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Electrolysis-enhanced anaerobic digestion of wastewater

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ABSTRACT

This study demonstrates enhanced methane production from wastewater in laboratory-scale anaerobic reactors equipped with electrodes for water electrolysis. The electrodes were installed in the reactor sludge bed and a voltage of 2.8–3.5 V was applied resulting in a continuous supply of oxygen and hydrogen. The oxygen created micro-aerobic conditions, which facilitated hydrolysis of synthetic wastewater and reduced the release of hydrogen sulfide to the biogas. A portion of the hydrogen produced electrolytically escaped to the biogas improving its combustion properties, while another part was converted to methane by hydrogenotrophic methanogens, increasing the net methane production. The presence of oxygen in the biogas was minimized by limiting the applied voltage. At a volumetric energy consumption of 0.2–0.3 Wh/L_R, successful treatment of both low and high strength synthetic wastewaters was demonstrated. Methane production was increased by 10–25% and reactor stability was improved in comparison to a conventional anaerobic reactor.

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1. Introduction

The recent demand in renewable sources of energy has boosted application of anaerobic digestion (AD), which is reflected by the increased number of anaerobic digesters installed world-wide (Kassam et al., 2003). Wastewaters of various complexity can and are treated by anaerobic digestion (Alvarez and Lema, 2010; Fang et al., 2011; Salminen and Rintala, 2002; Steyer et al., 2006; Tait et al., 2009). However, its application for energy recovery is limited by the presence of hydrogen sulfide in the biogas, the slow hydrolysis of complex organic matter under anaerobic conditions, the high sensitivity of anaerobic microorganisms to variations in wastewater composition and the requirement of influent with a high concentration of organic matter (Leitao et al., 2006).

Several studies have demonstrated increased methane production and chemical oxygen demand (COD) removal under microaerobic conditions, i.e. at very low dissolved oxygen concentrations (Jagadabhi et al., 2010; Jenicek et al., 2008, 2010; Shen and Guiot, 1996; Zitomer and Shrout, 1998). This improvement was attributed to the enhanced hydrolysis of complex organic matter (Both-eju et al., 2009; Johansen and Bakke, 2006; Zhu et al., 2009). The microaerobic environment can be created by limited reactor aeration (Jenicek et al., 2008; Johansen and Bakke, 2006; Pirt and Lee, 1983; Shen and Guiot, 1996; Zhou et al., 2007; Zitomer and Shrout, 1998) as well as by feeding small amounts of H₂O₂ to the reactor (Tartakovsky et al., 2003).

In the study presented below, the microaerobic conditions were created and maintained by water electrolysis. To avoid oxygen-related inhibition of anaerobic metabolism, the applied voltage was adjusted to minimize the presence of oxygen in the biogas. The performances of the eAD (electrolysis-enhanced anaerobic digestion) and conventional AD reactors were compared to evaluate the effect of water electrolysis on COD removal and methane production.

2. Methods

2.1. Reactor setup and instrumentation

Two upflow anaerobic sludge bed (UASB) reactors with a liquid volume of 0.5 L (0.15 L headspace) each and one UASB reactor with a liquid volume of 3.5 L (1.1 L headspace) were used in the study. The reactors were made of glass (internal diameter of 48 and 100 mm for 0.5 and 3.5 L reactor, respectively) and had external recirculation loops. Water jackets and water heating systems were used to maintain the reactor liquid temperature at 35 °C. The reactor pH was controlled using a pH-controller (Cole-Parmer Instrument, Vernon Hills, IL, USA) equipped with a probe, which was inserted in the external recirculation line. The pH was maintained at 6.8–7.0 by the controlled addition of NaOH. The reactors were operated at a hydraulic retention times (HRT) between 6 h and 12 h. An upflow velocity of 2 m h⁻¹ was maintained in all reactors.

