Title: Interfacing anaerobic digestion with (bio)electrochemical systems: potentials and challenges

Running title: Review bioelectrochemical systems in anaerobic digestion

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Abstract

For over a century, anaerobic digestion has been a key technology in stabilizing organic waste streams, while at the same time enabling the recovery of energy. The anticipated transition to a bio-based economy will only increase the quantity and diversity of organic waste streams to be treated, and, at the same time, increase the demand for additional and effective resource recovery schemes for nutrients and organic matter. The performance of anaerobic digestion can be supported and enhanced by (bio)electrochemical systems in a wide variety of hybrid technologies. Here, the possible benefits of combining anaerobic digestion with (bio)electrochemical systems were reviewed in terms of (1) process monitoring, control, and stabilization, (2) nutrient recovery, (3) effluent polishing, and (4) biogas upgrading. The interaction between microorganisms and electrodes with respect to niche creation is discussed, and the potential impact of this interaction on process performance is evaluated. The strength of combining anaerobic digestion with (bio)electrochemical technologies resides in the complementary character of both technologies, and this perspective was used to distinguish transient trends from schemes with potential for full-scale application. This is supported by an operational costs assessment, showing that the economic potential of combining anaerobic digestion with a (bio)electrochemical system is highly case-specific, and strongly depends on engineering challenges with respect to full-scale applications.

Keywords: anaerobic digestion, bioelectrochemical system, biogas, methane, resource recovery

1. Introduction

The transition from a fossil fuel based economy to a bio-economy, which relies on renewable resources, indirectly imposes a central role on anaerobic digestion (AD) (Verstraete et al. 2005). Bio-refineries, for example, make use of a wide variety of organic feedstocks to manufacture chemical building blocks, such as ethanol, short- and medium-chain fatty acids, and other biohydrocarbons (Choi et al. 2015, Maity 2015). This results in the production of both liquid (*e.g.*, thin stillage and molasses wastewater) and solid (*e.g.*, bagasse) side and waste streams, which, in many cases, are subjected to treatment by means of AD with concomitant renewable energy recovery in the form of biogas (Alkan-Ozkaynak and Karthikeyan 2011, Fuess and Garcia 2015, Rabelo et al. 2011, Satyawali and Balakrishnan 2008). These waste streams often pose a challenge to the AD process, due to their high salinity, total ammonia nitrogen (TAN) concentration, high sulphate concentration and/or acidic character (Barrera et al. 2014, Fang et al. 2011a, Jimenez et al. 2003). An example of such a problematic stream is vinasse, originating from bioethanol production (Rodrigues Reis and Hu 2017). This underscores the need for complementary technologies to stabilize the AD process by reducing toxicity of ammonia, sulphide and/or salinity, and to improve effluent quality. Additionally, it creates opportunities for the recovery of nutrients, such as N, P, S and K.

Whereas AD is an established, mature technology with a long history of full-scale applications (Abbasi et al. 2012, McCarty 1981), more recently, (bio)electrochemical systems ((B)ESs) emerged for recovery of energy and nutrients from various organic waste streams (Arends and Verstraete 2012, Logan and Rabaey 2012, Schroder 2011, Schroder et al. 2015). An ES consists of an anode and cathode electrode, usually separated by an ion selective membrane to create two separate compartments in which a current can be applied (electrolytic system) or produced spontaneously (galvanic system). For a BES, at least one of the electrode reactions (oxidation and/or reduction) is catalysed by microorganisms. When an (a)biotically catalysed reaction on

the cathode occurs at a higher potential, compared to a biotically catalysed reaction on the anode, a positive cell potential is the result, and energy can be gained from the combination of both reactions. This configuration is called a microbial fuel cell (MFC) (Logan et al. 2006). An example is the oxidation of acetate to CO₂, electrons and protons ($E^{0'} = -0.29$ V vs. SHE) at the anode and reduction of O₂ to water ($E^{0'} = 0.81$ V vs. SHE) at the cathode. When the cathode operates at a lower potential compared to the anode, additional energy needs to be provided, the system has a negative cell potential, and is termed a microbial electrolysis cell (MEC) (Logan et al. 2008). An example is the reduction of water to H₂ ($E^{0'} = -0.41$ V vs. SHE) at the cathode, coupled to the previously mentioned oxidation of acetate. The equilibrium potentials are reported versus the Standard Hydrogen Electrode (SHE), and were calculated based on the Growth Reference System (Heijnen 1999) at typical concentrations in microbial systems (Gildemyn et al. 2017).

At first glance, BES might seem a competitive technology compared to AD, *i.e.*, both technologies can be used to convert chemical energy contained in organic matter into electrical energy or into a gaseous energy carrier (H₂ or CH₄). However, treating waste streams containing high solids can be detrimental to BES performance, due to clogging and fouling issues on both electrodes and membranes (Logan and Rabaey 2012). Another important aspect intrinsic to a BES is that it relies on a surface based catalysis, which makes the overall conversion rates dependent on the size of the electrode and membrane surface in the reactor (Arends and Verstraete 2012). Several authors have reviewed configurations in which synergies between both technologies were proved successful (Arends and Verstraete 2012, Cheng and Kaksonen 2017, Pham et al. 2006). These synergies include, but are not limited to (1) removal of inhibiting levels of volatile fatty acids (VFA) *via* biological oxidation at the anode (Cerrillo et al. 2016), (2) (selectively) extracting organic and inorganic molecules by (biocatalysed) membrane electrolysis or electrodialysis (Desloover et al. 2015, Scoma et al. 2016, Zhang and Angelidaki

2015c), and (3) creating microaerobic conditions in AD by water electrolysis (Tartakovsky et al. 2011). Electrodialysis targets a transfer of salts from a feed solution to another solution by removing anions and/or cations through an anion exchange membrane (AEM) and/or cation exchange membrane (CEM), respectively, under the influence of a potential difference and in different configurations (Xu 2005). Membrane electrolysis is a single membrane process, using either an AEM or a CEM, with focus on electrochemical production or selective extraction (Andersen et al. 2014).

