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Opportunities for microbial electrochemistry in municipal wastewater treatment – an overview

Oskar Modin^{1*}, David J. I. Gustavsson²

¹ Division of Water Environment Technology, Department of Civil and Environmental Engineering, Chalmers University of Technology, SE-412 96, Gothenburg, Sweden

(E-mail: oskar.modin@chalmers.se)

² VA SYD, Box 191, SE-201 21 Malmö, Sweden

(E-mail: david.gustavsson@vasyd.se)

*Corresponding author: +46 31 772 2138

ABSTRACT

Microbial bioelectrochemical systems (BESs) utilise living microorganisms to drive oxidation and reduction reactions at solid electrodes. BESs could potentially be used at municipal wastewater treatment plants (WWTPs) to recover the energy content of organic matter, to produce chemicals useful at the site, or to monitor and control biological treatment processes. In this paper, we review bioelectrochemical technologies that could be applied for municipal wastewater treatment. Sjölunda WWTP in Malmö, Sweden, is used as an example to illustrate how the different technologies potentially could be integrated in an existing treatment plant and the impact they could have on the plant's utilization of energy and chemicals.

Keywords: Bioelectrochemical system; biogas; microbial electrolysis cell; microbial fuel cell; wastewater treatment

INTRODUCTION

Microbial bioelectrochemical systems (BESs) could potentially contribute to more sustainable treatment of municipal wastewater. In BESs, living microorganisms serve as catalysts for oxidation or reduction reactions on solid electrodes. This makes it possible to directly convert the chemical energy stored in dissolved organic matter in wastewater into electrical energy. However, production of electric power is only one of many possible applications. BESs could also be used for denitrification, generation of energy carriers and other valuable chemicals, or be used as sensors.

BESs can be classified as microbial fuel cells (MFCs), which generate electrical power, or microbial electrolysis cells (MECs), which consume electrical power to generate a valuable product. Examples of an MFC and an MEC are shown in Figure 1. Further details about the operating mechanisms of BESs can be found in several review papers (e.g. Logan *et al.* 2006; Rabaey *et al.* 2007; Rozendal *et al.* 2008b; Hamelers *et al.* 2009; Lefebvre *et al.* 2011; Pant *et al.* 2012).

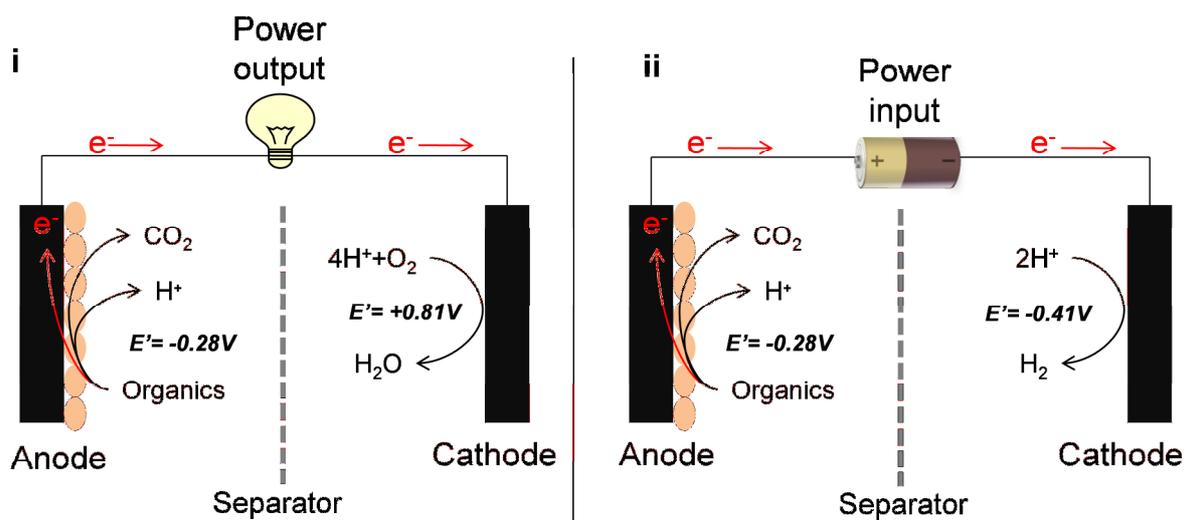


Figure 1. Examples of BESs illustrated by (i) an MFC generating electric power and (ii) an MEC generating hydrogen. E' represents the reduction potentials for the shown reactions at pH 7 assuming the organics are acetate. Theoretically, the maximum voltage output from the MFC is 1.09 V and the minimum voltage input to the MEC is 0.13 V.

