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Integrating BES in the wastewater and sludge treatment line

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19.1 INTRODUCTION

Traditionally, wastewater treatment has been a combination of physical, biological, and chemical treatment methods. Physical methods of treatment include settling and sand filtration, biological methods include aerobic activated sludge, denitrification, and anaerobic digester treatment systems, while chemical methods include phosphate removal, dye and endocrine disruptor removal, and disinfection systems. All of these methods have been adopted and optimized to...
raise the quality and clarity of the final effluent stream and to minimize the quantity and severity of pollutants and harmful pathogens to be released into the environment. Biological oxygen demand (BOD) and chemical oxygen demand (COD) levels in untreated municipal wastewater are typically low and the use of aerobic activated sludge systems has become a conventional treatment method in developed nations to reduce these levels even further to meet minimum quality standards (Tchobanoglous et al. 2003). Activated sludge systems rely on oxygen transfer from air into the mixed liquor, which conventionally is accomplished by large blowers that are energy intensive. Burton (1996) has estimated that aeration in activated sludge systems may account for 1% of all electricity consumed in the US. Thus, conventional treatment systems are not sustainable.

To make matters worse, activated sludge systems mainly convert soluble constituents to suspended biomass (i.e. waste activated sludge [WAS]), which can then be removed from the water by physical methods, such as settling. As a consequence, vast quantities of sludge accumulate in the treatment line and must be further treated or removed. Biomass in sludges can bio-accumulate toxic substances from the influent, making sludge treatment or biosolids reuse complicated (Rulkens 2008). Various methods have been proposed and utilized for circumventing the disposal of WAS, including treatment of influent or the accumulated sludge with anaerobic digesters (Rulkens 2008; Seghezzo et al. 1998). This is a more sustainable treatment method because methane in biogas can partly offset the energy consumption of conventional wastewater treatment. With the advent of BES we can now potentially transform chemical energy stored in organic substrates directly to electrical energy through bacterial metabolism even at conditions outside the optimum range for anaerobic digestion (Angenent et al. 2004; Logan 2005).

Here, we will discuss how BES may be integrated in the wastewater and sludge treatment line with the overarching goal to increase the sustainability of waste treatment. Each section represents a description of one or two plant flow diagram(s) in which a BES is utilized, which is also visualized in Figure 19.1 A–G. Each section heading indicates which flow diagram will be discussed (A–G). We realize that wastewater must be prepared before entering BES by, for example, screens, dissolved air flotation, or settling basins to remove solids. In addition, a buffer tank may be necessary to control pH (e.g. by recirculating cathode effluent) and to equalize fluctuations in wastewater flow and strength. We have omitted these pre-treatment steps in the flow diagrams (except for when the buffer tank is used as a preacidification tank). Many more variations of flow diagrams that include BES are possible, and our goal is merely to stimulate the reader’s imagination.
Figure 19.1. Flow diagrams of wastewater and sludge treatment line that incorporate BES. Each section in this chapter describes one or two of these alternatives (A–G)
19.2 BES AS THE SINGLE BIOLOGICAL TREATMENT UNIT (A) OR FOLLOWED BY AN ACTIVATED SLUDGE SYSTEM AS A POLISHING STEP (B)

The question of where to apply BES systems within the wastewater treatment line can be addressed through consideration of the anodic and cathodic bacterial metabolisms. Most research has been performed on bacterial metabolism in the anode compartment of BES where organic constituents can be oxidized with an electrode as the electron acceptor. Undefined mixed cultures that include electrode-respiring bacteria can metabolize a wide variety of organic substrates, including simple sugars, lipids, proteins, polysaccharides, and fatty acids (He et al. 2005; Heilmann and Logan 2006b; Huang and Logan 2008; Huang et al. 2008; Liu et al. 2005a; Min et al. 2005; Rabaey et al. 2003). Because of the metabolic diversity of undefined mixed cultures, BES systems have the flexibility to contribute to wastewater COD reduction in a variety of locations in the treatment line. Although oxygen may be the terminal electron acceptor at the cathode of BES, which is typical for microbial fuel cells (MFCs), most biochemical processes in the anode chamber proceed close to thermodynamic equilibrium, leaving little excess energy for biomass growth. The advantages of producing lower quantities of excess sludge compared to activated sludge systems and a potential for electricity generation (rather than energy consumption) make the technology attractive for secondary wastewater treatment (MFC instead of activated sludge) or as a pretreatment step to remove the bulk of organic constituents before activated sludge systems (Figure 19.1A and B).