The main aim of this review is to provide a critical evaluation of potential synergetic benefits of coupling AD with (bio)electrochemical technologies in a holistic framework that exceeds technical feasibility to potential full-scale applicability and economic validity. Crucial aspects in terms of overall energy recovery, process stability, value of extracted products (in the case of membrane electrolysis) and technical feasibility are considered. The direct influence of the (bio)electrochemical component on the AD microbial community is discussed. In consideration of this information, suggestions are made for successful strategies to combine AD with (B)ESs.

2. Potential processes combining anaerobic digestion and (bio)electrochemical systems

2.1. Inorganics removal and/or recovery for process stabilization and resource recovery

Anaerobic digestion requires a minimum concentration of both macronutrients and trace elements to ensure optimal conditions for each stage of the process (Pobeheim et al. 2010). The optimal level of each element strongly depends on the operational conditions, and a wide range of values are reported (Schattauer et al. 2011, Singh et al. 1999). Micronutrient addition and/or co-digestion strategies could improve AD process stability (Cresson et al. 2006, Mata-Alvarez et al. 2011).

2.1.1. Electrochemical extraction of monovalent cations

Macronutrient limitation is usually not an issue, but instead, inhibition of especially methanogenesis can occur due to too high concentrations of total ammonia ($\text{NH}_3 + \text{NH}_4^+$), which is mainly caused by the free ammonia (NH_3) fraction, and other salts (Chen et al. 2008, De Vrieze et al. 2012). A wide range of total ammonia concentrations, *i.e.*, between 1.7 and 14 g N L⁻¹, causing 50% methanogenesis inhibition (IC_{50}) is reported, and this depends on several factors, such as pH (Reaction 1), temperature, synergistic and antagonistic effects, acclimation, and reactor configuration (Chen et al. 2008).

Similar wide ranges of IC_{50} are reported for Na^+ (4.4 to 26.9 g Na^+ L⁻¹) and K^+ (5.9-28 g K^+ L⁻¹), which demonstrates the need for a case-specific evaluation (Chen et al. 2008, Fang et al. 2011b, Feijoo et al. 1995).

Several full-scale AD plants operate at total ammonia concentrations and salinity values up to 6.0 g N L⁻¹ and 60 mS cm⁻¹, respectively (De Vrieze et al. 2016b, De Vrieze et al. 2015,

Sundberg et al. 2013). In combination with high pH values, > 7.5-8.0, this leads to VFA accumulation and suboptimal process performance, the so-called “inhibited steady-state” (Angelidaki and Ahring 1993, Hansen et al. 1998). High concentrations of ammonium, > 4.0 g N L⁻¹, and other cations (mainly Na⁺ and K⁺) offer the potential for efficient removal or recovery by means of (bio)electrochemical technologies (Angelidaki and Ahring 1993, De Vrieze et al. 2016c, Rajagopal et al. 2013).

The electrochemical removal and recovery of ammonium (NH₄⁺) and other cations for AD process stabilization can be implemented at different process stages and a variety of approaches, ranging from pre-treatment, *in situ*, side stream and post-treatment technologies (Table 1, Figure 1). In most cases, the electrochemical unit relies on the extraction of ammonium and other cations through a cation exchange membrane (CEM) after which recovery in a “clean” catholyte stream is possible (Figure 2a). The main advantage of ammonium extraction over other cations lies in the fact that a stripping/absorption unit can be coupled with the electrochemical extraction unit. Due to the increased pH in the cathode compartment, ammonia is mainly present in the free ammonia form, which prevents back diffusion through the CEM. This high cathodic pH enables continuous removal of free ammonia from the cathode compartment, thus, maintaining a substantial driving force for ammonium transfer across the membrane (Desloover et al. 2012, Ippersiel et al. 2012). To maintain the driving force for non-volatile cation extraction (*e.g.*, Na⁺ and K⁺), an additional concentration step, such as reverse osmosis, is required (Mondor et al. 2008).

Pre-treatment strategies are often used for direct total ammonia extraction from feedstocks, such as manure, which can result in high total ammonia concentrations, up to 20 g N L⁻¹ in the concentrated extracting solution (Ippersiel et al. 2012, Mondor et al. 2008). Direct removal of ammonium and/or other cations from the digester can take place through a side stream extraction unit in a recirculation loop of, for example, an upflow anaerobic sludge blanket

(UASB) system, as described by Desloover et al. (2015). Alternatively, *in situ* extraction via a submerged electrochemical extraction unit can be applied for direct desalination and toxicity reduction in continuous stirred tank reactor (CSTR) digesters (Zhang and Angelidaki 2015a, c). A similar system can be used for post-treatment of either the total digestate (Desloover et al. 2012) or only the liquid fraction of the digestate (Kim et al. 2015) for total ammonia recovery or effluent polishing.

One of the main problems with membrane-based systems lies in scaling and other forms of membrane fouling, which results in decreased membrane fluxes, membrane destruction, increased power input requirements and/or poor effluent quality (Mondor et al. 2009). Pre-treatment of the digestate and additional research concerning membrane fouling will be required to ensure adequate performance of these extraction systems.

2.1.2. Electrochemical sulphur recovery and the cryptic sulphur cycle

Hydrogen sulphide is an inhibitory component in AD with a wide IC_{50} concentration range of 20-1000 mg S L⁻¹ for H₂S (Chen et al. 2008, Hulshoff Pol et al. 1998, Isa et al. 1986, Karhadkar et al. 1987, Koster et al. 1986, Lens et al. 1998, Visser et al. 1996). It is also a corrosive gas that may cause damage to the CHP unit (Weiland 2010). Electrochemical sulphide toxicity remediation can take place *via* (1) the introduction of a sacrificial anode, which induces precipitation of metal sulphides (Zamalloa et al. 2013), (2) polarity switching for sulphide recovery as elemental sulphur or other sulphur species (Desloover et al. 2015, Dutta et al. 2009), or (3) continued, high potential anodic oxidation of the sulphide (Zhao et al. 2009) and subsequent deflaking of sulphur coatings from the anode electrode for recovery of elemental sulphur (Vaiopoulou et al. 2016). An alternative approach is sulphur recovery from the effluent of UASB systems (Dutta et al. 2010, Zhang et al. 2009), which allows better steering of the recovery process, but does not allow for direct reduction of H₂S in the biogas.