One of the 0.5 L reactors (R-1) and the 3.5 L reactor (R-2) were equipped with electrodes for water electrolysis (eAD reactors). The other 0.5 L reactor (R-0) was operated in a conventional

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Fig. 1. Schematic diagram of an UASB reactor with electrodes for in situ water electrolysis.

anaerobic (AD) mode. The electrodes were placed at the reactor bottom to be situated in the sludge bed. Each electrode set consisted of a titanium mesh anode with Ir-MMO coating (Magneto Special Anodes B.V., The Netherlands) and a stainless steel (#316) mesh cathode. The electrode dimensions were 4 × 5 cm and 5 × 10 cm for 0.5 and 3.5 L reactors, respectively, with a distance of 0.5 cm and 0.2 cm between the electrodes for 0.5 and 3.5 L reactors, respectively. A controllable power supply (PW18–1.8AQ, Kenwood USA Corp, Long Beach, CA, USA) was used for voltage or current control. The diagram of the experimental setup is shown in Fig. 1.

Each 0.5 L reactor was seeded with 0.2 L of a mesophilic anaerobic granular sludge from a wastewater plant (A. Lassonde Inc., Rougemont, QC, Canada), which had a VSS content of 45–55 g L⁻¹. The 3.5 L reactor was seeded with 0.5 L of the anaerobic sludge. The 0.5 L reactors were fed with a low-strength synthetic wastewater (sWW) solution containing trace metals and were operated at several hydraulic retention times (HRTs). Table 1 provides a summary of R-0 and R-1 operation. The 3.5 L reactor was fed with three separate streams containing a concentrated stock solution of sWW, trace metal solution, and bicarbonate buffer. The feed rate of the sWW stock solution was adjusted to obtain

Table 1
Performance of 0.5 L UASB reactors R-0 (anaerobic) and R-1 (electrolysis-enhanced).

HRT h	OLR $g_{COD} L_R^{-1} d^{-1}$	Reactor #	$P_{app} mW/L_R$	$Q_{CH_4} L L_R^{-1} d^{-1}$	$Q_{H_2} L L_R^{-1} d^{-1}$	$Y_{CH_4}^{app} L g^{-1}$	$Y_{CH_4}^{adj} * L g^{-1}$
11.8	1.4	R-0	0	0.33	0	0.28	0.28
		R-1	140	0.46	0.005	0.44	0.35
8.3	2.0	R-0	0	0.51	0.0	0.30	0.30
		R-1	260	0.75	0.018	0.46	0.36
6	2.5	R-0	0	0.49	0.0	0.24	0.24
		R-1	260	0.80	0.016	0.40	0.31

* Based on projected hydrogen production vs. applied current.

Table 2

Performance of the 3.5 L UASB reactor (R-2) in anaerobic digestion (AD) and electrolysis-enhanced anaerobic digestion (eAD) modes of operation.

OLR $\text{g}_{\text{COD}} \text{L}_{\text{R}}^{-1} \text{d}^{-1}$	Operation mode	P_{app} (mW/L _R)	Q_{gas} (L L _R ⁻¹ d ⁻¹)	CH ₄ (%)	CO ₂ (%)	H ₂ (%)	H ₂ S (%)	$Y_{\text{CH}_4}^{\text{app}}$ (L g ⁻¹)	$Y_{\text{CH}_4}^{\text{adj}}$ * (L g ⁻¹)
1.7	AD	0	0.61	82	8	0	0.02	0.33	0.33
	eAD	0.20	0.79	80	7	3.7	0	0.41	0.35
15.5	AD	0	3.52	72	20	0	0.3	0.27	0.27
	eAD	0.22	4.60	66	17	7.5	0	0.29	0.27

* Based on projected hydrogen production vs. applied current.

different organic loads (Table 2). The influent stream of the sWW had a conductivity of 2–4 mS cm⁻¹, depending on the sWW strength.

Biogas production was measured on-line by electronic bubble counters. Biogas composition was determined by the GC method as described below. In addition, the 3.5 L reactor was equipped with an online methane analyzer (Ultramat 22P, Siemens, Germany). A PC equipped with a PC-1200 acquisition board (National Instruments, Austin, TX, USA) was used for data acquisition (gas flow and gas composition measurements, reactor pH, temperature, and applied voltage). Also, samples were periodically withdrawn from the effluent lines for chemical oxygen demand (COD) and volatile fatty acid (VFA) analyses.