BESs can be traced back to 1911 when it was noted that the microbial degradation of organic matter gave rise to an electromotive force in an electrochemical cell (Potter 1911). However, the discovery received relatively little attention during the 20th century, partly because of the low power output (Schröder 2011). The interest in BESs resurged at the turn of the century when it was shown that microorganisms present in wastewater could oxidise organics and generate current without the addition of external electron transfer mediators (Kim *et al.* 2001). This discovery together with a rising interest in sustainable technologies for energy, fuel, and chemical production in a time of growing concern about peak oil (Murray & King 2012) and global warming (Broecker 1975) has resulted in a tremendous increase in the number of scientific papers about BESs during the last ten years. However, today there are still no full-scale applications of BESs for municipal wastewater treatment. Thus far, the only well-known practical applications of BESs are the use of a benthic MFC to power a meteorological buoy (Tender *et al.* 2008), the use of MFCs to charge a cell phone (Ieropoulos *et al.* 2013), and the commercialization of an MFC-based sensor for biochemical oxygen demand (BOD) (<http://korbi.en.ecplaza.net/>). However, several start-up companies are trying to commercialize the technology (Pant *et al.* 2011).

For BESs to play a role in future municipal wastewater treatment plants (WWTPs), the technology must first be proven in existing plants. The goal of this paper is to review the different bioelectrochemical technologies that potentially could be integrated with an existing municipal WWTP. We use Sjölanda WWTP, located in Malmö in southern Sweden, as an example to illustrate how BESs could fit into the process solution of an existing plant.

OVERVIEW OF BIOELECTROCHEMICAL TECHNOLOGIES

MFCs generating electric power

Electric power generation using an MFC is the most studied BES application (Figure 1). Organic compounds are oxidized by microorganisms using the anode as electron acceptor. The electrons flow through an external circuit to the cathode where oxygen is reduced (Logan *et al.* 2006). Electrical energy can be recovered from the external circuit because the overall reaction, oxidation of organics and reduction of oxygen, is thermodynamically favourable. In

theory, the maximum voltage that can be generated in one MFC is around 1.1 V. In practice, the voltage will be lower because of internal losses such as activation overpotentials associated with the kinetics of electrode reaction, ohmic losses associated with electron transfer through wires and ion migration through the electrolyte, and concentration overpotentials associated with inefficient mass transfer of reagents and products near electrodes (Clauwaert *et al.* 2008a). Open circuit voltages as high as 0.8 V have been observed in an MFC operated with municipal wastewater (Ahn & Logan 2010). The operating cell voltage corresponding to the maximum power output will, however, be lower; it was around 0.38 V in the study by Ahn and Logan (2010). To produce practically useful voltages (~12 V), several MFCs have to be stacked in series which introduces additional challenges with voltage reversal in some cells (Aelterman *et al.* 2006b; Oh & Logan 2007).

The highest power density generated by an MFC is 2080 W m⁻³, which was achieved in a well-designed 30-mL reactor fed with a nutrient medium containing 100 mM acetate and 100 mM phosphate buffer (Fan *et al.* 2012). In general, higher power densities have been observed with nutrient media containing phosphate buffer and e.g. acetate as carbon source than with real wastewater (Pant *et al.* 2010b). A summary of the performance of single-chamber MFCs operated with real municipal wastewater is shown in Table 1. It should be noted that most of the studies were performed at elevated temperatures.

Table 1. Performance of single-chamber MFCs for electricity production using pre-settled municipal wastewaters.