High potential (a)biotic oxidation of H_2S on the anode can yield elemental sulphur that can be re-oxidised to sulphur oxyanions or polysulphide, and these compounds can subsequently function again as an electron acceptor for biological oxidation of organics (Rabaey et al. 2006, Sun et al. 2009). This sulphur cycling is known as the “cryptic sulphur cycle” (Hansel et al. 2015, Kappler and Bryce 2017). Hence, a higher organics removal could be due to (1) sulphur cycling and/or (2) higher COD conversion to CH_4 by the methanogens, due to the lower H_2S toxicity. From an engineering point of view, sulphur removal and recovery through a hybrid AD-(B)ES approach should be considered and evaluated on the macro-scale.

2.1.3. Electrochemical phosphorus recovery: a different perspective

The recovery of phosphorus, in contrast to ammonia, other cations and sulphide, is not related to toxicity issues, rather the need for resource recovery (Tyagi and Lo 2013). Phosphate recovery can take place by means of electrodialysis *via* an anion exchange membrane (Figure 2b) (Ebberts et al. 2015, Mondor et al. 2008). Alternatively, a MEC can be used for direct struvite precipitation and recovery from AD effluents (Cusick et al. 2014). The availability of soluble phosphate for direct recovery is an important issue, as it often precipitates with multivalent cations, such as Ca^{2+} and Fe^{2+} (Carliell and Wheatley 1997, De Vrieze et al. 2016c). Hence, additional solubilisation treatment strategies, such as microwave treatment (Liao et al. 2005), are needed to increase the availability of phosphate for (electrochemical) recovery as a refined product.

2.2. Effluent polishing: residual COD removal

The VFA are intermediates in biomethane production, and their production causes a pH decrease. Methanogenic archaea that convert these VFA to CH_4 and CO_2 create alkalinity, in the form of bicarbonate, which causes a pH increase (Appels et al. 2008). Process imbalances

and the presence of toxic compounds can affect the less robust archaea first, causing an accumulation of the toxic VFA and concomitant pH decrease (Ahring et al. 1995). Removal of excess VFA is critical to sustain biogas production. Changing the operational parameters, *e.g.*, lowering the organic loading rate and elimination of potentially inhibiting compounds from the feedstock, can be an option, but (bio)electrochemical technologies can also provide the necessary stabilization through removal of the produced VFA (Table 2). These electrochemical technologies can also be used for additional effluent polishing, especially in the case of UASB systems (Table 2).

The removal of VFA from the digester, especially UASB-types characterized by low suspended solids concentrations, can be accomplished by adding an electrochemical cell in the recirculation loop. By means of a bioanode, the VFA can be used by an electroactive biofilm as an easily available carbon source for oxidation, leading to the production of electrical power in a MFC. The direct additional power production by the MFC is often marginal compared with the total CH₄ production of the digester, but the removal of VFA toxicity can give a strong indirect boost to CH₄ production (Weld and Singh 2011). The application of (B)ESs in (M)EC modes provides a suitable alternative, both for *in situ* VFA removal (Sasaki et al. 2010, Zhang et al. 2013a, Zhang et al. 2013b) and additional effluent polishing (Goncalves et al. 2012, Qu et al. 2012). The required power input per unit of COD removed can be up to a factor 1000 higher for electrochemical oxidation techniques compared to microbial electrolysis systems (Table 2). The H₂, which is generated at the cathode in MEC mode for VFA removal, can be injected in the digester to produce more CH₄. Alternatively, it can be added to the biogas to improve its performance as fuel in, for example, a spark ignition engine (Karim et al. 1996), though this does reduce the caloric value of the biogas if the CH₄ content is higher than 30 %. Recovery of the excess VFA, instead of removal, can be realised by driving the VFA across an anion exchange membrane, using an electrochemical extraction unit, such as electrodialysis or

a membrane electrolysis cell (Figure 2b) (Andersen et al. 2014). A pH higher than the pKa of the VFA (ensuring the VFA to be negatively charged) and a higher molar concentration relative to other anions in the broth (*e.g.*, bicarbonate, chloride, sulphate, phosphate, nitrate) are both necessary to obtain energy-efficient recovery (Andersen et al. 2014). As those conditions are often not met in AD, the recovery of VFA has, thus far, only been investigated for fermentation processes (Andersen et al. 2015, Xu et al. 2015). In cases of VFA accumulation exceeding 10 g COD L⁻¹, as sometimes observed in full-scale AD plants (De Vrieze et al. 2015), it could become economically attractive to extract the VFA to both reduce VFA toxicity and obtain a concentrated VFA stream that can be valorised (Andersen et al. 2016). Another advantage of the electrolysis approach is that the cathode, which is in contact with the AD mixed liquor during VFA extraction, produces hydroxyl ions that increase the pH and H₂ gas, which can be added to the biogas. Intermittent use of the electrolysis cell for extraction of VFA above a threshold concentration, or for pH control when the reactor acidifies, could be a suitable process control strategy without input of chemicals, although the intermittent use can have a negative impact on system economics.

2.3. Electrochemical biogas upgrading to biomethane

Biogas produced from organic substrates through AD, represents a reliable and flexible renewable energy source. Biogas can be valorised as a fuel for on-site heat and power generation *via* a combined heat and power (CHP) unit (Szarka et al. 2013), or, if properly upgraded, used as a natural gas substitute for domestic and industrial use and as a fuel for transportation (Ryckebosch et al. 2011). Raw biogas is composed mainly of CH₄ (40-75 %) and CO₂ (25-60 %), but for biogas to work as an effective renewable energy source that can be introduced into the existing gas grid, the energy density of biogas (*i.e.*, CH₄ content) needs to be increased to 96% or even higher (Munoz et al. 2015, Pöschl et al. 2010).

Three strategies have been developed to upgrade biogas into natural-gas-quality biomethane: (1) removing CO₂ from biogas *via* physical-chemical postprocessing technologies; (2) supplying a reduced substrate (*e.g.*, hydrogen gas) to the digestion process to biologically convert CO₂ to CH₄ *in situ* (using the anaerobic digester microbiome); and (3) converting CO₂ from biogas into added-value products in an *ex situ* reactor technology, *e.g.*, H₂-based (bio)methanation of CO₂ to CH₄ or microalgae-based CO₂ fixation (Martin et al. 2013, Muñoz et al. 2015). At industrial scale, biogas upgrading is nowadays performed by physical-chemical processes for CO₂ separation (*e.g.*, absorption, adsorption or gas permeation). Recently, several biotechnological approaches for *in situ* and *ex situ* CO₂ removal have been assessed at laboratory or pilot scale, and show potential for cost-effective and sustainable biogas upgrading with low chemicals and/or energy requirements (Bauer et al. 2013, Muñoz et al. 2015).

