A novel membraneless bioelectrochemical system termed rotatable bioelectrochemical contactor (RBEC) was fabricated and evaluated for its ability to recover useful energy (here methane) from a low organic strength wastewater. We studied the operational characteristics of the RBEC by operating it as a three-electrode electrolysis cell. A stack of conductive disks (each subdivided into two half disks), similar to rotating biological contactors, were rotated with one-half disk immersed in the wastewater and the other into the gas headspace. By carrying out regular half rotations (180° rotation) the anode became the cathode and vice versa. This operation resulted in the buildup of a biofilm that could catalyze both an anodic acetate oxidation and a cathode-driven methanogenesis. Methane production rate was directly proportional to the applied electrical energy. Increase in current density (from 0.16 to 4.1 A m⁻²) resulted in a faster COD removal (from 0.2 to 1.38 kg COD m⁻³ day⁻¹) and methane production (from 0.04 to 0.53 L L⁻¹ day⁻¹). Of the electrons flowing across the circuit, over 80% were recovered as methane. Such methane production was electrochemically driven by the headspace-exposed cathodic half disks, which released the methane directly to the gas-phase. Energy analysis shows that the new design requires less energy for COD removal than what is typically required for oxygen supply in activated sludge processes. Because the system could operate without wastewater recirculation against gravity; additional pH buffer chemicals; ion-exchange membranes or electrochemical catalysts, it has desirable characteristics for process up-scale. Further, the current report shows the first example of a BES with identical biofilm (due to intermittent polarity inversion) on both electrodes.

1. Introduction

Traditional aerobic treatment of municipal wastewaters requires forced aeration which is energy intensive (approximately 1 kWh per kg of COD removed in activated sludge processes) (1). With the ever-rising economic and environmental constraints, many municipal wastewater treatment plants (WWTPs) around the world are developing strategies to minimize their energy expense for wastewater treatment such as advanced activated sludge treatment. Recent work has aimed at being energy neutral or even recovers useful energy from the treatment processes. For instance, the WWTP at Strass, Austria has approached over 100% energy self-sufficiency primarily through (i) cutting the energy demand for both sewage pumping and aeration in the aerobic biological processes and (ii) efficiently recovering electrical/heat energy from the methane produced from the anaerobic digestion of wasted sludge (2).

Apart from “sludge-based” anaerobic digestion, bioelectrochemical systems (BESs) such as microbial fuel cells (MFC) and microbial electrolysis cells (MEC) have been suggested as a new approach to recover useful energy from wastewaters (3–5). These systems allow removal of dissolved organic pollutants by electrochemically active bacteria, which dissimilatively couple the oxidation of the organics with an electrochemical reduction of an insoluble electrode (anode). Electrons accepted by the anode are conveyed via an external electric circuit to a counter electrode (cathode), where a suitable chemical species is finally reduced. In MFC there is sufficient energy in the system to drive a spontaneous flow (downhill reaction) of electrons from anode to cathode. However, in MEC additional electrical energy is required to drive an otherwise nonspontaneous and/or sluggish cathodic reaction (e.g., hydrogen production) where the cathodic potential is more negative than the anodic potential. Since electrochemically active bacteria can oxidize the organics without undergoing aerobic assimilation metabolism, BES-based wastewater treatments are expected to yield significantly less wasted sludge compared to conventional aerobic activated sludge processes.

Currently, the use of BES for wastewater treatment has not found industrial application yet (6). Many challenges remain to hinder process scale-up. In essence, two generic obstacles are identified:

1. The creation of a pH split between the anode (proton production) and the cathode (proton consumption) (3, 7–9). This has been shown to virtually shut down the bacterial driven electron flow and hence the degradation of the organic pollutant. As wastewaters are usually poorly buffered, this limitation is commonly addressed by dosing buffer chemicals, which is not practical in large-scale applications.

2. A strong cathodic overpotential for the transfer of electrons to the terminal electron acceptor (10–13). This slows down the cathodic reaction or requires a higher electrical energy input to overcome such limitation.