COD influent (mg L ⁻¹)	Temp. (°C)	Area power density ^a (mW m ⁻²)	Volumetric power density (W m ⁻³)	Operating voltage (V)	COD removal (%)	CE ^b (%)	Reference
210-220	30	26	0.19	0.21	40-80	3-12	(Liu <i>et al.</i> 2004)
200-300	30	146	3.7	0.32	75	20	(Liu & Logan 2004) ^c
200-300	30	28	0.7	0.14	55	28	(Liu & Logan 2004) ^d
246	30	43-72	10.8-18	0.36-0.47	42-79	~6	(Min & Logan 2004)
300	25	103	5.8	0.25	71	18.4	(You <i>et al.</i> 2006)
255	30	464	15.5	0.34	40-50	27	(Cheng <i>et al.</i> 2006)
345	23	207 ^e	5.2	0.38	83	18	(Cusick <i>et al.</i> 2010)
440-490	23	177 ^e	5.4	0.25	23	38	(Ahn & Logan 2010)
440-490	30	170 ^e	5.2	0.25	33	26	(Ahn & Logan 2010)
671	22	42		0.23	28	0.71	(Nimje <i>et al.</i> 2012)
390	30	185	9.3	0.36	80	8.6	(Hays <i>et al.</i> 2011)
232±84	30	62-120 ^e	1.8-3.3	0.30-0.35 ^f	>90	15-22	(Ahn & Logan 2012)
232±84	30	19 ^{e,f}	0.5 ^f	0.26 ^f	52	6 ^f	(Ahn & Logan 2012)

^aBased on anode surface area unless otherwise specified

^bCoulombic efficiency, i.e. efficiency with which organic matter is converted into electrical current

^cOperated without a proton exchange membrane

^dOperated with a proton exchange membrane

^eBased on cathode surface area

^fCalculated from data given in the article

MFCs for denitrification

Conventional enhanced nitrogen removal at municipal WWTPs is the two-step process of autotrophic nitrification and heterotrophic denitrification. Typically, organic compounds in the wastewater are used as electron donors for denitrification. However, at low carbon-to-nitrogen ratios, dosage of external carbon source is needed. Autotrophic denitrifiers utilise inorganic sulphur or iron compounds, hydrogen, ammonia, or nitrite (Zumft 1997).

Sakakibara and Kuroda (1993) used electrolysis to produce hydrogen for autotrophic denitrification. However, denitrifiers can also directly utilise a cathode as electron donor

(Gregory *et al.* 2004). Clauwaert *et al.* (2007) demonstrated the concept of simultaneous anodic acetate oxidation and cathodic nitrate reduction from two separate liquid streams in an MFC. Virdis *et al.* (2008) used a single synthetic wastewater stream adding a separate nitrification step in the flow line between the anode and the cathode. However, ammonium diffusion from the anode compartment to the cathode compartment decreased nitrogen removal efficiency down to 67-70%. Virdis *et al.* (2010) improved their concept by promoting simultaneous nitrification and denitrification in the cathode compartment and increased the nitrogen removal to 94%. However, 29% of the nitrogen load was emitted as nitrous oxide (N₂O) making the removal unsustainable because N₂O is a very potent greenhouse gas (GHG) with a global warming potential (GWP₁₀₀) of 296 kg CO_{2e} kg⁻¹ N₂O (Forster *et al.* 2007), and the carbon footprint of the WWTP will be multiplied several times (Gustavsson & Tumlin 2013). Normal levels of N₂O emissions are below 1% of the nitrogen load (Kampschreur *et al.* 2009). Virdis *et al.* (2009) showed that the N₂O production could be minimised by decreasing cathodic potential in a system with a separate nitrification reactor. Xie *et al.* (2011) combined a regular MFC with a denitrifying MFC. Nitrification took place in the aerobic cathode of the MFC. The system removed 97.3% of the total nitrogen and produced power densities of 14 and 7.2 W/m³ in the regular and denitrifying MFCs, respectively. Zhang and He (2012) built an MFC consisting of an aerobic and a denitrifying cathode compartment connected to the same anode. All the studies cited above were conducted with various nutrient media prepared in the laboratory. Zhang *et al.* (2013) operated 4-L MFCs with real primary settled wastewater for over 400 days. They achieved 65-70% COD removal at 11-h hydraulic retention time. When a denitrifying MFC was connected, the total nitrogen removal reached 76%. Energy balances considering the energy requirements for pumping were positive for the MFCs operated without nitrogen removal with an output of 19 Wh kg⁻¹COD. With denitrification, the net energy balance was negative with a consumption of 53 Wh kg⁻¹COD .

Except for the risk of high N₂O emissions, nitrogen removal in an MFC has several positive aspects compared to conventional nitrogen removal: no large-volume recycling streams are required for pre-denitrification, electricity can be produced, no organic carbon is required for denitrification, and low biomass production due to autotrophic denitrification. As shown in the review above, various reactor configurations have been developed for denitrifying MFCs; however, few have been tested with real municipal wastewater.