2.3.1. *In situ* biogas upgrading

Several recent studies have evaluated the performance of systems in which H₂ is directly introduced into the anaerobic digester to increase the CH₄ content of the biogas. This *in situ* approach for biogas upgrading employs hydrogenotrophic methanogens capable of using CO₂ as carbon source and electron acceptor and H₂ gas as electron donor (Reaction 2) (Thauer et al. 1993).

Direct H₂ injection aims to stimulate and enrich autotrophic methanogenic archaea, consistently found in mixed anaerobic cultures, by actively supplying reducing equivalents to the anaerobic food web (Luo and Angelidaki 2013). The chemoautotrophic bioconversion of CO₂ to CH₄ as a strategy for *in situ* biogas upgrading has been reported using (1) direct H₂ injection, either

continuous (Luo and Angelidaki 2013, Luo et al. 2012) or pulsed (Agneessens et al. 2017), and (2) a poised electrode for direct transfer of electrons (or dissolved H₂ gas) to the hydrogenotrophic methanogens (Xu et al. 2014a). In a study performed by Luo et al. (2012), H₂ gas was injected into a thermophilic digester at a flow rate around four times higher than the CO₂ production rate, corresponding to the stoichiometric H₂:CO₂ ratio (4:1) for biomethanation (Reaction 2). The biological H₂ uptake lowered the CO₂ content from 38 % to 15 %, and CH₄ production increased with 22 %, compared to a control reactor without H₂ addition. The direct supplementation of H₂ to a digester may adversely affect the functioning of the microbial community, as it can lead to an increase in pH > 8, due to the consumption of bicarbonate buffer by hydrogenotrophic methanogens. This may lead to (partial) inhibition of methanogenic activity. Higher H₂ partial pressures may also induce propionate and butyrate accumulation, because the thermodynamic equilibrium of the syntrophic associations is shifted (McInerney et al. 2009, Schink 1997, Thauer et al. 1977), and oxidation of short-chain carboxylic acids is thermodynamically not favourable at H₂ partial pressures above 10⁻² kPa (Siriwongrungson et al. 2007). It is crucial for the hydrogenotrophic methanogens to effectively consume the H₂, preferably at a rate equal to its injection rate, to avoid these adverse effects. The supplementation of H₂ gas directly to the digester for *in situ* upgrading is accompanied by operational challenges, as undersupplementation of H₂ gas will lead to an excessive CO₂ content in the biogas, while oversupplementation may lead to the accumulation of VFA. The poor solubility of H₂ in water (7.7×10^{-6} mol m⁻³ Pa⁻¹) (Sander 2015) is known to limit the H₂ gas-to-liquid mass transfer rates, and subsequent CH₄ production rates, since under conditions where H₂ mass transfer is limiting, the biomethanation efficiency decreases drastically. The main limitation of *in situ* upgrading arises from the fact that anaerobic digesters are not designed to maximize the gas-liquid mass transfer, as is done in gaslift reactors (Muñoz et al. 2015). Xu et al. (2014a) demonstrated a system in which biomethanation was not limited

by dissolution of H₂ in the liquid phase, as electrons for CO₂ reduction were supplied *in situ* using a graphite cathode. In this system, simultaneous biogas production and upgrading (< 10 % CO₂) was achieved in the cathode chamber of the BES.

2.3.2. *Ex situ* biogas upgrading

Since *in situ* biogas upgrading might interfere with the conventional digestion process, biogas production and upgrading can be separated and optimized independently. *Ex situ* biogas upgrading can be accomplished by combining biogas and H₂ in an external bioreactor, containing either a pure or mixed culture of hydrogenotrophic methanogens, or by feeding biogas to the cathode compartment of a CH₄-producing BES. The use of a BES to produce CH₄ from CO₂ *via* the interaction of methanogens with a solid-state electron donor has been studied intensively in the past years, but the mode of electron transfer from the cathode to the methanogens is still unclear (Geppert et al. 2016). In a process called “electromethanogenesis”, methanogens can directly accept electrons from the cathode for reduction of CO₂ to CH₄ (Reaction 3) (Cheng et al. 2009, Geppert et al. 2016, Villano et al. 2010), and extracellular enzymes can facilitate electron transfer (Deutzmann et al. 2015).

The direct bioelectrochemical reduction of CO₂ at a biocathode has not yet been confirmed or characterized, since microbial or abiotically generated H₂ might still have acted as a mediating component between the electrode and the “electromethanogens”. It was suggested that both direct electron and H₂-mediated transfer contributed to bioelectrochemical CH₄ production, and that the cathode potential is the key parameter affecting the electron transfer mechanism (Villano et al. 2010). To address this interesting biological question on the electron transfer

mechanism, accurate H₂ sensing techniques are needed that can operate (1) at low H₂ partial pressure, and (2) close (within μm) to the electrode surface.

The scalability and implementation potential of bioelectrochemical CO₂ removal as a strategy for biogas upgrading is highly unknown, since no pilot scale studies have been conducted in the public domain. The H₂-mediated conversion of CO₂ seems to be more practical in terms of operational simplicity. A thermophilic lab-scale biomethanation reactor with continuous injection of a synthetic biogas stream that consisted of 60% H₂, 25% CH₄, and 15% CO₂ (4:1 ratio of H₂:CO₂), resulted in a maximum CH₄ content in the product gas of ~95% (Luo and Angelidaki 2012). In another study, a final CH₄ content of ~97% was achieved by combining hydrogenotrophic methanogens in the cathode compartment with electrolytic extraction of excess CO₂ (Jin et al. 2017b).

2.4. Direct control of the anaerobic digestion process

2.4.1. *In situ* water electrolysis

Direct control of the AD process through water electrolysis can take place by adjusting the pH or by providing suitable conditions for hydrolysis and methanogenesis, both of which are considered bottlenecks in AD (Appels et al. 2008, Batstone et al. 2009, Chen et al. 2008, Rajagopal and Beline 2011). Water electrolysis leads to the production of H₂ at the cathode and O₂ at the anode, and can, depending on the buffer capacity of the mixed liquor, coincide with an increase in pH at the cathode and decrease in pH at the anode through the production of OH⁻ and H⁺, respectively (Reactions 4 & 5, Figure 2).