The amount of electric power that can be generated from wastewater using BES depends on the number of electrons harvested from the oxidation of organic substrates within the wastewater. This number of electrons harvested is directly proportional to the COD removed and expressed as coulombic efficiency (CE) (Logan et al. 2006). In other words, the CE calculation evaluates the number of electrons captured versus the total number of electron equivalents released during the oxidation of wastewater constituents. At constant CEs, a higher COD concentration of the wastewater would result in a greater current density. Since the COD concentration of the wastewater flow decreases through the treatment line (not taking the sludge line into consideration), the introduction of BES at the start would be logical. However, CE levels for real wastewater treatment are generally low (Table 19.1). The relatively high CE levels for MFCs have been achieved with synthetic wastewater that was rich in carboxylic acid substrates (Table 19.2), such as acetate, which are directly usable by bacteria (Brock 1966).
Real wastewater consists of many constituents (either soluble or suspended) that are not directly usable by bacteria and that must be first hydrolyzed and digested in a food web. Examples include particulate and colloidal substrates, and hydrolytic processes to solubilize these constituents to easy-to-metabolize substrates are often rate limiting (Dimock and Morgenroth 2006; Ginestet et al. 2002). This results in a complex food web in the anodic compartment that will expend significant amounts of energy and time – energy that can never be recovered as electric power and time that results in the requirement of large reactor volumes – for microbial breakdown. Thus, significantly lower CEs for complex wastewaters that involve complex microbial food webs are anticipated (Marcus et al. 2007). Many bacteria in such a food web are, thus, not directly involved with electrode reduction (Liu et al. 2005a; Min and Logan 2004; Rabaey et al. 2005), which may lead to crowding of electrode-respiring bacteria that often require direct interaction with the anode. We have observed the formation of a thick biofilm on the electrodes of a 6-L MFC treating real brewery wastewater with vast quantities of suspended solids (data not shown).
This resulted in methane formation in the outer biofilm layers due to insulation of the electrode and the accumulation of particulate matter from the wastewater inside the anode chamber. Rabaey et al. (2005) also observed this latter phenomenon. A solution to this problem may be to screen solids more efficiently and to place a preacidification step before BES (Section 19.3), which is a conventional treatment step before high-rate anaerobic treatment of industrial wastewaters, such as brewery wastewater.

It is highly unlikely that oxidation of organic wastewater constituents in the anode chamber of BES will ever be a stand-alone technology (Figure 19.1A). First, the effluent BOD concentration may still be higher than the local regulations allow. Second, the anaerobic conditions of the anode chamber do not fulfill the requirements to support biological nutrient removal. In the case of nitrification/denitrification, a separate aerated reactor or zone is necessary to convert ammonia-N into nitrate-N (nitrification). However, denitrification may take place in BES as a cathodic process (Clauwaert et al. 2007) – see Section 19.6. In the case of phosphorus removal, no report has evaluated if this process occurs in BES. Some phosphate may diffuse from the anode chamber to the cathode chamber when an anion exchange membrane is present, but this is against the ionic forces and unlikely to be sufficient to meet discharge requirements. Thus, an aerobic/anoxic polishing step after BES may be required similar to conventional anaerobic digester implementation in the treatment line. Here, this is envisioned as an activated sludge process in the flow diagram after BES (Figure 19.1B).