2.2. Chemicals, media composition, and analytical methods

Chemicals were obtained from Sigma–Aldrich Canada (Oakville, ON, Canada). Trace metals solution contained (in mg L⁻¹): AlK(-SO₄)₂·12H₂O 6; H₃BO₃ 1; Ca(NO₃)₂·4H₂O 535; Co(NO₃)₂·6H₂O 7.5; Cu(SO₄) 3; Fe(SO₄)·7H₂O 540; MgSO₄ 197.3; Mn(SO₄)·H₂O 150; Na₂(MoO₄)·2H₂O 2.3; NiSO₄·6H₂O 7; Na₂SeO₄ 1.3; and ZnSO₄·7H₂O 3.5. Synthetic wastewater fed to 0.5 L reactors contained (in mg L⁻¹): Peptidase 350, beef extract 140, (NH₄)HCO₃ 50, urea 4, NaCl 35, CaCl₂·2H₂O 20, K₂HPO₄ 20, and MgSO₄·2H₂O as proposed by Zaveri and Flora (2002). One millilitre of trace metal solution was added per L of the synthetic wastewater. The stock solution of synthetic wastewater for the 3.5 L reactor operation contained (g L⁻¹): Peptidase 50, beef extract 50, yeast extract 30, KH₂PO₄ 1.5, K₂HPO₄ 1.75, and NH₄HCO₃ 17. The bicarbonate buffer used for operation of the 3.5 L reactor was composed of 1.36 g L⁻¹ of NaHCO₃ and 1.74 g L⁻¹ of KHCO₃. The phosphate buffer used for the activity tests was composed of (g L⁻¹) K₂HPO₄ 4.0; Na₂HPO₄ 2.7; NaH₂PO₄·H₂O 1.1.

Analytical measurements of COD, suspended solids (SS), and volatile suspended solids (VSS) were carried out according to Standard Methods (APHA, 1995). Volatile fatty acid (VFA) concentration in the effluent was determined using a gas chromatograph (Sigma 2000, Perkin–Elmer, Norwalk, Connecticut, USA) equipped with a 91 cm × 4 mm i.d. glass column packed with 60/80 Carbowax C/0.3% Carbowax 20 NH₃PO₄ (Supelco, Mississauga, Ontario, Canada). Gas-phase concentrations of methane, hydrogen, and carbon dioxide were measured by gas chromatography (Sigma 2000, Perkin–Elmer, Norwalk, Connecticut, USA) equipped with a thermal conductivity detector. More details are provided in Morel et al. (2007). Gas-phase concentrations of H₂S was measured by a gas chromatograph (Photovac Voyager, Perkin Elmer, Waltham, MA, USA) with a PID detector (Column C). The column temperature was 60 °C and the carrier gas was air.

2.3. Activity tests

The acetoclastic and hydrogenotrophic activity of the anaerobic sludge was evaluated in batch activity tests. The tests were done in triplicates, in 60 mL serum bottles maintained under anaerobic conditions. The anaerobic sludge samples withdrawn

from the reactors were diluted in phosphate buffer in a final volume of 10 mL and a concentration of approximately 5 g VSS L⁻¹. To measure acetoclastic activity, an initial acetate concentration of 4 g L⁻¹ was added to the bottles, which were subsequently flushed with N₂/CO₂ (80%/20%) and then incubated on a rotary shaker (New Brunswick Scientific Co., Edison, NJ, USA), at 100 rpm and at 35 °C. The volume of biogas accumulated in the bottle headspace was measured using a burette (gas displacement method).

In hydrogen consumption tests, for hydrogenotrophic activity, the bottles were flushed with H₂/CO₂ (80%/20%), then pressurized (a gauge pressure of 10–15 kPa) with H₂/CO₂, and incubated in a rotary shaker, at 400 rpm and at 35 °C. The concentration of CH₄ and H₂ in the headspace were measured periodically. H₂ quantity in the bottle headspace (in mg) was calculated with respect to headspace pressure. At the end of each test the VSS content of the bottles was determined.