MECs for production of energy carriers

Hydrogen

In an MEC, the energy content of dissolved organic matter can be recovered as hydrogen (Liu *et al.* 2005; Rozendal *et al.* 2006a; Logan *et al.* 2008). The operational principle is similar to an MFC. However, the cathode is kept anaerobic, which allows hydrogen ions to be reduced to hydrogen gas. The overall reaction, i.e. oxidation of organics and reduction of hydrogen ions, is thermodynamically unfavourable, which means that a voltage input is necessary to drive the reactions. In theory, a voltage of at least 0.13 V is required (Figure 1). In practice, an input voltage of at least 0.2 V will be needed (Call & Logan 2008). Compared to MFCs, MECs do not need a supply of oxygen to the cathode, which facilitates construction. On the other hand, a system to collect and process the produced gas is needed. Because MECs are operated with anaerobic cathode compartment, diffusion of oxygen into the anode compartment can be avoided and higher coulombic efficiencies are obtained (Cusick *et al.* 2010), which means that a larger fraction of the removed organic matter is used to generate current in the system.

Several studies have explored MECs for hydrogen production with nutrient medium containing acetate as feed to the biological anode. Such systems have achieved high energy efficiencies (i.e. energy content in the produced hydrogen relative to the input of electrical energy) of up to 406% (Call & Logan 2008). A few studies have been carried out with real wastewater (Ditzig *et al.* 2007; Cusick *et al.* 2010; Escapa *et al.* 2012; Heidrich *et al.* 2013). Cusick *et al.* (2010) used carbon fiber brush anode and Pt-catalyzed cathode in a 28 mL reactor operated at a cell voltage of 0.9 V. They achieved an energy efficiency of 104% and a H₂ production rate of 0.28 m³ m⁻³ d⁻¹. They also directly compared lab-scale MFC and MEC operation for energy recovery from municipal wastewater. Although the energy recovery was higher with the MFC (0.22 vs 0.14 kWh kg⁻¹COD for the MEC), the monetary value was higher for the MEC because of the high price of hydrogen compared to electricity (MEC: 0.19 \$ kg⁻¹COD, MFC: 0.021 \$ kg⁻¹COD) (Cusick *et al.* 2010). Both Escapa *et al.* (2012) and Ditzig *et al.* (2007) investigated various input voltages in mL-scale MECs and achieved good performance at 0.5 V. Heidrich *et al.* (2013) constructed a 120-L pilot-scale reactor containing electrode cassettes with carbon-felt anodes and stainless steel cathodes. The domestic wastewater fed to the reactor had a temperature of 13.5-21.0°C during the study period. The reactor was mostly run at an input voltage of 1.1 V. Pure H₂ gas was produced at 0.015 m³H₂ m⁻³d⁻¹ and 70% of the electrical energy input needed to run the reactor was recovered as H₂ gas. The net energy requirement for COD removal was 2.3 kJ kg⁻¹COD, which is comparable to typical values for activated sludge.

Methane

In MECs designed for hydrogen production, methane will often also be produced by hydrogenotrophic methanogens (Clauwaert & Verstraete 2009). This is usually considered a nuisance and different strategies have been employed to avoid methane formation (Wang *et al.* 2009); for example, periodic exposure of the reactor to air (Call & Logan 2008) or removing bicarbonate from the liquid medium (Rozendal *et al.* 2008a). However, MECs can also be designed to generate methane gas (Clauwaert *et al.* 2008b). It has been suggested that an MEC could improve combustion properties of biogas by mixing in some hydrogen (Aelterman *et al.* 2006a), which however may not be advisable if the biogas is upgraded to natural gas quality and sent to the natural gas pipe system since hydrogen-containing gas has different safety regulations. Although methane has a 20% lower energy value than hydrogen, many WWTPs currently have an infrastructure in place to valorize methane. Methane can be generated on the cathode indirectly via hydrogen or directly by biocatalysis (Cheng *et al.* 2009; Villano *et al.* 2010). There are no reports on methane MECs operated with municipal wastewater. However, in some wastewater-fed MEC designed for hydrogen production, methane has been a major constituent of the produced gas. In the first pilot-scale MEC trial, a 1 m³ reactor containing graphite fiber brush anodes and stainless steel mesh cathode was used to treat winery wastewater. During the startup of the reactor, gas production was low (0.09 m³ m⁻³ d⁻¹) and contained 33% H₂. After increasing the temperature of the reactor to 31°C and adding acetic acid, the gas production increased up to 0.28 m³ m⁻³ d⁻¹; however, in this latter phase of the experiment the methane content of the gas was 86% and hydrogen was not detected. Most of the biogas production was not associated with current, but was produced directly from organic compounds in the wastewater (Cusick *et al.* 2011).

