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Evaluation of low cost cathode materials for treatment of industrial and food processing wastewater using microbial electrolysis cells

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ARTICLE INFO

Article history:
Received 21 September 2012
Received in revised form
13 November 2012
Accepted 20 November 2012
Available online 20 December 2012

Keywords:
MEC
Energy recovery
Methanol
Wastewater
Molybdenum disulfide

ABSTRACT

Microbial electrolysis cells (MECs) can be used to treat wastewater and produce hydrogen gas, but low cost cathode catalysts are needed to make this approach economical. Molybdenum disulfide (MoS_2) and stainless steel (SS) were evaluated as alternative cathode catalysts to platinum (Pt) in terms of treatment efficiency and energy recovery using actual wastewaters. Two different types of wastewaters were examined, a methanol-rich industrial (IN) wastewater and a food processing (FP) wastewater. The use of the MoS_2 catalyst generally resulted in better performance than the SS cathodes for both wastewaters, although the use of the Pt catalyst provided the best performance in terms of biogas production, current density, and TCOD removal. Overall, the wastewater composition was more of a factor than catalyst type for accomplishing overall treatment. The IN wastewater had higher biogas production rates (0.8–1.8 m^3/m^3-d), and COD removal rates (1.8–2.8 kg-COD/m^3-d) than the FP wastewater. The overall energy recoveries were positive for the IN wastewater (3.1–3.8 kWh/kg-COD removed), while the FP wastewater required a net energy input of −0.7–−1.2 kWh/kg-COD using MoS_2 or Pt cathodes, and −3.1 kWh/kg-COD with SS. These results suggest that MoS_2 is the most suitable alternative to Pt as a cathode catalyst for wastewater treatment using MECs, but that net energy recovery will be highly dependent on the specific wastewater.

1. Introduction

Bioelectrochemical systems are novel processes that utilize exoelectrogenic bacteria to oxidize organic compounds and generate electrical current through the transfer of electrons to the anode. In a microbial electrochemical cell (MEC), the electrons produced by bacteria are consumed at the cathode in the reduction of H^+ to H_2. MEC hydrogen production requires the addition of power from an external electrical source larger than ~ 0.2 V [1–3]. MECs have achieved high hydrogen yields (3.65 mol-H_2/mol-acetate) [4], and at lower applied voltages energy efficiencies of up to 400% (the energy in the hydrogen gas produced, relative to the electrical energy input) [5]. Higher applied voltages can be used to increase

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0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2012.11.103

hydrogen production rates, although this reduces the energy yields [6]. Applied voltages >0.8 V can result in electrical energy efficiencies <100% [7], depending on the hydrogen gas recovery. Consequently, there is a tradeoff in setting process goals, with higher voltages chosen to increase the rate of treatment, and lower voltages used to maximize energy recovery. Typically, voltages of 1 V or less are used in MEC tests to ensure good rates and reasonable energy recoveries.

Minimizing the costs of the electrode materials, and avoiding the use of precious metals are two goals for the development of economical wastewater treatment using MECs [8]. One of the most critical materials to the performance of the MEC, and also one of the most expensive, is the catalyst used for hydrogen evolution from the cathode. Pt is used in many MECs, although recently several alternative materials have been proposed, including stainless steel (SS), molybdenum disulfide (MoS_2), iron, nickel oxide, nickel alloys, and tungsten carbide [9–14]. Stainless steel (SS) is one of the least expensive of these materials, and the use of high surface area SS electrodes can produce good rates of hydrogen evolution compared to some alternative materials [9,15,16]. Brushes and mesh made from SS type 304 were both shown to produce current densities comparable to those obtained with Pt and carbon cloth cathodes using acetate as a substrate for the bacteria [17,18]. One disadvantage of SS, however, is that it has relatively high overpotentials, for example 0.85 V larger than Pt on carbon cloth [13,19]. MoS_2 is a relatively inexpensive catalyst that can have lower overpotentials than SS. It can be used as a coating on the SS mesh, or as particles bound to carbon cloth. When MoS_2 particles were used in a cathode in electrochemical tests (with carbon black and a Nafion binder), the hydrogen evolution reaction overpotential in perchlorate and phosphate buffer was reduced from 1.04 V to 0.105 V [13].