The methane production and hydrogen consumption rates were calculated by dividing the quantity of methane produced or hydrogen consumed by VSS values and time intervals between the measurements.

2.4. Yield calculations

The apparent methane yield ($Y_{\text{CH}_4}^{\text{app}}$, L of CH₄ produced per g of COD consumed) was calculated for the periods of stable reactor operation using the known quantity of carbon source fed to the reactor, measurements of biogas production, and measurements of the effluent soluble COD as follows:

$$Y_{\text{CH}_4}^{\text{app}} = \frac{F_{\text{gas}} C_{\text{CH}_4} / 100}{F_L (\text{COD}_{\text{in}} - \text{COD}_{\text{out}})} \quad (1)$$

where F_{gas} is the biogas flow rate (L d⁻¹); C_{CH_4} is the methane percentage in the biogas (%); F_L is the liquid flow rate (L d⁻¹); COD_{in} and COD_{out} are the concentration of COD in the reactor influent and reactor effluent, respectively (g L⁻¹). Since the influent stream may contain particulates, measurements of total COD (tCOD) of the influent were used for yield calculations. Particulates in the effluent stream contain biomass, consequently soluble COD (sCOD) measurements of the effluent were used in Eq. (1). The adjusted methane yield ($Y_{\text{CH}_4}^{\text{adj}}$), which takes into account methane production from hydrogen was calculated as:

$$Y_{\text{CH}_4}^{\text{adj}} = \frac{F_{\text{gas}} C_{\text{CH}_4} / 100 - Q_{\text{H}_2} / 4}{F_L (t\text{COD}_{\text{in}} - s\text{COD}_{\text{out}})} \quad (2)$$

where Q_{H_2} is the estimated production of hydrogen due to water electrolysis (L d⁻¹). COD consumption by aerobic microorganisms was not considered in this calculation. Electrolytic production of H₂ was measured in abiotic tests (i.e. in the absence of anaerobic sludge), which were carried out at 35 °C using the same solution of nutrients and trace metals as during normal reactor operation. H₂ production was then correlated with applied current using a linear regression equation:

$$Q_{\text{H}_2} = k_{\text{H}_2} \times I \quad (3)$$

where Q_{H_2} is the H_2 flow rate ($L d^{-1}$), k_{H_2} is the regression coefficient estimated by the least squares method of data fitting ($L A^{-1} d^{-1}$), and I is the current (A).

3. Results and discussion

3.1. Wastewater treatment tests in 0.5 L UASB reactors

Electrolysis-enhanced treatment of low-strength wastewater was first studied in the 0.5 L UASB reactor R-1. To see the effect of water electrolysis on anaerobic digestion the second reactor of 0.5 L (R-0) was simultaneously operated without the electrodes. By measuring the H_2 flow in the abiotic test performed prior to R-1 start-up, the regression coefficient $k_{H_2} = 8.4$ (Eq. (3)) was obtained ($R^2 = 0.98$, based on 9 measurements). Energy consumption for hydrogen production was relatively high and varied between 8–11 Wh/ L_{H_2} , depending on the applied voltage. The high energy consumption was attributed to a large distance between the electrodes (0.5 cm) and parasitic currents due to hydrogen oxidation in the absence of a proton-exchange membrane.

After R-0 and R-1 were seeded with anaerobic sludge, the reactors were operated at an influent COD concentration of 656 ± 57 mg/L and a retention time of 11.8 h. R-1 operation was started at an applied voltage of 3 V. Since at this applied voltage O_2 measurements in the biogas showed less than 1% O_2 , the voltage was increased to 3.5 V (35 mA, corresponding to 0.25 Wh/ L_R) and was maintained at this level throughout the test. At this applied voltage the O_2 concentration of the biogas varied between 2% and 4%.