Anaerobic digestion is often used at WWTPs for treatment of waste sludge and BESs could potentially be used to stimulate the activities of digesters. Sasaki *et al.* (2011) placed the cathode of a BES into an anaerobic digester and observed improved methane production and COD removal, as well as a higher ratio of methanogens to total prokaryotes suspended in the reactors. Guo *et al.* (2013) integrated both the anode and cathode with the anaerobic digester

and observed hydrogen production followed by improved methane production in the bioelectrochemically stimulated digesters compared to controls. By anodic oxidation of volatile fatty acids in the reactor, the pH could be maintained at a higher level and hydrogen generated at the cathode could be further converted into methane by hydrogenotrophic methanogens (Guo *et al.* 2013).

BESs for production of chemicals

Production and onsite utilization of alkali

In BESs, it is common to use cation exchange membranes (CEM) to separate the anode and cathode compartments. CEMs contain negatively charged groups fixed to the polymer matrix, which allow the transfer of cations through the membrane but exclude anions. When CEMs are used in BESs, transport of cations such as Na^+ , K^+ , NH_4^+ , Ca^{2+} and Mg^{2+} often dominate due to their high concentrations in wastewater (Rozendal *et al.* 2006b). This leads to a pH decrease (alkalinity consumption) in the anode compartment due to the acidifying oxidation of organics and a pH increase (alkalinity production) in the cathode compartment due to proton consumption by e.g. oxygen reduction to water or proton reduction to hydrogen gas. In MFCs this is usually considered a problem; however, the phenomenon could also be utilised to harvest an alkaline solution in the cathode chamber (Rabaey *et al.* 2010). An important aspect of this application is that the flow rate through the anode chamber must be much larger than the flow rate through the cathode chamber to avoid the development of a low anode pH that could negatively affect the biological activity. Rabaey *et al.* (2010) operated an MEC with fixed anode potential and acetate as electron donor at the anode. The system generated up to 1015 A m^{-3} anode volume, and produced an alkaline solution corresponding to 3.4 wt % NaOH at an energy input of 1.06 kWh kg^{-1} NaOH. When wastewater from a brewery was used as anode feed, currents up to 367 A m^{-3} were achieved and the alkali production was significantly lower.

Instead of producing a concentrated alkali, a BES could be used to redistribute alkalinity between process streams in a WWTP. Sludge liquor produced from the anaerobic digestion of sludge contains high ammonium concentration, which is often nitrified before being fed back into the treatment plant. Nitrification consumes alkalinity, which must be added, e.g. in the form of NaOH. Since the influent wastewater flow is much larger than the sludge liquor flow, alkalinity could be redistributed from the influent wastewater without a large change in concentration, to the sludge liquor where it could support nitrification. Modin *et al.* (2011) demonstrated this concept using synthetic wastewater and sludge liquor. The same concept can also be used to strip ammonia from sludge liquor and recover it in acid. In a study using real sludge liquor as catholyte, up to 79% of the ammonia could be recovered. Hydrogen generation was achieved simultaneously (Wu & Modin 2013).

Production of hydrogen peroxide

Hydrogen peroxide (H_2O_2) can be produced in the cathode of BESs by oxygen reduction (Rozendal *et al.* 2009). The reduction of O_2 to H_2O_2 has a standard reduction potential of 0.28 V at pH 7. This means that an MFC can drive the production of H_2O_2 without an external input of electrical power (Modin & Fukushi 2012). However, higher production rates can be achieved by applying a voltage. Rozendal *et al.* (2009) used an acetate-containing nutrient medium as anolyte and produced a 0.13 wt % H_2O_2 solution in the cathode chamber at an applied voltage of 0.5 V, which meant an energy input of 0.93 kWh kg^{-1} H_2O_2 . Modin and Fukushi (2012) also used an acetate-containing nutrient medium as anolyte and produced a H_2O_2 concentration of 0.5% with an energy consumption of 1.77 kWh kg^{-1} H_2O_2 . When they

switched anolyte to raw municipal wastewater, the current in the system dropped to about 20% of the value with acetate medium, and the produced H₂O₂ concentration was only 0.01% (Modin & Fukushi 2012). In a reactor with larger anode, a concentration exceeding 0.2% could be produced at an energy cost of 8.3 kWh kg⁻¹ H₂O₂ with real municipal wastewater as anode feed (Modin & Fukushi 2013). The studies cited above used gas-diffusion cathodes catalysed by carbon nanoparticles. Lower concentrations were produced using graphite rods submerged in the liquid (Fu *et al.* 2010). Fenton's reagent, which is a strong oxidant consisting of H₂O₂ and an iron catalyst, was generated in-situ in an MFC with an iron-containing cathode (Feng *et al.* 2010).