Optimal performance of the AD process requires a narrow pH range of 6.8 to 7.5, mainly due to the sensitivity of the methanogenic archaea (Appels et al. 2008, Chen et al. 2008, Gujer and Zehnder 1983). Conventionally, pH control in AD takes place through the direct addition of NaOH or H₂SO₄. Both chemicals are subject to strict safety regulations during transport, storage and usage, and after transport the chemicals are often diluted to the desired concentrations for use. This emphasizes the benefit of on-site production of acids and bases at controllable concentrations and rates through, *e.g.*, electrochemical technologies (Blanc and Molof 1973, Logan and Rabaey 2012). By introducing a cathode into the anaerobic digester, or by recirculating the mixed liquor through the cathodic compartment of an electrochemical cell, the pH could be increased (Reaction 4), thereby limiting adverse effects on the microbial community, resulting from VFA or H₂S toxicity (Agler et al. 2011, Hulshoff Pol et al. 1998). In contrast, combining an anode with the digester would result in a decrease in pH, which can counteract the free ammonia (NH₃) toxicity, often observed for AD of N-rich feedstocks (Calli et al. 2005, Moestedt et al. 2016). Anodic and cathodic pH control only depends on the current that is provided, and thereby allows accurate chemical-free pH control (Andersen et al. 2015). While the production of protons and hydroxyl ions can be used for indirect steering of the process by creating optimal conditions for the microbial community, the production of O₂ and H₂ can also contribute directly to the metabolic pathways in the hydrolytic and/or methanogenic stage. Medium-intensive (3-5 L O₂ L⁻¹ d⁻¹) or high-frequency (every 2 hours) pulsed micro-aeration has been shown to redirect the AD process to fermentation by selectively inhibiting the methanogenesis stage, and still allowed high-rate VFA production (Xu et al. 2014b). As methanogenesis inhibition in AD is undesired, O₂ supply must be carefully regulated to limit its effect to increased hydrolysis and sulphide scavenging, and avoid negative impacts on methanogenesis (Jagadabhi et al. 2010, Xu et al. 2014b). The beneficial effect of O₂ supply through water electrolysis appears to be case-specific (Lim and Wang 2013), as contradictory

results were obtained in different studies. Koch et al. (2015) reported no positive effect of water electrolysis on CH₄ production during batch digestion of corn silage. In contrast, Tartakovsky et al. (2011) observed a 10-25% improvement in CH₄ production during continuous digestion of synthetic wastewater in a UASB. The difference might be explained by calculating the oxygen loading rate vs. the organic loading rate. No effect was observed when 0.07 g O₂ g⁻¹ COD was applied (Koch et al. 2015), while a positive effect was observed at 0.2 g O₂ g⁻¹ COD (Tartakovsky et al. 2011). This shows that by accurately controlling the current, O₂ can be supplied to the digester in the required concentration or rate to balance hydrolysis and methanogenesis. However, feed composition and reactor configuration also need to be carefully considered when comparing results, as these will determine the rate of O₂ consumption, which will influence its eventual impact on the AD process. The supply of H₂ from the cathode to the digester can stimulate *in situ* biogas upgrading through hydrogenotrophic methanogenesis (see section 2.3.1).

2.4.2. Biosensors for process stability monitoring

In contrast to direct process steering, on-line monitoring of process stability in AD can be made possible by (bio)electrochemical technologies, especially for VFA measurements. These systems are based on biological VFA oxidation at an anode, resulting in current production that should be proportional to the actual VFA concentration in the mixed liquor, which represents the most basic biosensor configuration (Kaur et al. 2013, Kretzschmar et al. 2016). Other organic compounds commonly present in the mixed liquor, such as alcohols and soluble sugars, can also be oxidized at the anode, which will lead to an overestimation of the actual VFA concentrations. To avoid this issue, the electrolytic extraction of VFA from the mixed liquor can be carried out either from the cathode compartment (Jin et al. 2017a), or from a central compartment (Jin et al. 2016) through an AEM to the anode compartment.

The effectiveness of bio-sensors has mainly been demonstrated for synthetic wastewaters and/or wastewaters with low suspended solids, *e.g.*, in the recirculation loop of an upflow anaerobic fixed-bed reactor (Liu et al. 2011). The application of a biosensor with a *Geobacter anodireducens* dominated anode in an anaerobic digester treating a mixture of maize silage and cow manure allowed accurate VFA measurements (Kretzschmar et al. 2018). However, long-term stability in CSTR digesters remains to be validated. The concentration range over which accurate measurements can be carried out tends to show a strong variation. For example, the optimal range was shown to be 5-40 mg L⁻¹ propionate (Kaur et al. 2013) or 60-6000 mg L⁻¹ acetate equivalents (Jin et al. 2017a). Compounding the issue, the distinction between different VFA is complicated by differences in their redox state (number of electrons needed for oxidation) (Kaur et al. 2013). Hence, for reliable on-line application of these biosensors, especially for full-scale AD, further optimization using actual waste streams, extension of the optimal detection range, and long-term stability will be necessary (Arends 2017).

3. Electrochemical effects on the anaerobic microbiology

3.1. Physical-chemical niche creation in a homogenous environment

An anaerobic digester, particularly in a CSTR configuration, is usually considered as a homogeneously distributed reactor system. By adding electrodes into a digester, additional surface area is created, and, depending on the electrode material, allows for biofilm formation (De Vrieze et al. 2014, Yang et al. 2004). Consequently, a gradient of substrates, products and nutrients will be created within the biofilm. Biofilm growth also allows retention of slow growing microorganisms (*i.e.*, with a growth rate lower than the sludge retention time) in the reactor (De Vrieze et al. 2016a). The electrodes can also function as baffles that impact the hydrodynamics of the reactor system. These surface effects do not directly impact key electrochemical reactions, and the electrode mostly serves as a suitable carrier material for the slow-growing methanogenic community. Nonetheless, these effects need to be considered when setting up a suitable experimental design, and it is recommended that control reactors with electrodes in open circuit (*i.e.*, no current) and without electrodes are included to distinguish electrochemical and surface effects (De Vrieze et al. 2014).