Once the reactor was at a steady-state, the HRT of both reactors was decreased from 11.8 to 8.3 h and then to 6.0 h, while maintaining the same influent concentration of wastewater. Consequently, the organic loading rate (OLR) increased from 1.4 to 2.7 $g_{COD} L_R^{-1} d^{-1}$ (Table 1).

At all HRTs, the soluble COD (sCOD) in the effluent of both reactors were quite low (100–150 mg/L), with a COD removal efficiency of $85 \pm 4\%$ and 804% for R-0 and R-1, respectively. Also, effluent total COD (tCOD) values in both reactors varied between 150–250 mg/L. The comparison of COD removal efficiencies was inconclusive (based on a t -test with a 0.95 significance level) since both reactors demonstrated good sCOD removal efficiencies while standard deviations of the COD measurements were high. Also effluent concentration of tCOD was relatively high. The latter was attributed by an upflow velocity of $2 m h^{-1}$ used for reactor operation, which led to solids washout. While COD removal was similar, R-

Fig. 2. Methane production in R-0 and R-1 reactors. Methane production from H_2 in R-1 is estimated using applied current measurements.

Fig. 3. Methane production rates observed in batch activity tests on different substrates for R-0 and R-1 reactor samples.

0 and R-1 showed a significant difference in biogas production rate and biogas composition. Methane production was significantly higher in R-1. Estimation of the apparent methane yield according to Eq. (1) suggested $Y_{CH_4}^{app}$ values of 0.24–0.3 L_{CH_4}/g_{COD} and 0.40–0.46 L_{CH_4}/g_{COD} for R-0 and R-1, respectively (Table 1). Because the methane in R-1 was produced not only from COD but also from electrolytic hydrogen, the $Y_{CH_4}^{app}$ value in R-1 exceeded the stoichiometric maximum of 0.35 L_{CH_4}/g_{COD} . Consequently, the methane yield in R-1 was recalculated with respect to CH_4 production from H_2 ($Y_{CH_4}^{adj}$, Eq. (2)) resulting in lower methane yield estimations (R-1 operation at low organic loads likely led to sludge digestion thus increasing the yield values, which explains a yield of $0.36 L g^{-1}$ in Table 1). These calculations are illustrated in Fig. 2, where methane production rates observed in R-0 and R-1 are compared and methane production from electrolytic hydrogen is shown. At all HRTs, a summation of methane production in R-0 with the estimated methane production from electrolytic hydrogen gives values, which are less than the total methane production observed in R-1, which indicates that water electrolysis increased methane production beyond hydrogen conversion to methane.

Batch activity tests corroborated measurements of methane production in R-0 and R-1 (Fig. 3). Microaerobic conditions in R-1 created by electrolytic production of oxygen did not decrease the acetoclastic methanogenic activity. In fact the acetoclastic activity, both on acetate and sWW, was slightly higher for the sludge that originated from R-1. Both R-0 and R-1 featured high hydrogenotrophic activity with statistically insignificant differences between the measurements. An estimation of methane production potential in the reactors based on the acetoclastic methanogenic activity in bottle tests suggests values of $390 mL g_{VSS}^{-1} d^{-1}$ as compared to about $250 mL g_{VSS}^{-1} d^{-1}$ observed in the reactors. The latter estimation was based on the reactor VSS content of 6 g measured at the end of the experiment and considered influent and effluent COD concentrations. The difference in the estimated rates of methane production was indicative of substrate-limiting conditions in the reactor. Indeed, the reactors were operated at a low organic load, while the bottle tests were performed under substrate non-limiting conditions to observe the maximum potential activity of the sludge.

3.2. Wastewater treatment tests in a 3.5 L UASB reactor

The tests executed in the 3.5 L UASB reactor (R-2) were aimed at confirming the results obtained in the 0.5 L reactors and at study-

ing COD removal and methane production at high organic loads. As in the previous test, electrolytic production of H_2 was measured in the abiotic test prior to inoculation. The regression coefficient $k_{H_2} = 10.4$ was obtained for H_2 production based on Eq. (3) ($R^2 = 0.99$, $n = 5$). Depending on the applied voltage, energy consumption for hydrogen production varied between 4.5–7.0 Wh/L $_{H_2}$.