We have previously demonstrated that both of the above limitations can be partly addressed by allowing an electroactive biofilm to alternately catalyze the anodic oxidation and cathodic reduction (polarity inversion) in a bioelectrochemical cell (14). However, the described process was not designed to approach large-scale application, largely because of the use of expensive ion exchange membranes. Here, we describe a novel reactor configuration to overcome both of the above problems by using intermittent inversion of polarity of the cell and by encouraging the growth of bacteria also on the cathode to catalyze the cathodic reaction. Similar to the design of conventional rotating biological contactors (RBC), a specific rotating disk bioelectrochemical system (here termed rotatable bioelectrochemical contactor, RBEC) has been developed with electrically conductive half disks that are either exposed to the liquid phase (wastewater) or the gas phase. Unlike most other BES configurations, the RBEC requires no mechanical recirculation of wastewater, and no physical membrane between the anodic and cathodic half cell as the oxidation—reduction interface is formed by the water surface. These features could be useful for process up-scale.
The aim of this paper was to evaluate whether the proposed combination of RBC and polarity inversion of a BES enables microbial-electrosynthesis of energetic products from a synthetic wastewater. We operated the new RBEC reactor as a three-electrode microbial electrolysis cell, with a potentiostat to provide additional electrical energy to facilitate conversion of organics (here acetate) in the liquid phase into an energy-rich gas product (e.g., hydrogen or methane). The performance of the system was quantified based on COD removal, electron and energy balance.

2. Materials and Methods

2.1. Configuration of the Rotatable Bioelectrochemical Contactor. The rotatable bioelectrochemical contactor (RBEC) consists of three major components: (1) a reactor vessel; (2) a rotatable electrode disk assembly; and (3) a computer controllable stepper motor unit (Figure 1).

2.1.1. Reactor Vessel. The reactor vessel consists of a cylindrical Perspex transparent water pipe (298 mm length; 140 mm diameter) with the two ends covered by two separate square Perspex end-plates (160 × 160 mm) (the total internal volume of the reaction vessel is about 3 L). A rubber O-ring was mounted between each end-plate and the Perspex pipe to ensure air and water tightness. After mounting the rotatable electrode disk assembly the total working volume of the RBEC reactor was 1.75 L. This value is used to calculate COD removal rates, hydraulic retention time (HRT), and gas production rate of the process.

2.1.2. Rotatable Electrode Disk Assembly. The rotatable electrode disk assembly consists of a Perspex horizontal central rotatable shaft (Figure 1A). Each disk consists of two halves: an upper gas phase-exposed and a lower liquid-submerged halve. Each half consists of a stainless steel mesh, which serves as both current collector and physical support for the carbon fiber electrode sheets (see Figure S1, Supporting Information). They were mounted onto both sides of the mesh using stainless steel clips (Figure 1B). A short length of Perspex plastic ring was used to connect each pair of electrode disks with the central shaft and to maintain a constant distance with the neighboring disks. The estimated total projected surface area of the water submerged half disks is 947 cm². This value is used for calculating the current densities. After loaded with the wastewater (1.75 L), a portion of the upper half disks were also immersed in the water (ca. 5 mm from the bottom edge).
to enable ionic flux between the anodic and cathodic half disks without using an ion exchange membrane or separator.

2.1.3. Computer Controllable Stepper Motor Unit. Regular rotation of the electrode disks was performed by using a computer controllable stepper motor unit, which consists of a stepper motor, a stepper motor driver, and an analog output device (Labjack U12). The stepper motor was tightly mounted onto the side plate of the reactor vessel. A gear disk (one-to-seven reduction) was used to convey the mechanical action of the motor to the central rotatable shaft. The stepper motor and its driver were calibrated to ensure the rotation could be controlled precisely such that the lower edge of the upper disks could remain partly submerged in the water after each rotation (e.g., full turn, 360° or half turn, 180° at fixed time intervals).