Reduction of CO₂

One of the most recent topics in BES research is microbial electrosynthesis (MES). This refers to the reduction of carbon dioxide by cathodic microorganisms to produce organic compounds (Centi & Perathoner 2009; Nevin *et al.* 2010). Abiotic electrochemical reduction of carbon dioxide has not proven practical, and using living microorganisms as cathode catalysts could be a way forward (Nevin *et al.* 2010). The anaerobic digester at a WWTP produces a fairly concentrated stream of carbon dioxide that potentially could be upgraded to a valuable chemical product. Cheng *et al.* (2009) reported that methanogenic microorganisms were capable of carbon dioxide reduction to methane using a cathode as direct electron donor. Villano *et al.* (2010) observed that methane was produced both by abiotically produced hydrogen via hydrogenotrophic methanogenesis and via direct extracellular electron transfer. Nevin *et al.* (2011) demonstrated that several acetogenic microorganisms can reduce carbon dioxide to acetate and other multicarbon compounds using a cathode as electron donor. A mixture of acetate, methane, and hydrogen was produced by a mixed microbial community enriched on a cathode (Marshall *et al.* 2012). Other chemicals that potentially could be produced include ethanol (Steinbush *et al.* 2010) and caproate (Van Eerten-Jansen *et al.* 2013).

Microbial electrochemical sensors

Biochemical oxygen demand (BOD) is an important parameter in WWTPs. It is a measure of the amount of biodegradable organics in wastewater and is used to dimension and assess treatment processes. The conventional method to measure BOD takes 5-7 days and requires skilled personnel. In WWTPs, the activated sludge process is used to remove dissolved organic material. Aeration of activated sludge represents a major energy cost, so optimization of this process is desirable for WWTPs. Because of the lack of reliable online sensors for BOD concentration, other parameters such as dissolved oxygen, water flow, total suspended solids, and air flow rates are used to control the activated sludge process (Hedegård & Wik 2011).

The MFC has emerged as an alternative to the conventional BOD test. In an MFC, microbes convert organic compounds directly into an electrical current, which is easy to measure. Thus, MFCs have been suggested as online sensors for BOD concentration (Kim *et al.* 2003a). Several types of MFC-based BOD sensors have been investigated. The correlation parameter (i.e. the parameter that is measured and correlated to BOD concentration) is either current (i.e. voltage over a resistor) or charge (i.e. coulombs transferred through a circuit for a specified time interval). In cases when the current is correlated with BOD concentration, the wastewater is fed continuously through the anode chamber of the MFC and the current is measured as the voltage across a resistor (e.g. Moon *et al.* 2004). In cases when charge is correlated with BOD concentration, the wastewater is fed batchwise to the anode chamber and the charge is calculated by integrating the current over a specific time interval (e.g. Kim *et al.* 2003a)

A summary of the MFC-based BOD sensors described in the literature is provided in Table 2. In most cases the measurable concentration range is up to a few hundred mg L⁻¹ and the response time ranges from a few minutes to several hours. The response time for a downshift step in concentration is usually longer than an upshift concentration change (Moon *et al.* 2004; Di Lorenzo *et al.* 2009a; Di Lorenzo *et al.* 2009b).

Table 2. MFC-based BOD sensors described in the literature.