19.3 PREACIDIFICATION OF ORGANIC WASTEWATER BEFORE BES (C)

Very high CEs have been achieved with MFCs for simple, easy-to-metabolize, organic substrates, such as acetate (Table 19.2). These higher CEs were reported because the anodic food web does not need to support hydrolysis and digestion of high-molecular-weight constituents compared to anodic food webs in MFCs treating complex wastewater. Rather, electrode-respiring bacteria can readily ingest and oxidize the simple organic substrates, regenerate reducing equivalents with anaerobic respiration processes, and deposit electrons to the anode electrode (Gregory et al. 2004; Lovley 2006, 2008). Thus, aside from meeting cell maintenance and growth energy requirements, the bacteria can efficiently transform the simple organic substrates into electricity. This will result in a less-complex food web, lower biomass concentrations, and a higher concentration of electrode-respiring bacteria in the anode. We can enforce such an efficient BES
by outsourcing the rate-limiting hydrolysis and digestion steps into a preacidification tank (Figure 19.1C). We anticipate that feeding mostly carboxylic acids rather than complex wastewater will increase CEs and kinetic rates, resulting in much smaller anode volumes.

Wastewater preacidification is a process commonly used to accelerate soluble organic constituent conversion and some hydrolysis. It is a required pretreatment step before upflow anaerobic digesters to prevent excessive growth of filamentous bacteria in the upflow bioreactor at high food-to-microorganism ratios, which can cause bulking of granular sludge (Alphenaar 1994). However, it must be realized that solids in the preacidification tank effluent can be high, which necessitates the use of a solids separation unit between the preacidification unit and BES. The residence time in preacidification tanks are typically short enough to prevent methanogenesis and to only promote carboxylic acid formation (i.e. acetate, butyrate, and propionate) from anaerobic microbial conversion of soluble organic constituents, such as sugars and proteins. Hydrogen and carbon dioxide gases are by-products of preacidification, and carbon dioxide increases the alkalinity of the wastewater by solution-gas equilibrium, limiting (to some extent) the pH drop associated with the formation of the carboxylic acids (often the pH level in the preacidification tank still must be equalized by, for example, circulating cathodic effluent; see Section 19.5). Finally, preacidification does slightly decrease the COD concentration of the wastewater, but this disadvantage will be greatly compensated for by the ease of carboxylic acid to electric current conversion (Figure 19.1C).

### 19.4 Anaerobic Digesters for Sludge Stabilization Followed by BES (D)

We have introduced WAS above, which is the biological product of activated sludge systems. Primary sludge is separated from wastewater up front of the treatment line by mechanical filtration and/or settling (Tchobanoglous et al. 2003). Often these two sludge streams are combined for further treatment in anaerobic digesters to lower the amount of biosolids and to recover energy (Kalyuzhnyi 2008; Rulkens 2008). For the purposes of this chapter, we will just focus on WAS treatment by a two-step process that consists of a thermophilic anaerobic digester system followed by BES (a combination of primary sludge and WAS could also be an excellent substrate for such a process). WAS is fed into the first phase in which hydrolysis removes solids and methane is formed. Next, separated carboxylic acids from the digestion effluent are introduced into the anode of the BES (e.g. MFC) to be converted into current (Figure 19.1D).
A lab-scale system that included anaerobic digester effluent flow into the anode of a MFC was reported by De Schamphelaire and Verstraete (2009).