2.2. Bacterial Inoculum and Medium. A return activated sludge collected from a local domestic wastewater treatment plant (sequencing batch reactors activated sludge process) was used as the initial inoculum. It was stored at 4 °C prior use. A synthetic wastewater with only minimal amount of pH buffer was used throughout the study. It consisted of (mg L−1) the following: NH4Cl 125, NaHCO3 125, MgSO4·7H2O 51, CaCl2·2H2O 300, FeSO4·7H2O 6.25, and 1.25 mL L−1 of trace element solution, which contained (g L−1): ethylenediamine tetra-acetic acid (EDTA) 15, ZnSO4·7H2O 0.43, CoCl2·6H2O 0.24, MnCl2·4H2O 0.99, CuSO4·5H2O 0.25, NaMoO4·2H2O 0.22, NiCl2·6H2O 0.19, Na2SeO4·10H2O 0.21, H3BO3 0.014, and NaWO4·2H2O 0.050. Sodium acetate (10 to 20 mM) was used as the electron donor. Yeast extract (about 1 g L−1 final concentration) was added as bacterial growth supplement. The pH of the synthetic feed was adjusted to 6.9–7.5 using 1 M HCl or 4 M NaOH.

2.3. Operation and Monitoring. 2.3.1. General Operation. In this work, we operated the RBEC as a microbial electrolysis cell using a three-electrode scanning potentiostat as a power supply (Model no.362, EG&G, Princeton Applied Research, Instruments Pty. Ltd.) (Figure 1C). The working electrode half disk to intermittently serve as the anode and cathode, and the reference electrode, respectively. The reactor was initially inoculated with the activated sludge (about 10% v/v) and was operated with an air-cathode for about three months (initially in a batch mode and then switched into continuous mode) (results to be published elsewhere). All electrode potential (mV) described in this paper refers to values against Ag/AgCl reference electrode (ca. +197 mV vs standard hydrogen electrode). Unless specified differently, the potential of the submerged half disks (i.e., anode) were controlled at a fixed level by the potentiostat (−300 to 0 mV). This potential range was chosen to facilitate anodic acetate oxidation (15, 16).

The electrode disks were regularly rotated (frequencies are specified in text) for a half-turn (180°) or half turn, 180° at fixed time intervals).

2.3.2. Gas Production. The enclosed headspace design of the RBEC reactor offers opportunity to recycle, recover, or control of gaseous byproducts (Figure 1C). Anaerobic condition in the headspace was obtained by continuously purging the headspace with pure nitrogen gas (1 L min−1) for about 10 min. Biogas production from the RBEC was continuously monitored with a gas counter connected to the headspace. The gas counter was regularly calibrated by injecting a known volume of N2 into the reactor headspace to determine the gas volume per count. This allows the calculation of the biogas production rate (BPR) (L biogas L−1 reactor day−1). The methane or hydrogen production rate (L CH4 or H2 L−1 reactor day−1) was calculated by multiplying the volumetric fractions (v/v) of each gas in the headspace as determined from the GC measurement by the BPR (17).

2.3.3. Electrochemical Monitoring. A computer program (LabVIEW version 7.1 National Instrument) was developed to control and monitor the bioprocess. The electrode potentials of the upper and lower half disks and the electric current between the two half disks (taken directly from the potentiostat) were recorded at fixed time intervals via the program interfaced with a data acquisition board (DAQ) (National Instrument NI4350). The data were regularly logged into an Excel spreadsheet.

2.3.4. Chemical Analysis. Methane, hydrogen, and carbon dioxide volumetric fractions (v/v, %) in the headspace were determined using a Varian Star 3400 Gas Chromatograph (GC) coupled with a thermal conductivity detector. The carrier gas was high purity nitrogen at a flow rate of 30 mL min−1. Separation of different gas species in the sample was performed on a Pora-PakQ packed column (2 m × 5 mm (internal diameter)) maintained at 40 °C. Detector and inlet temperatures were maintained at 40 and 120 °C, respectively. Gas sample was taken from the reactor headspace via a gastight rubber bung using a 10-µL plastic disposable syringe. About 50–100 µL of the gas sample inside the plastic syringe were manually injected into the GC using a 100 µL gastight syringe (Hamilton). Standard curves of each measured gas were established by injecting a known volume of high purity standard gas into the GC. COD of the influent and effluent was measured according to a standard method (18).