The effectiveness of these various cathode catalysts for effective wastewater treatment has not been well investigated. There are many studies on hydrogen production with simple organic substrates, such as acetic acid, butyric acid, and lactic acid, with Pt catalysts [4,20–22]. However, there are fewer tests using complex source of organic matter such as effluents from bioprocesses as cellulose fermentation or anaerobic digestion, or different types of wastewaters (domestic, winery, potato, dairy and piggery) [5,23–28]. SS has only been tested using a single wastewater [25], and MoS_2 has not previously been used with actual wastewaters. The organic and inorganic components of the wastewater can affect not only catalyst efficiency but also catalyst longevity, as they can irreversibly adsorb on the catalyst and lead to its poisoning [29,30]. The purpose of this study was to explore more practical applications of MEC systems by using low-cost catalysts (SS and MoS_2) and two actual wastewaters as feedstocks. These wastewaters were chosen to be much different in composition: the food processing wastewater contained high concentrations of complex carbohydrates, while the industrial wastewater (from a specialty chemicals manufacturing facility) had a lower concentration of biodegradable organic matter and a high concentration of methanol. Tests using these wastewaters were also conducted using MECs with cathodes containing a Pt catalyst in order to better understand the performance of these materials relative to Pt. The effectiveness of these catalysts for effective wastewater treatment was evaluated in terms of current densities, time for treatment, COD removal, and energy recovery.

2. Materials and methods

2.1. Wastewater

Industrial wastewater samples were collected from a chemical manufacturing facility in Kentucky. The sample was collected from a neutralization pit, representative of a blend of multiple different waste streams, prior to the aerobic treatment process currently being used at this site. Food processing wastewater samples were collected from the discharge pipe of a food processing plant. Samples were placed on ice, shipped overnight to the laboratory, and stored at 4 °C. Wastewater samples were fully characterized upon arrival (Table 1). Wastewater served both as microbial inoculum and substrate in all experiments.

2.2. Reactor construction and operation

Twelve single-chamber MECs (six for each wastewater sample) consisted of Lexan cubes drilled to contain a cylindrical chamber 4 cm long by 3 cm in diameter (empty volume = 28 mL). An anaerobic culture tube was glued to the top of the reactor to collect hydrogen gas (1.6 cm inner diameter and 6 cm length; 12 mL capacity). Anodes were heat-treated graphite fiber brushes (PANEX 33 160K, Gordon Brush, 2.5 cm diameter and 2.5 cm long) [31].

Table 1 – Wastewater characteristics.

Parameters	Industrial	Food processing
pH	6.68 ± 0.30	6.35 ± 0.25
Conductivity (mS/cm)	2.04 ± 0.02	2.53 ± 0.04
TCOD (kg/m^3)	4.07 ± 0.18	8.10 ± 0.62
SCOD (kg/m^3)	3.81 ± 0.16	1.83 ± 0.20
BOD (kg/m^3)	0.8	2.00 – 5.00
TS (kg/m^3)	1.34 ± 0.09	4.76 ± 0.10
TSS (kg/m^3)	0.06 ± 0.01	2.43 ± 0.09
Inorganic compounds		
Phosphorous (mg/L)	8.9	57.3
Sulfate (mg/L)	55.5	686 ± 25
Nitrate (mg/L)	<5	5.7 ± 0.1
Nitrogen Ammonia (mg/L)	0.25	9.5 ± 0.9
Organic compounds		
Total carbohydrates (mg-COD/L)	386 ± 7	1940 ± 17
Soluble carbohydrates (mg-COD/L)	240 ± 6	920 ± 12
Solvents and alcohols (mg/L)		
Acetone	52.85 ± 1.8	0
Methanol	1537.4 ± 48.6	0
Ethanol	18.3 ± 4.8	11.3 ± 2.1
Propanol	2.1 ± 1.9	1.5 ± 0.2
Butanol	0	0
Volatile fatty acids (mg/L)		
Acetate	182.4 ± 34.4	116.3 ± 7.5
Propionate	0	20.5 ± 3.7
Butyrate	0	29.5 ± 8.7