R-2 operation was started in the conventional anaerobic (AD) mode with the electrodes disconnected from the power supply. An influent sWW concentration of 660 mg/L (HRT = 9 h) was maintained at the startup corresponding to low-strength wastewater. At a steady state, which was estimated once the biogas flow and COD removal rates stabilized, only 80 mg L $^{-1}$ of sCOD was measured in the effluent with a $Y_{CH_4}^{app} = 0.33$ L $_{CH_4}$ /g $_{COD}$.

Water electrolysis was started after two weeks of reactor operation in AD mode. A current of 150 mA corresponding to a current density of 43 mA L $_{R}^{-1}$ was maintained by the controllable power supply (5.2 V, 0.2 W L $_{R}^{-1}$). Under these conditions the oxygen concentration in the biogas remained below 2%. The startup of water electrolysis resulted in an almost immediate increase in biogas production from 2.1 to 2.7 L d $^{-1}$. The biogas composition changed from 82% CH_4 , 8% CO_2 , and 0.02% H_2S to 80% CH_4 , 7% CO_2 , 3.7% H_2 , and 1.6% O_2 (with N_2 and water vapor for the balance). Importantly, the H_2S concentration in the biogas decreased below the detection limit of the analytical method. At a steady state the $Y_{CH_4}^{app}$ was 0.41 L g $^{-1}$ and sCOD concentration in the effluent was 70 mg L $^{-1}$ (Table 2). Overall, at energy consumption for water electrolysis of 0.19 Wh/L $_R$, methane production was increased by 26%.

Following the low-strength wastewater treatment test, the reactor was re-inoculated with anaerobic sludge, which was not exposed to oxygen, and fed with a high-strength sWW containing 6040 mg $_{COD}$ L $^{-1}$ to study reactor performance at high organic loads (OLR = 15.5 g $_{COD}$ L $_{R}^{-1}$ d $^{-1}$). As in the previous test, at startup the power supply was disconnected to observe the performance of the reactor in AD mode. Within one week, reactor operation with high-strength sWW led to near failure of the AD process. Reactor overload was evidenced by the high concentration of VFAs and CODs, 430 mg L $^{-1}$ and 2440 mg L $^{-1}$ in the effluent respectively, a low removal efficiency (Fig. 4) and a decrease in methane production (Table 2). Organic overload also led to a progressive increase of H_2S concentration in the biogas, which in 10 days reached 0.3%.

The onset of water electrolysis led to an almost instant improvement of the reactor performance with COD removal efficiency increasing to 77% and effluent sCOD decreasing to 1420 mg L $^{-1}$, improved methane production, and a sharp drop in H_2S concentration (Table 2). CH_4 production increased by 23% at an applied power of 0.22 W/L $_R$ and the oxygen percentage in the biogas was below 2%. Although improved COD removal could be attributed to electrochemical oxidation of organic matter, signifi-

cantly higher current densities and applied voltages might be required for this process, leading to aerobic conditions in the reactor (Zaveri and Flora, 2002). Increased methane production during eAD operation was indicative of anaerobic conditions in the reactor. Also, methanogenic activity was confirmed in batch activity tests, which produced results similar to those obtained in R-0 and R-1 tests showing a specific rate of 64 ± 5 mL/(g-VSS day) of methane production from acetate. This value was similar to the specific activity on acetate observed in R-0 and R-1 tests and once again suggested the absence of oxygen-related inhibition of acetoclastic activity.