3. Results and Discussion

The described RBEC was initially operated in a batch mode with the submerged electrode half disks controlled at a potential of −300 mV, while the cathodic headspace remained aerobic (Figure 2). Anodic current was observed only when the synthetic wastewater was amended with acetate (Figure 2A). This shows that the system could establish electrochemically active biofilm at the rotatable half disks, allowing electrochemical oxidation of organics (acetate) in the wastewater.

To test whether the developed reactor could be operated as a microbial electrolysis cell for fuel gas production, the oxygen in the headspace was replaced by nitrogen and its effect was recorded (Figure 3).

3.1. Oxygen Removal of the Headspace Resulted in H2 and CH4 Production. Switching the system from an oxygen reducing cathode (air in cathodic headspace) to an anaerobic cathode (headspace flushed with N2) did not affect the anodic site of the reaction or the bacteria as the potentiostat maintained the anodic potential at a favorable potential (here −200 mV) (Figure 3). Therefore, the overall current flow of the system was not affected by removing oxygen from the cathodic headspace. However, by removing oxygen as the oxidant from the cathodic half cell the potentiostat lowered...
the cathodic potential from $-1100 \text{ mV to } -1300 \text{ mV}$, which is a relatively small increase in energy input considering that now $\text{H}_2$ as a fuel was produced. The hydrogen produced was proportional to the current density (see Figure S3, Supporting Information). This is in line with published work using MECs for hydrogen production (11). Resuming the headspace composition to air reversed the effect, showing that by using oxygen only a small energy saving could be achieved.

After operating the RBEC for over two weeks under fully anodic condition, hydrogen could no longer be detected in the headspace despite the system was still actively generating current. Instead, methane (up to 78% v/v) was found to be the major gas product. In the literature, it has been shown that biofilms in the presence of hydrogen producing electrodes enrich for the development of methanogenic microorganisms in MECs (17, 19, 20). As the inhibition of methanogens is practically cumbersome and the volumetric energy content of methane is higher than that of hydrogen, producing methane from the treatment of dilute synthetic wastewater using the RBEC appeared reasonable.

### 3.2. Intermittent Half Rotation Facilitated Biofilm Growth at Both Electrode Half Disks and Inverted the Polarity of the Methanogenic RBEC

The intermittent half turn rotation of the electrode disks had exposed all electrode surfaces of the RBEC to both the anodic and cathodic conditions. This is expected to generate identical biofilms on both electrode half disks (see Figure S4, Supporting Information), while the continued half rotation operation keeps reversing the cell polarity (Figure 4; the positive current after the half rotation signifies that the polarity of the system was inverted). Since methane and current were continuously produced during this period, it implies that the established biofilm was capable of catalyzing both (i) the anodic acetate oxidation ($\text{CH}_3\text{COO}^- + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 7\text{H}^+ + 8\text{e}^-$) when submerged in the medium and (ii) the cathode-associated methanogenesis when exposed to the headspace (either hydrogen formation: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ or cathodic methane formation: $\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$). If acetate was directly degraded by methanogens, no current would be produced.

The bidirectional electron flow is expected to avoid the localized pH effect at the electrodes during BES operation, similar to the effect of reversing polarity in normal MFC (14). Further, the membrane-less design and repetitive turning of the RBEC electrode disks results in a physical exchange of alkaline catholyte with acidic anolyte which also helps preventing the buildup of the pH gradient, which is problematic for continued BES operation (8, 21). Here (Figure 4), the operating pH of the wastewater was maintained at around neutral to a slightly alkaline condition with the influent and effluent pH of 7.00 and 7.76, respectively (HRT 14.6 h). Conventional pH control methods (dosing of buffers or acid/base) are therefore not required to operate the described process for methane production.