Another physical niche created by an electrode resides in the narrow liquid layer surrounding its surface where pH and gas gradients from the bulk liquid towards the electrode surface will arise. This is particularly the case when the electrochemical unit is operated at high currents (Reactions 4 & 5, Figure 2), and makes it extremely difficult for microorganisms to colonize the electrode surface. Depending on the conductivity of the mixed liquor, cell voltage, and electrode spacing, an electrical field is created, which can cause the formation of gradients of charged molecules in the system. However, the overall effect of such gradients also strongly depends on the local hydrodynamic conditions, *i.e.*, laminar or turbulent flow conditions. These aspects, thus far, have received little attention, but could allow for additional tools to steer or study microbial niche differentiation (Braff et al. 2013).

3.2. Altered microbial communities on electrodes

Microbial communities that develop on the electrodes have been found to be very distinct from those in the mixed liquor (De Vrieze et al. 2014, Koch et al. 2015). The extent of this difference seems to be related to the process conditions and feedstock composition. For example, *Methanosaeta* sp. were enriched on both the anode and cathode compared to the mixed liquor during AD of molasses (De Vrieze et al. 2014). Enrichment of *Geobacter* sp. was observed in the microbial community on the anode in a digester where silage was treated, while *Methanobacterium* sp. were enriched on the cathode (Koch et al. 2015). *Geobacter* sp. are known to interact with an electrode for use as a terminal electron acceptor during respiration of VFA (Bond and Lovley 2003, Richter et al. 2008), and it has been suggested that hydrogenotrophic *Methanobacterium* sp. isolates are capable of direct electron uptake (Beese-Vasbender et al. 2015).

The applied voltage can not only induce a shift in the microbial community close to or on the electrodes, but has also been shown to impact the mixed liquor microbial community. For example, by increasing the applied voltage, an archaeal community dominated by *Methanosaeta* shifted to a *Methanoregula* dominated archaeal community during AD of waste activated sludge (Chen et al. 2016). In the same study, the bacterial community also shifted upon changing the applied voltage, but no clear trends could be identified. The shift in the bulk microbial community with changing applied voltages can be an effect of the electric field, especially at high cell potentials, yet, this remains to be investigated. Given the often high mixing intensity and related turbulent conditions in CSTR digesters, the impact of the electric field on the microbial community is more likely indirect, as it will also influence pH and speciation of redox active components. If the scope is expanded from AD to general BESs, a trend is observed in which microorganisms, like *Geobacter* sp., colonize the anode (Dennis et

al. 2016, Malvankar et al. 2012), and certain homoacetogens, sulphate reducing bacteria (Arends et al. 2017) and hydrogenotrophic methanogens (Pozo et al. 2015) colonize the cathode, with very different microbial communities in the mixed liquor of the anodic and cathodic compartments (Arends et al. 2017, Dennis et al. 2016). This differentiation is most likely due to the ability of these microorganisms to actively exchange electrons with the electrode. The reasons for microbial colonization of cathodes and details of the microbe-cathode interaction, however, require further research. For example, *Acetobacterium* sp. are often found to colonize cathodes (Arends et al. 2017, Marshall et al. 2012, Patil et al. 2015), but do not appear to be capable of direct electron uptake from an electrode (Nevin et al. 2011). It seems likely that *Acetobacterium* sp. can instead efficiently scavenge H₂ from the electrode surface, like sulphate reducing bacteria and hydrogenotrophic methanogens.

Several studies have shown that the addition of conductive materials, such as carbon fabrics (Chen et al. 2014a), granular activated carbon (Liu et al. 2012) or biochar (Chen et al. 2014b), to the digester resulted in enhanced CH₄ production in lab-scale co-culture experiments. The addition of carbon cloth or biochar to lab-scale molasses digesters could not replicate these results in a mixed culture, as an enrichment of Methanosaetaceae was obtained (De Vrieze et al. 2016a), in contrast to the co-culture experiments being conducted with a *Methanosarcina* sp. (Chen et al. 2014b). Adding conductive materials to the mixed liquor of an AD reactor has the advantage that it does not require a large, fixed electrode to steer the process. Conductive particles can be used to influence the bioprocess by acting as a reservoir for charge storage (*i.e.*, capacitive particles), which can be charged by exoelectrogenic biofilms (Deeke et al. 2015, Liu et al. 2014). Regeneration and, especially, retention of these conductive materials needs to be carefully considered during the reactor design stage. A fluidized bed design with a relatively small (compared to reactor volume) fixed electrode has been proposed to re-oxidize reduced carbon particles (Deeke et al. 2015). The exact mechanisms of charge storage in or on these so-

called capacitive particles is still unknown, but seems to be linked to the charge storage capacity of the cytochromes in the cell wall of *Geobacter* sp. (Tejedor-Sanz et al. 2017), or merely the charge/discharge properties of the material.

Introducing electrodes into AD can have a major impact on the availability of nutrients, electron donors, electron acceptors and physico-chemical conditions, which in turn can have a strong effect on the microbial community in the digester. However, there is no strong consensus on the mechanisms of how these different factors interact to achieve macro-scale performance enhancement. An interesting avenue for further research is to elucidate the impact of electrode associated communities on mixed liquor performance in the framework of a bioaugmentation strategy. If certain microorganisms that have beneficial properties for processes in the mixed liquor can thrive on the electrode surface, and are able to colonize or seed the mixed liquor, pre-colonized electrodes could be used as a bioaugmentation strategy.

4. Engineering challenges: economic and practical feasibility

The techno-economic potential of combining AD with a (B)ES to reduce toxicity, recover nutrients and/or increase CH₄ production in full-scale digesters depends on multiple parameters (Figure 1). The hybrid AD-(B)ES systems should not lead to a higher cost and energy consumption than the single AD process, and the (B)ES itself should not be more costly than alternative technologies in terms of infrastructure and energy consumption. To date, only estimates of capital costs for (B)ES technologies at the full scale are available (Rozendal et al. 2008). Hence, to avoid a speculative approach, here, only operational costs were considered. As the combination of AD with a (B)ES entails several possibilities, and is most likely location dependant, a specific operational cost assessment should be made for each case to come up with the best solution for which ultimately a full life cycle assessment, which is outside of the scope of this review, is needed. As an example, here, an operational costs assessment of applying electrochemical recovery of ammonia to obtain both increased CH₄ production rates and nutrient recovery was performed.