Because much of WAS is particulate cellular material, thermophilic temperatures (55°C), which increase the rate of solubilization, have been reported to double methane production at an 8-day HRT compared to mesophilic temperatures (35–37°C), and achieve volatile solids (VS) removal efficiencies up to 40% (Lafitte-Trouque and Forster 2002). Thermophilic pretreatment of WAS with anaerobic digesters would also allow for sufficient pathogen removal to obtain biosolids that can be more easily dispersed into the environment (class A biosolids) (Han and Dague 1997; Welper et al. 1997). However, high temperatures contribute to increased accumulation of carboxylic acids (also often referred to as volatile fatty acids or short-chain fatty acids) due to higher concentrations of free ammonia and propionate, which can inhibit methanogenesis (Bocher et al. 2008; Lier 1996; Lier et al. 1993). In the past, this problem has been tackled by placing additional thermophilic methanogenic reactors/compartments in series or by placing a mesophilic anaerobic digester after the thermophilic unit to remove propionate. With the advent of BES, an ideal polishing step can convert carboxylic acids efficiently into current without limitations, such as hydrolysis and digestion, which were described in Section 19.3 (Pham et al. 2006; Rulkens 2008) (Figure 19.1D).

We performed a simple estimation of the potential for energy production and sludge reduction with thermophilic anaerobic digestion of WAS followed by polishing with BES (Figure 19.2). A typical WAS stream contains 90% particulate COD and 10% soluble COD. Here, we assume 40% hydrolysis of particulate COD from WAS in the anaerobic digester (Mahmoud et al. 2004), which is a conservative estimate under thermophilic conditions. Assuming a 90% conversion of hydrolyzed soluble COD and influent soluble COD to methane (for a thermophilic reactor), 4.6% of the original influent COD (particulate and soluble COD) is left as soluble COD in the digester effluent. A typical WAS stream contains about 30,000 mg total COD/l, and therefore a digester effluent stream with 1,380 mg soluble COD/l (mainly as acetate and propionate) could be separated from total solids and fed to BES. With an average 65% CE for carboxylic acids (Table 19.2), we predict a total of ∼ 900 mg SCOD/l going to electric current in BES (3% of the COD fed). Under these assumptions, the digester would convert 41.4% of the total COD present into methane. Then, the total energy recovery from WAS may be improved by 7.2% by integrating BES in the sludge line when compared to thermophilic anaerobic digestion alone.
19.5 GENERATING CAUSTIC IN THE CATHODE OF BES TO CONTROL ANAEROBIC DIGESTER pH (E)

BES systems balance the electron flow from anode to cathode by transport of ions across the ion exchange membrane to maintain electroneutrality. Unlike proton exchange membrane fuel cells, BESs operate in a near neutral pH range, and therefore electroneutrality is maintained with ions other than protons or hydroxide ions (Zhao et al. 2006). Because protons or hydroxide ions are not involved in BES electroneutrality, cathode pH increases are experienced (Fornero et al. 2008; Rozendal et al. 2006a; Zhao et al. 2006). The cathode pH increase results from the cathode oxygen reduction reaction, which can be represented either as consuming protons or generating hydroxide ions (Larminie and Dicks 2003).

\[
\text{O}_2 + 4 \text{e}^- + 4 \text{H}^+ \rightarrow 2 \text{H}_2\text{O} \quad \text{(Proton consumption)}
\]

\[
\text{O}_2 + 4 \text{e}^- + 2 \text{H}_2\text{O} \rightarrow 4 \text{OH}^- \quad \text{(Hydroxide generation)}
\]
Regardless of how the cathode oxygen reduction stoichiometry is represented, the net effect is an increase in the cathode pH, resulting in a pH gradient across the ion exchange membrane, which negatively impacts the BES potential by 0.059 V/pH according to the Nernst equation (Zhao et al. 2006). Also, electroneutrality can be maintained in two different ways: 1. with a cation exchange membrane for which cations are selectively transferred from the anode to the cathode; and 2. with an anion exchange membrane for which anions are selectively transferred from the cathode to the anode. It is now clear that the cathode pH increase occurs whether a cation or anion exchange membrane is used (Fornero et al. 2008). Thus, the catholyte pH requires attention independent of the ion exchange membrane selection (Fornero et al. 2008).