### 3.3. Methane Production Was Directly Proportional to Electrical Current, Indicating an Electrochemical Nature of Its Formation

In principle the methane found could have been formed from acetoclastic methanogenesis in the liquid phase. In order to test whether the methane formed came truly as an electricity flow from acetate oxidation in the liquid phase.

**FIGURE 2.** Aerobic operation (cathode exposed to air) of the potentiostatically controlled RBEC reactor. The disks were rotated (360°) once per 15 min. The submerged anode disks were poised at $-300 \text{ mV vs Ag/AgCl}$. At about $6 \text{ h}$, continuous feeding began (initial COD loading rate was 1.58 kg·m$^{-3}$·day$^{-1}$). At 18.2 h: influent flow rate was doubled to 6 mL·min$^{-1}$ (HRT 4.9 h) and resulted in an abrupt decrease in medium temperature from 22 to 16 °C causing a current drop. At 22.2 h: resumed temperature to 22 °C increased the current back to its original level.

**FIGURE 3.** Effect of different gas compositions in the reactor headspace on (A) anodic current and the (B) cathode potential (i.e., counter electrode). Submerged anode disks were poised at $-200 \text{ mV vs Ag/AgCl}$. Electrode disks stayed stationary throughout the experiment. The reactor was operated in a batch mode at room temperature (22 ± 2 °C).

**FIGURE 4.** Changes in current and electrode potentials in the methane generating RBEC during intermittent disk-flipping operation. The electrode disks were rotated for a half turn in every 2 h. The submerged anodic half disks were potentiostatically controlled at about $-50 \text{ mV vs Ag/AgCl}$. A synthetic wastewater with 20 mM acetate (pH 7) was continuously fed through the system at a flow rate of 2 mL·min$^{-1}$ (COD loading rate 11 kg·m$^{-3}$·day$^{-1}$, HRT 14.6 h). Note: positive current after the half rotation indicates that the polarity of the system was actually inverted. Effluent pH = 7.76.
phase to the methanogenic cathode, a higher voltage was applied to increase the current flow. This enhanced current flow increased both acetate disappearance (measured as COD) and methane production rates (Figure 5). In fact, rate of methane production and COD depletion was directly proportional to the current (Figure 5).

To obtain an electron balance, the steady-state electron flow rates representing various paths in the methanogenic RBEC were compared (Figure 6). Clearly, a large portion of the electrical current was captured as methane in the RBEC. At cathodic potentials of −1200 and −1600 mV, 82 and 88% of the electron flow in the RBEC were recovered as methane. The estimated energy balance (energy recovered as CH₄ minus electrical energy input) of the methanogenic RBEC was 0.14 ± 0.09 kWh kg COD⁻¹.

Energetically, the submerged anodic disks represent a more favorable electron acceptor than producing methane via acetoclastic methanogenesis. With an anodic potential of −200 mV (Ag/AgCl), the anodic reaction acetate⁻ + 2H₂O → 2CO₂ + 7H⁺ + 8e⁻ enables a GIBB's Free Energy Change (ΔG°⁻) of −216 kJ·mol⁻¹, which is 6-fold more energetic than the acetoclastic methanogenic reaction: acetate⁻ + H⁺ → CH₄ + CO₂ (ΔG°⁻ = −36 kJ·mol⁻¹) (22). The energetics behind the microbial preference for more positive electron acceptors is a known phenomenon (23).

The question whether the methane producing archaea can accept electrons directly from the cathode for a one-step methane formation, still remains open. This study did not show whether hydrogen may have acted as a mediator; however, in the literature, a hydrogenotrophic methanogen (Methanobacterium palustre) was found to be able to catalyze the direct cathodic reduction of carbon dioxide into methane (24). Further studies are warranted to elucidate the mechanism(s) of the electrode-linked methanogenesis in the RBEC.