Correlation parameter	Concentration range	Response time	Reference
Charge	< 206 mg L ⁻¹	30 min (6.45ppm), 10h (206.4 ppm)	(Kim <i>et al.</i> 2003a)
Charge	80-150 mg L ⁻¹	45 min	(Kim <i>et al.</i> 2003b)
Current	< 100 mg L ⁻¹	60 min	(Chang <i>et al.</i> 2004)
Current	Tested 50 & 100 mg L ⁻¹	5 min (upshift) 11 min (downshift)	(Moon <i>et al.</i> 2004)
Current	2-10 mg L ⁻¹	60 min	(Moon <i>et al.</i> 2005)
Charge	50-200 mg L ⁻¹	1 h	(Kim <i>et al.</i> 2009)
Current	25-25,000 mg L ⁻¹ glucose	3-5 min	(Kumlanghan <i>et al.</i> 2007)
Current	< 350 mg L ⁻¹	40 min (upshift)	(Di Lorenzo <i>et al.</i> 2009a)
Charge	< 500 mg L ⁻¹	2 h (downshift)	
Current	Tested 70 & 250 mg L ⁻¹	3.5 h (upshift) 14 h (downshift)	(Di Lorenzo <i>et al.</i> 2009b)
Current	17-78 mg L ⁻¹	30 min (at 17 mg L ⁻¹) 10 h (at 78 mg L ⁻¹)	(Peixoto <i>et al.</i> 2011)
Charge	32-1280 mg L ⁻¹	5-20 h	(Modin & Wilén 2012)

MFCs have also been investigated as toxicity sensors. Kim *et al.* (2007) investigated how organophosphorous compounds, Pb, Hg, and PCBs affected the electric current generation in an MFC. The additions of these compounds to the influent to the MFC inhibited current output. Patil *et al.* (2010) compared biofilm-based MFCs and planktonic cell MFCs as toxicity sensor. They found that planktonic cell were much more sensitive to toxic shocks and therefore more suitable as toxicity sensor. MFCs could also be used for real-time monitoring of anaerobic digesters. Liu *et al.* (2011) placed an MFC in an aerobic digester and monitored how the current was correlated with other parameters in the digester.

Other applications

BES could potentially play a role in phosphorous recovery at WWTPs. By utilizing the localized pH increased at the cathode, struvite could be obtained in a hydrogen-producing MEC (Cusick & Logan 2012). Fisher *et al.* (2011) used an MFC to mobilize phosphate from FePO₄ in sewage sludge for subsequent recovery as struvite.

BESs could also be a way of integrating municipal wastewater treatment with other processes such as desalination and solid waste management. By placing alternating anion- and cation exchange membranes between the anode and cathode in an MFC, water desalination can be accomplished in the central compartments (Cao *et al.* 2009). Such a system could be used as pre-treatment for a reverse osmosis process (Mehanna *et al.* 2010). BESs could recover metals such as copper on the cathode (Ter Heijne *et al.* 2010; Tao *et al.* 2011). Municipal solid waste

incineration fly ash contains high concentrations of various metals such as copper and zinc. The metals can be leached out from the ashes using acids. The dissolved organics in pre-settled municipal wastewater could be used to power electrolytic recovery of the metals from the leachate solutions (Modin *et al.* 2012).

INTEGRATING BESs INTO A WWTP

The primary goal of WWTPs is to treat wastewater to certain discharge limits. This can already be achieved with currently available technologies. Bioelectrochemical technologies could potentially contribute by reducing the net energy- or chemical consumption, or by providing better technology for monitoring processes at the plants. However, applying BESs at full-scale WWTPs is not trivial. Scale-up from the mostly laboratory-scale systems that have been investigated to date is an important issue. Moreover, we must consider which of the possible technologies will make the biggest contribution to a treatment plant, in terms of e.g. reduced energy or chemical consumption, at an acceptable cost.

Scale-up issues

Scaling up BESs is challenging and lower performance with larger reactors has been observed (Dewan *et al.* 2008). Issues related to scale up include cost of reactor materials, conductivity of electrodes and wastewater, performance in stacked cells, current densities with real wastewater, and stability of electrochemically active biofilms.