While an alkaline BES catholyte can negatively impact electric power, the accumulation of caustic in the catholyte can be beneficial to buffer preacidification of wastewater streams (Figure 19.1E) or some other process in the treatment line. For example, if BES uses a replenished catholyte, the alkaline catholyte produced by the oxygen reduction reactions can be discharged into the preacidification tank to partly compensate the pH decline from the production of carboxylic acids (see Section 19.3 for details on preacidification). Thus, a BES system used in parallel with high-rate anaerobic digestion can treat part of the preacidified wastewater stream and control the pH without the need of external alkalinity (Figure 19.1E). This may present a nice cost saving for the industry that is treating its wastewater by anaerobic biotechnology.

19.6 DENITRIFICATEATON IN THE CATHODE OF BES TO REMOVE NUTRIENTS FROM WATER (F)

Wastewater treatment systems typically not only employ biological treatment units to decrease the amount of organic carbon (activated sludge treatment and sludge conversion processes), but also to remove nutrients, such as soluble nitrogen. Conventionally, nitrogen is removed as molecular nitrogen in a two-step process: 1. reduced nitrogen species (i.e. ammonium) are oxidized by autotrophic nitrifying bacteria; and 2. generated nitrate is reduced to molecular nitrogen by heterotrophic denitrifying bacteria. Since denitrification is a reductive process, it can be coupled to reduction reactions with the cathode as an electron donor and microorganisms as biocatalysts (Figure 19.1F). For this cathodic process, the microbes perform autotrophic denitrification rather than the more conventional heterotrophic denitrification. The main advantage of using a biocathode to reduce nitrate is the absence of noble metal catalysts on the cathode (Clauwaert et al. 2007; He and Angenent 2006; Jia et al. 2008;
Virdis et al. 2008). In the wastewater treatment line, nitrate can originate from different sources. Examples include nitrate-rich industrial wastewater or ground water (Clauwaert et al. 2007); nitrate generation in activated sludge systems or other separate operation units from ammonium-rich waste streams; and nitrate generation in aerated compartments from ammonium-rich anode effluent from BES (Virdis et al. 2008). In the latter alternative, the anolyte becomes the catholyte after an additional treatment step. Then, the aeration and cathodic processes can act as additional COD polishing steps after anodic wastewater treatment. This may nearly eliminate the residual COD concentration of the anode effluent (Virdis et al. 2008; Fornero et al. 2008).

Using a denitrifying cathode system is advantageous for both the wastewater treatment process and BES beyond the circumvention of noble metal catalysts – anaerobic denitrifying cathodes omit the aeration of the cathode and/or the catholyte and, as a result, can prevent oxygen crossover from the cathode to the anode with negative effects on CE. Even though the theoretical potential difference for the organic substrate/nitrate couple is lower than the organic substrate/O2 couple (Clauwaert et al. 2007), solubility and catalytic advantages of nitrate compared to oxygen may guarantee a comparable measured potential difference.

In this section we have discussed that an autotrophic denitrification process can occur in the cathode with the electrode as the electron donor (Figure 19.1F). As part of an additional flow diagram, we have envisioned molecular hydrogen produced in BES cathodes as the electron donor for autotrophic denitrification in a separate process unit (Section 19.7). This may be the necessary flow diagram when the anolyte cannot become the catholyte due to incompatibilities in regard to, for example, conductivity. Regardless of the most advantageous configuration, the resulting autotrophic denitrification requires a much lower carbon/nitrogen ratio than conventional heterotrophic denitrification (step two for nitrogen removal mentioned above), which is a tangible advantage because alternative carbon sources, such as methanol, do not have to be procured. Additional advantages of autotrophic versus heterotrophic denitrification are: 1. prevention of organic carbon carryover to the final effluent, and 2. decrease in biomass yield, resulting in lower biosolids production (Rezania et al. 2007).