3.4. Energetic Consideration. The described system required net electrical energy input to facilitate the methane production (in contrast to traditional anaerobic digestion). The estimated energy balance (energy recovered as CH₄ minus electrical energy input) of the methanogenic RBEC depends on the applied voltage (Figure 7). The higher the applied voltage, the faster the reaction (COD removal) but the lower the energy recovery. Attempting to obtain a positive energy yield would come at the cost of a lowered COD removal rate (here 0.2 kg COD m⁻³ day⁻¹) (Figure 7). This agrees with a recent report that a methanogenic MEC could produce a negative energy yield (−0.14 ± 0.35 kWh kg COD⁻¹), and the invested electrical energy was not completely recovered from the produced biogas (17).

Considering that aerobic wastewater treatment technologies have a very negative energy balance, the current system may represent promise for the treatment of the organic fraction of wastewater (Table 1). It is also flexible in either allowing energy neutral operation or faster organic removal, simply by controlling the applied voltage and hence the electrical current of the system.

3.5. Implication of This Work. Overall, we have documented here a new BES design (here RBEC) for energy recovery from a liquid stream. The tested system was operated...
as a MEC to accelerate the bioelectrochemical conversion (current) of chemical energy contained in the wastewater into a gaseous fuel (here methane). In this respect, the system has carried out the same overall reaction as traditional anaerobic digesters. From a practical standpoint, the additional energy input (voltage and turning of disks) and complexity of the system may not seem justified. However considering that we studied the degradation of dilute wastewater where activated sludge systems are normally used, the energy balance looks favorable (Table 1).

3.5.1. A New Option for Large Scale BES-Wastewater Treatment. The design of the RBEC is similar to the conventional rotating biological contactors (RBC), which has been widely established in the industry. From an engineering standpoint, retrofitting existing RBC reactors into RBEC may be a more practical up-scaling option compared with other BES designs. Below are several RBEC features that may favor process up-scaling:

Membrane-less Design. The system does not require any membrane separator as the upper and the lower electrode half disks are physically and electrically separated from each other. This should reduce capital cost.

Minimal Requirement of Wastewater Recirculation against Gravity. Unlike most other BES configurations, the RBEC does not require mechanical recirculation (i.e., energy input) of wastewater against gravity as the oxidation-reduction interface lies horizontally instead of vertically against the water surface.

Cathode Surrounded by the Gas-Phase. The headspace-exposed cathodic half disks serve as ‘gas diffusion cathode’ allowing the release of the gaseous byproduct (here methane) directly into the gas phase.

No expensive chemical catalyst such as platinum is required: It becomes widely accepted that the use of platinum cannot be justified (financially and functionally) for BES aiming at wastewater-related application. Here, the biofilm could catalyze both anodic and cathodic reactions in the RBEC without any chemical catalyst at the electrode.

3.5.2. Up-Scaling Limitation and Outlook. It is conceivable that by increasing the number of electrode disks per volume of the RBEC, the volumetric current density and thus the bioelectrochemical conversion rate of the process can be enhanced. However, by using orders of magnitudes larger electrode disks (i.e., increased disk diameter) the charge-balancing ions need to migrate a longer distance to maintain the system’s electroneutrality. As a one-dimensional increase in electrode disk diameter leads to a two-dimensional increase in disk surface area, the ionic flux and hence ohmic resistance eventually become limiting with increasing reactor scale. Rather than up-scaling the disk sizes, a more modular up-scaling could be considered as it has been implemented for processes such as reverse osmosis desalination systems.

At this early stage of a novel process concept, the focus is on understanding, investigating, and quantifying the principles involved, which could be useful for other BES processes. For instance, in the described process the non-methanogenic steps (hydrolysis, fermentation, VFA oxidation, acetoclastic reaction) of anaerobic digestion are physically separated from the pure methanogenic step, which uses electrons and CO2. Whether this unique methanogenic system can be exploited or whether the described process could be combined synergistically with traditional anaerobic digestion occurring in the anolyte (provided the retention time is sufficiently long) are questions to be investigated separately.

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Supporting Information Available
Illustration of the electrode disks, schematic diagram showing the flipping action of the electrode disks, hydrogen generation performance, scanning electron microscopy of the carbon electrode sheets. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


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