3.3. Comparing eAD and AD processes

At a first glance water electrolysis, which results in oxygen formation, is expected to negatively affect the activity of strictly anaerobic methanogenic microorganisms. Nevertheless, in our tests both at low and high organic loads water electrolysis was observed to have a positive impact on methane production. This was indicated from the comparison of methane production between the reactors operated under anaerobic and electrolysis-enhanced conditions (Figs. 2 and 4) and by measuring acetoclastic and hydrogenotrophic methanogenic activity in the batch tests (Fig. 3). The low current density led to limited oxygen formation, creating micro-aerobic conditions, which did not prevent methane production. Since the biomass granules in the UASB reactors are typically larger than 500 μ m in diameter and the oxygen penetration depth does not exceed 50 μ m (Quarmby and Forster, 1995; Thaveesri et al., 1995), the electrolytic oxygen might be consumed in the outer biofilm layer (Botheju et al., 2009; Jenicek et al., 2008; Jenicek et al., 2010; Kato et al., 1997; Shen and Guiot, 1996; Tan et al., 1999; Tartakovsky et al., 2006; Zhou et al., 2007).

However, even if excessive production of electrolytic oxygen does not inhibit methanogenic activity in the biofilm granules, avoiding an over supply of oxygen is important since it would divert part of the organic matter from methane production to aerobic metabolism. Also, the presence of unused oxygen in the biogas should be avoided. By limiting the applied power and therefore the amount of electrolytic oxygen, a near-complete consumption of oxygen (95–99%) by facultative anaerobic microorganisms was achieved with oxygen in the gas phase in a range of 2–5% (R-1) and 1–2% (R-2). The presence of oxygen might be further reduced by a feedback control of the applied voltage, which could be automatically adjusted depending on the on-line measurements of O_2 in the biogas.

The increased methane production in the eAD reactors can be attributed to several factors, including improved hydrolysis of organic matter, production of additional methane from electrolytic

Fig. 4. (A) COD removal and (B) Methane production during AD and eAD modes of R-2 operation. Methane production from H_2 is estimated based on applied current.

hydrogen, stimulation of acetoclastic methanogenic activity due to micro-aerobic conditions, and H₂S removal from the reactor liquid. Many studies have demonstrated an improved hydrolytic activity under micro-aerobic conditions (Jagadabhi et al., 2010; Jenicek et al., 2008, 2010; Pirt and Lee, 1983; Zhu et al., 2009). This improvement was evident during R-2 operation at a high OLR, where a sufficient amount of slowly hydrolysable organic matter was fed to the reactor, and the anaerobic digestion was hydrolysis-limited. The electrolysis led to a decrease of the sCOD concentration in the reactor effluent and a corresponding increase in methane production, while an accumulation of solids in the reactor was not observed.

Methane production from the electrolytic H₂ was evident at a low OLR. A comparison of H₂ recovered in the biogas during eAD tests with H₂ production in abiotic tests showed that 90–98% of electrolytic H₂ was converted to methane. Since the COD removal efficiencies at a low OLR were similar with and without electrolysis, it was concluded that methane production mainly increases due to H₂ conversion to CH₄ by hydrogenotrophic methanogens. Similar calculations for the high OLR test in R-2 showed that 23% of H₂ was converted to methane.

Furthermore, microaerobic conditions were observed to result in increased acetoclastic methanogenic activity of a mixed culture containing methanogenic and facultative fermentative microorganisms (Shen and Guiot, 1996; Zitomer and Shrouf, 1998). It can be hypothesized that the fermentative microorganisms not only consumed oxygen thus protecting the methanogens from its toxicity, but also produced metabolites and co-factors, which were used in methanogenic anabolism.

Oxygen produced by water electrolysis also resulted in a near complete removal of H₂S, as can be seen from a comparison of H₂S levels in the off-gas of the 3.5 L reactor operated in AD and eAD modes (Table 2). The AD mode of operation led to H₂S build-up. Water electrolysis resulted in an almost immediate drop of H₂S concentration in the biogas to below 1 ppm. Importantly, H₂S oxidation occurred in the reactor liquid as opposed to H₂S removal from the biogas. High levels of sulfates in wastewater promote the proliferation of the sulfate-reducing bacteria leading to H₂S formation and a decrease of the methanogenic activity due to HS[−] toxicity (Bhattacharya et al., 1996; Raskin et al., 1996). H₂S removal from the reactor liquid due to a chemical, microbiological (Guiot et al., 1998), or electrochemical reaction helped to maintain methanogenic activity in spite of high sulfate levels in the reactor influent.