The electrochemical power input per unit of nitrogen recovered from various waste streams ranges from 12.0 to 17.2 kWh kg⁻¹ N (Desloover et al. 2015, Desloover et al. 2012, Luther et al. 2015). These values are similar to or even higher than the energy required for nitrogen fixation *via* the classic Haber-Bosch process, which consumes 10-12 kWh kg⁻¹ N (Maurer et al. 2003). The cost of electrochemical extraction does not take additional concentration and cleaning steps into account, which will potentially further increase its energy cost. Hence, mere nitrogen recovery from AD cannot be considered an economically viable approach, and must be coupled with additional CH₄ production or other energy recovery strategies. A decrease in total ammonia concentration from 6.0 to 1.5 kg N m⁻³ resulted in a 4-fold increase in CH₄ production during AD of manure (Angelidaki and Ahring 1993, Rajagopal et al. 2013). At a volatile solids (VS) content of 45 kg m⁻³ manure and a non-inhibited yield of 0.2 m³ CH₄ kg⁻¹

VS, this would lead to a CH₄ yield potential of 9.0 m³ CH₄ m⁻³ manure, compared with an inhibited yield of 2.25 m³ CH₄ m⁻³ manure. Based on an energy content of 10 kWh m⁻³ CH₄ and an electrical efficiency of 40% for the CHP unit (Deublein and Steinhauser 2008, Szarka et al. 2013), this could give an additional 27 kWh of electricity per m³ of manure if the ammonia concentration is reduced from 6.0 to 1.5 g N L⁻¹. The removal of ammonia can be accomplished *via* electrochemical extraction, but comes at an estimated average cost of 14.6 kWh kg⁻¹ N, resulting in an additional electricity consumption of 65.7 kWh m⁻³ manure. Considering these aspects, the additional electricity produced through increased CH₄ production can cover only 41% of the energy required for ammonia removal and recovery.

This gap can be partially covered by the simultaneous cathodic production of H₂, which could reduce the actual energy consumption by 4.3 kWh kg⁻¹ N (Luther et al. 2015). In the case when this H₂ is used to upgrade the biogas to higher CH₄ levels, 53% of the energy gap could be covered, assuming an electrical efficiency of 40% for the CHP unit. The recovery of ammonia reduces the energy consumption of the aerobic post-treatment process, which, for example, corresponds to 6.3 kWh m⁻³ for manure. This is due to the lower electricity consumption for aeration in, for example, the anammox process (Maurer et al. 2003), which is commonly applied for the post-treatment of the liquid fraction of anaerobic digestate (De Vrieze et al. 2016c, Magri et al. 2013). This increases the energy coverage to 62 % for the overall process. The anodic production of O₂ could also increase CH₄ production through enhanced hydrolysis (Lim and Wang 2013, Xu et al. 2014b), but the magnitude of this effect is difficult to estimate. Similarly, the combination of the ammonia extraction cell with the digester could reduce the H₂S content in the biogas (Desloover et al. 2015, Zamalloa et al. 2013), thus, eliminating the need for additional biogas polishing, and contributing up to 10% of the biogas economic value (Abatzoglou and Boivin 2009, Munoz et al. 2015).

In this operational cost assessment, combining AD with an electrochemical extraction unit

565 appears to be favourable (Table 3), as a net energy production of 24.8 kWh per m³ (energy
566 coverage of 138%) of manure could theoretically be obtained. An important aspect lies in the
567 fact that the energy needed for the Haber-Bosch process is avoided, since ammonia is recovered.
568 The actual outcome will differ case by case, depending on, for example, the energy efficiency
569 of ammonia stripping, which can strongly differ as a function of the ammonia concentration
570 and desired removal efficiencies (De Vrieze et al. 2016c, Siegrist 1996). A thorough
571 comparison and evaluation of different strategies, both with and without a combined AD-(B)ES
572 is essential in finding optimal real-world solutions. The hybrid AD-(B)ES technology should
573 be (1) considered both in terms of operational and capital costs, and (2) compared with the
574 reference situation to determine its full-scale potential.

5. (Bio)electrochemical assistance of anaerobic digestion: real potentials vs. hypes

The strength of the AD-(B)ES combination resides in the complementary character of both technologies, as they occupy different niches for the treatment of solid and liquid waste streams (Arends and Verstraete 2012). The AD process can be considered as the technology *par excellence* for renewable energy recovery from organic waste streams (Verstraete et al. 2005), while (B)ES could serve as an assisting technology for (1) nutrient recovery, (2) effluent polishing, (3) biogas upgrading, and (4) process control. The presence of solids remains a possible issue for the AD-BES hybrid technology, which highlights the complementary of both technologies, and limits the applicability of (B)ES technologies in combination with AD to low-solids streams. To overcome the limits of surface-based catalysis, well-balanced approaches to increase available surface without resorting to a microporosity that would be obsolete, can be used. These include the application of conductive particles (Dang et al. 2016, Rotaru et al. 2018, Zhao et al. 2017) and 3-dimensional electrodes, yet, diffusion limitation and pore blocking are important issues, hampering, at present, widespread application (Santoro et al. 2017). To obtain high rates, high current densities are needed, *e.g.*, for CO₂ conversions, which coincides with high internal resistances and operational costs (Logan et al. 2006). Hence, a well-balanced decision should be made between a high-rate abiotic electrochemical unit that can operate at high salinities to reduce internal resistance or a biological system operating within certain boundaries, but that allows a more efficient and more targeted process, depending on the role of the BES in the digester. The versatility of (B)ES will allow them to replace existing technologies that are less cost- and energy efficient. For example, the electrochemical extraction of ammonia could outcompete classic stripping, and effluent polishing *via* a MFC could recover energy contained in the residual effluent COD, rather than oxidizing it to CO₂ *via* a conventional activated sludge process (Kim et al. 2015). The techno-economic potential for full-scale application will not only depend on the economic picture of the hybrid AD-(B)ES technology,

but also on the potential for retrofitting of existing AD plants. Electrochemical technologies that cannot compete with existing technologies will not make it to full-scale applications, and are at risk to be limited to specific niche or for research applications only. In contrast, those technologies that can outcompete existing technologies in terms of higher energy- and/or cost-efficiency, and that possess a strong potential for retrofitting, have real potential for (bio)electrochemical assistance of full-scale AD processes. In any case, it is recommendable that future studies include at least the power input per kilogram of product recovered and power input per additional cubic meter of CH₄ produced to allow overall prospect of any novel concept to be properly assessed.

