has been examined as a substrate for hydrogen production. It is reasonable to expect that domestic wastewater could be used to make hydrogen in the BEAMR process as either acetate or wastewater can be used to generate electricity in an MFC. However, the amount of hydrogen that could be recovered and the required voltage needed to make the BEAMR process work cannot be predicted, and must be tested. In tests conducted previously with MFCs, maximum power densities and CEs with wastewater have been consistently lower than those achieved using acetate. For example, a maximum power density of $661\ \mathrm{mW/m^2}$ was produced in a single chamber MFC using acetate, but only $146\ \mathrm{mW/m^2}$ was achieved using domestic wastewater [5,7]. The recovery of hydrogen based on the measured current in the BEAMR has varied, from 90–100% [1] to $57 \pm 0.1\%$ [2]. Previous BEAMR tests have only examined hydrogen production via intermittent gas release, but it has been shown in hydrogen fermentation tests that continuous gas release can increase overall hydrogen yields [8]. To examine the potential for hydrogen generation from domestic wastewater, we examined hydrogen production in a reactor with a plain carbon electrode versus a system with the anodic chamber filled with a bed of conductive graphite granules, and the effect of intermittent or continuous gas release.

2. Methods

2.1. Reactor construction

Previous research with MFCs has shown that performance can be improved by reducing electrode spacing [9]. A two-chambered reactor was therefore constructed so that the chambers were directly adjacent to each other with a cation exchange membrane (CEM; Nafion^{TM} 117; Dupont Co., USA; projected surface area of $11.4\ \mathrm{cm^2}$) held between the two faces using an O-ring, and rubber gaskets (Fig. 1). Each rectangular chamber (292 mL capacity filled to either 192 or 256 mL) of the reactor contained an electrode (projected surface area of $26.5\ \mathrm{cm^2}$) placed 1.8 cm from the CEM (Fig. 2). Experiments were conducted using reactor headspace volumes of 100 or 36 mL (as indicated). This reactor is larger than our previous BEAMR system [1]. The larger liquid and gas volumes used for the reactor made it easier to sample the reactor and not alter reactor conditions. The anode was nonwet-proofed carbon paper (Phosphoric Acid Fuel Cell Electrode, Toray Carbon Paper; De Nora North America, Somerset, NJ, USA) and the cathode was carbon paper with a Pt loading on the membrane facing side of $0.5\ \mathrm{mg/cm^2}$ (A-3 EFCG; De Nora North America, Somerset, NJ, USA). Copper wire was attached to the electrodes and all exposed metal surfaces were sealed with a nonconductive epoxy (Dexter Corp., NJ, USA). In some tests the anode chamber was filled with graphite granules (total volume of 131 mL; particle size of 2–6 mm ($\frac{1}{4}$ in × #10 mesh; Product 100, Graphite Sales, Inc., Chagrin Falls, OH, USA)) to increase the surface area of the anode and proximity of the anode to the CEM (packed-bed mode), reducing the liquid volume to 135 mL. The total anode surface area increased to $1041\ \mathrm{cm^2}$, assuming a specific surface area of $A_s = 6\theta/d$ [10] where $d = 4$ mm is the granule diameter and $\theta = 0.53$ is the bed porosity [11].

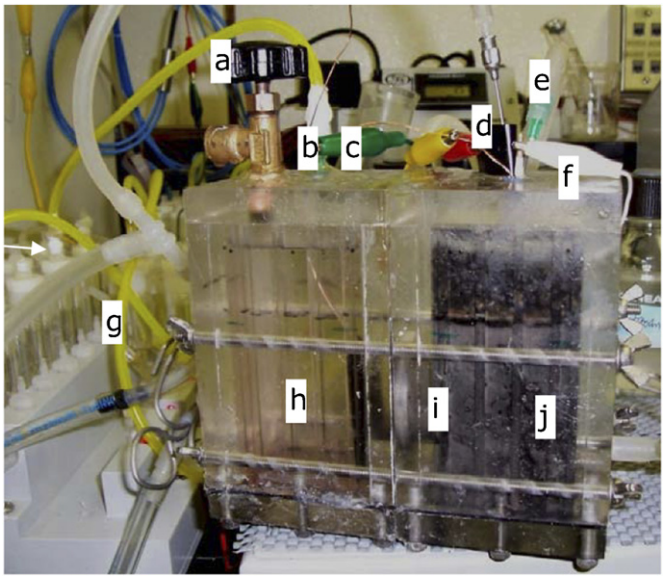

Fig. 1. Two-chambered acrylic BEAMR reactor shown with the anode chamber filled with granules. (a) Tube to respirometer, (b) headspace sampling valve, (c) wire to anode, (d) wire to cathode, (e) nitrogen sparge, (f) reference electrode, (g) bubble meters, (h) cathode chamber, (i) Nafion membrane, (j) anode chamber.

When operated in BEAMR mode, a resistor ($11.5\ \Omega$) was connected in series with a power source (model 3645 A DC Power Supply; Circuit Specialists, Inc., Mesa, AZ, USA) in order to allow measurement of the current in the circuit. Since the measured voltage drop across the external resistor is only about 2% of the total applied voltage, the voltage applied to the reactor was not corrected for this loss. The power source positive lead was connected to the anode and the negative lead connected to the resistor and then to the cathode. A multimeter (model 2700, Keithley Instruments, Inc.; Cleveland, OH,