19.7 GENERATING CHEMICAL REAGENTS AT CATHODES FOR TREATMENT PURPOSES (G)

A recent development in the field of BES research has been the transition from power to chemical producing systems in which energy released from anodes is stored as chemicals in the cathode. It is possible to integrate the production of
some of these specific chemicals in the wastewater treatment line (Figure 19.1G). Here, the production of molecular hydrogen and hydrogen peroxide species and their application for the treatment process will be discussed:

*Molecular hydrogen* can be produced at the cathode of BESs by addition of a small voltage (> 0.2 V in practice) and maintaining an anaerobic cathode (Liu et al. 2005b; Rozendal et al. 2006b), according to the following reaction:

\[ 2e^- + 2H^+ \rightarrow H_2 \]  (Hydrogen generation)

This invention, which has also been called bio-catalyzed electrolysis, can produce hydrogen gas that can be utilized for wastewater denitrification purposes. With BES, the hydrogen required for denitrification can, thus, be produced *in situ*, which eliminates acquisition, shipment, and storage of hydrogen. Two process configurations can be used: 1. a single reactor configuration in which hydrogen generation and denitrification take place simultaneously in the cathodic chamber of BES (note the difference with the biocathode system – here hydrogen rather than the electrode is the electron donor); and 2. a two-step system where hydrogen is produced in a BES cathode and fed to an anoxic denitrification tank (Kiss et al. 2000) (Figure 19.1G). It is likely that the latter (two-step) process would be the preferred configuration due to microbial poisoning of the metal catalyst on the cathode.

*Hydrogen peroxide* can also be electrogenerated by incomplete cathodic reduction of dissolved oxygen (Brillas and Casado 2002; Duran Moreno et al. 2004; Figueroa et al. 2009). The H$_2$O$_2$ produced *in situ* can be activated by soluble Fe$^{2+}$ to produce a strong oxidant (Fenton’s reagent). This can be used for removal of hard-to-degrade wastewater components, such as dyes in textile wastewater (Figueroa et al. 2009) and environmentally toxic anilines (Brillas and Casado 2002). The choice of electrode material will be a key factor for the electro-production of hydrogen peroxide due to the sluggish kinetics, however, this process is considered a highly promising technique to deal with challenging contaminants. Thus far, only abiotic electrochemical cells have been employed to generate hydrogen peroxide, but a bioelectrochemical system that would already be integrated in other wastewater treatment processes (i.e. anodic processes), would be a perfect *in situ* generator of hydrogen peroxide at the cathode (Figure 19.1G).

19.8 OUTLOOK

BES technology integrated in the wastewater and sludge treatment line did not exist at full scale when this chapter was written. Even though, at the time, these
systems may have had potential to accomplish a more sustainable wastewater
treatment system, they may not (have) come to fruition due to scale-up problems
and a nonlinear power (rate) drop with increasing reactor volumes (Dewan et al.
2008). On the other hand, problems are there to be solved and BES may find a
niche beyond our present-day imagination. Generation of high-value products
from the electrons stored in the organic constituents of wastewater may make
BES sustainable, economical, and beneficial in wastewater and sludge treatment
lines. In addition, lowering the carboxylic acids concentrations in thermophilic
digester effluent with BESs, such as MFCs, may present a logical and feasible
alternative due to the presence of high concentrations of easy-to-metabolize
substrate. Gaining all the advantages of BESs by combining, for example, flow
diagrams D and G may be necessary to guarantee success.

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REFERENCES

Netherlands.

Angenent, L.T., Karim, K., Al-Dahhan, M.H., Wrenn, B.A. and Domínguez-Espinosa, R.
(2004) Production of bioenergy and biochemicals from industrial and agricultural

Anaerobic digestion of secondary residuals from an anaerobic bioreactor at a
321–329.


Brillas, E. and Casado, J. (2002) Aniline degradation by Electro-Fenton and peroxi-
coagulation processes using a flow reactor for wastewater treatment. *Chemosphere*


Management Opportunities*, Electric Power Research Institute, Inc. (EPRI),
Community Environmental Center, St. Louis, MO.

Clauwaert, P., Rabaey, K., Aelterman, P., De Schamphelaire, L., Pham, H.T., Boeckx, P.,