6. Conclusions

Combining anaerobic digestion with (bio)electrochemical system allows the development and optimisation of hybrid systems, due to their complementary character. Although from a technical point of view multiple combinations are possible, upscaling feasibility and economic viability are crucial factors that determine the true potential of a full-scale hybrid technology. Hence, combining anaerobic digestion with a (bio)electrochemical system can be considered case-specific, due to a high variety of possibilities, and requires integrated engineering to tackle specific challenges.

619 **Acknowledgements**

620 Jo De Vrieze is supported as postdoctoral fellow by the Research Foundation Flanders (FWO-
621 Vlaanderen). Jan Arends is supported by the European Research Council *via* Starter Grant no.
622 310023 ‘ELECTROTALK’. Kristof Verbeeck is supported by FWO-Vlaanderen through a
623 Ph.D. scholarship. Korneel Rabaey is supported by Research Foundation Flanders (FWO-
624 Vlaanderen) project G018814N. The authors would like to thank Erika Fiset and Tyler Arbour
625 for critically reading the manuscript, and Tim Lacoere for his assistance with the graphics. All
626 authors declare no conflicts of interest.

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1069 **Table 1** Overview of various (bio)electrochemical strategies for ammonium and/or other cation removal and/or recovery before, during or after
 1070 the anaerobic digestion process. Power consumption is expressed per unit of nutrient (N or S) recovered and a negative sign indicates power
 1071 production. MFC = microbial fuel cell, MEC = microbial electrolysis cell, ED = electrodialysis, EC = electrochemical cell, NA = not available.

Main goal				Removal	Increase	CH ₄	Power consumption	Reference	
	Nutrient	Configuration	Cell mode	(%)*	production (%)		(kWh kg ⁻¹ product)		
N and S recovery	N	Pre-treatment	MFC	85-90	NA		-16.8	(Zhang and Angelidaki 2015b)	
N and S recovery	S	Pre-treatment	MFC	81-93	NA		-4.8	(Zhang and Angelidaki 2015b)	
N recovery	N	Pre-treatment	MEC	40-94	NA		NA	(Sotres et al. 2015)	
N recovery	N	Pre-treatment	ED	87	NA		4.94-5.95	(Ippersiel et al. 2012)	
N recovery	N	Pre-treatment	ED	NA	NA		NA	(Mondor et al. 2008)	
Reduce toxicity	NH ₃ N	<i>In situ</i>	MFC	40.8	112		-8.77	(Zhang and Angelidaki 2015a)	
								(Zhang and Angelidaki 2015c)	
Reduce toxicity	NH ₃ N	Side stream	EC	43-62	NA		13	(Desloover et al. 2012)	
Reduce toxicity	NH ₃ K	Side stream	EC	33-68	NA		NA	(Desloover et al. 2012)	

Reduce toxicity	NH ₃ N	Side stream	EC	28	450	17	(Desloover et al. 2015)
Prevent toxicity	salinity Na	<i>In situ</i>	MEC	NA	75.5	NA	(Zhang et al. 2012)
Effluent polishing	N	Post-treatment	MFC	77.5	NA	NA	(Kim et al. 2015)

1072 *Nutrient removal does not imply recovery in a usable form

1073 **Table 2** Overview of various (bio)electrochemical strategies for volatile fatty acid removal and/or recovery before, during or after the anaerobic
1074 digestion process. MFC = microbial fuel cell, MEC = microbial electrolysis cell, ED = electrodialysis, EC = electrochemical cell, NA = not
1075 available.

Main goal	Configuration	Cell mode	Removal (%)	Increase CH ₄ production (%)	Power consumption (kWh kg ⁻¹ COD removed*)	Reference
VFA removal	Side stream	MFC	0	0-3	NA	(Weld and Singh 2011)
Increase COD removal	<i>In situ</i>	Fixed redox	45-56	45-56	0.0028	(Sasaki et al. 2010)
Increase COD removal	<i>In situ</i>	MEC	7.1	NA	0.61	(Zhang et al. 2013b)
Increase COD removal	<i>In situ</i>	MEC	8.8	25	0.35	(Zhang et al. 2013a)
Effluent polishing	Post-treatment	EC	66-78	NA	1067-1234	(Qu et al. 2012)
Effluent polishing	Post-treatment	EC	75-88	NA	36-39	(Goncalves et al. 2012)

1076 *COD removed is considered as COD removal directly attributed to the (B)ES

Table 3 Overview of the estimated energy consumption and savings related to the extraction of ammonium from a manure digester. The calculations were made for a cattle manure stream, as described by Angelidaki and Ahring (1993). Energy consumptions are presented with a negative sign and energy savings with a positive sign.

Process step	Energy consumption/saving (kWh m ⁻³ manure)
Electrochemical NH ₄ ⁺ extraction	-65.7
Haber Bosch energy saving	49.5
Additional methane production	27.0
Electrochemical H ₂ production (40% efficiency <i>via</i> biogas upgrading)	7.7
Residual ammonia removal <i>via</i> partial nitritation/anammox	6.3
Net energy production	24.8

1083 **Figures:**

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1085 **Figure 1** Schematic overview of the various combinations and possibilities of an anaerobic
 1086 digester with a bioelectrochemical system for pre-treatment, *in situ*, side stream and post-
 1087 treatment of both digestate and biogas.

Figure 2 Schematic overview of the influence of water electrolysis, which leads to H_2 production at the cathode and O_2 at the anode. Depending on the buffer capacity of the mixed liquor, this can coincide with an increase in pH at the cathode and decrease in pH at the anode through the production of OH^- and H^+ , respectively. This allows the selective extraction of (a) cations through a cation exchange membrane and (b) anions and carboxylates through an anion exchange membrane for targeted resource recovery.