The low solubility of H₂ in water lead to its escape to the gas phase resulting in 2–7% H₂ in the biogas. The presence of H₂ has been shown to have a positive impact on biogas quality. A mixture of 8–20% H₂ and natural gas, known as Hythane, was demonstrated to increase the flammability range, decrease energy requirements for ignition, and reduce NO_x emissions (Ortenzi et al., 2008).

In addition to increased methane production, in situ water electrolysis also helped to stabilize reactor pH. This was in particular evident in the high OLR test, where no addition of NaOH was required to maintain a pH above 6.8, chosen as a setpoint for the pH controller. Also, the H₂ consumption by the hydrogenotrophic methanogens decreased the CO₂ percentage in the biogas since one mol of CO₂ is consumed for each mol of CH₄ produced according to 4H₂ + CO₂ → CH₄ + 2H₂O. Overall, by using a relatively low input of energy (0.2–0.3 Wh/L_R), the anaerobic digestion process required less intervention for operation and methane production was increased.

A comparison of energy input with the gain in methane production showed that in the case of 3.5 L reactor operation at an OLR of 1.7 g_{COD} L_R^{−1} d^{−1}, energy consumption (60.6 kJ) was higher than the energy content of the additionally produced methane (0.6 L of CH₄ corresponding to 24.9 kJ, Table 2). However, at an OLR of

15.5 g_{COD} L_R^{−1} d^{−1} energy consumption remained almost unchanged at 66.5 kJ, while methane production increased by 3.8 L corresponding to a gain of 150 kJ.

Interestingly, a detailed analysis of material balances in AD and eAD reactors at a low OLR suggested a gap between the estimated amounts of CH₄ produced from electrolytic H₂ and the experimentally measured CH₄ production (Figs. 2 and 4). Both in R-1 and R-2 methane production was higher than expected based on H₂ production calculated according to Eq. (3). Although this discrepancy could be attributed to enhanced COD removal or digestion of anaerobic sludge, effluent sCOD concentrations in R-0 and R-1 were similar and a comparison of volatile suspended solids (VSS) in R-0 and R-1 at the end of the test showed similar values. Therefore, we hypothesize that the amount of electrolytically produced H₂ was underestimated when using results of the abiotic tests because of improved electrolysis efficiency in the presence of anaerobic sludge, i.e. due to catalytic properties of microorganisms present in the reactor liquid or in the biofilm covering the electrodes. Apparently, this electrocatalytic activity of the microorganisms reduced energy consumption. In abiotic tests energy consumption for H₂ production varied between 8–11 Wh/L_{CH₄}^{−1} (R-1 test), which corresponds to 32–44 Wh/L_{CH₄}^{−1} with respect to the stoichiometry of CH₄ formation from H₂. At the same time, energy consumption for methane production from hydrogen during the eAD test was estimated at 18–27 Wh/L_{CH₄}^{−1}. Even a lower estimation of 9.1 Wh/L_{CH₄}^{−1} was obtained based on the results of the low OLR test in R-2. Notably, recent studies demonstrated biocatalytic activity of microorganisms in microbial electrolysis cells (Jeremiassen et al., 2010; Rozendal et al., 2008; Tartakovsky et al., 2008). Our results suggest a need for a detailed study on bioelectrochemical activity of anaerobic microorganisms on methane production in the eAD system.

4. Conclusions

By conducting water electrolysis in the sludge bed of UASB reactors at a low current density the process performance was improved in several ways. The micro-aerobic conditions increased the rate of hydrolysis of organic matter thus improving COD removal efficiency and methane production. Electrolytic H₂ improved the combustion properties of the biogas and increased net methane production through hydrogenotrophic methanogenesis. The microbial activity consumed almost all of the oxygen while the H₂S concentration in biogas was significantly reduced. Finally, a comparison of the material balances suggested that the efficiency of water electrolysis improved due to the electrocatalytic activity of the microorganisms.

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