- *Cost of reactor materials:* Often materials used in laboratory-scale setups, e.g. carbon cloth and platinum-catalysed electrodes, are too expensive for full-scale wastewater application. However, alternatives exist and several researchers have investigated inexpensive electrode materials, catalysts, membranes, and current collectors (see e.g. Logan 2010; Pant *et al.* 2010a).
- *Conductivity:* Municipal wastewater has low conductivity compared to the nutrient solutions that have been used in most laboratory studies. This means that anode and cathode must be placed very close to each other to minimize ohmic losses related to ion migration. For example, at a wastewater conductivity of 1 mS cm^{-1} and a current density of 10 A m^{-2} , the ohmic losses would be 1 V per cm distance between anode and cathode. Furthermore, carbon materials, which are often used as electrodes, are 400-500 times less electrically conductive than copper and resistive losses can be high as electrodes as scaled-up. To solve conductivity issues related to scale-up, anode and cathode could be pressed against opposite sides of ion-conductive membranes and current collectors made of e.g. stainless steel could be integrated with carbon electrode materials.
- *Stacked cell performance:* Full-scale BESs would consist of many smaller reactors connected in parallel or in series. For example, stacks of MFCs electrically connected in series would be required to achieve practically useful output voltages. Because of certain variability in the capacity for current generation by individuals reactors in the stack, this could lead to voltage reversal in some reactors and long-term inactivation of the microbes (Oh & Logan 2007). This problem could be solved using various types of control circuits (Kim *et al.* 2011; Andersen *et al.* 2013). It is likely also beneficial to try to ensure that all reactors in a stack have the same hydraulic conditions and are fed with wastewater containing the same concentration of organic substrate.
- *Current density:* The highest current densities in BESs have been obtained with well-buffered nutrient media containing high concentrations of acetate (e.g. Fan *et al.* 2012). It is still unclear what current densities can be obtained with real municipal wastewater. The current density is an important parameter as it determines the required size of reactor.

- *Stability of biofilm:* Full-scale BESs should be operated for long time with stable performance. Research indicates that long-term (>5 years) stable performance of electrochemically active biofilms is possible (Kim *et al.* 2003a). However, further research on how electrochemically active communities respond over time to the varying conditions in municipal wastewater is needed.

Perspectives - using Sjölunda WWTP as an example

Sjölunda WWTP is used as an example to illustrate the possible impact of different BESs (details of the theoretical calculations carried out in this section are shown in the supplementary material). The plant has an average load of about 300,000 population equivalents (P.E.) (1 P.E. = 70 g BOD₇ person⁻¹ day⁻¹) and its process layout is shown in Figure 2 (Hanner *et al.* 2003). The discharge limits for BOD₇, nitrogen and phosphorus are currently 12 mg L⁻¹ (monthly average), 10 mg L⁻¹ (yearly average) and 0.3 mg L⁻¹ (monthly average), respectively. The electrical energy consumption at the plant is approximately 50 MWh d⁻¹, about 2,184 ton COD of carbon source is dosed annually to the post-denitrification reactor (mostly methanol), and about 900 ton yr⁻¹ of 50% NaOH is added to the sludge liquor nitritation reactor.

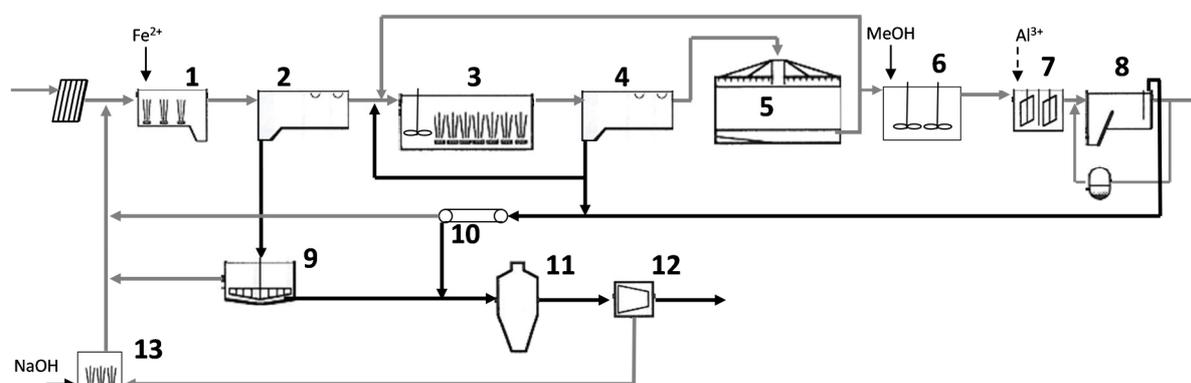


Figure 2. Simplified process layout for Sjölunda WWTP. The main stream is treated by (1) ferrous sulphate dosage for phosphorous precipitation, (2) pre-settler, (3) activated sludge with pre-denitrification, (4) secondary settler, (5) nitrifying trickling filters, (6) post-denitrification in moving bed biofilm reactors, (7) alum dosage and (8) flotation for removal of suspended solids. The sludge is thickened in a gravity thickener (9) or gravity belt thickener (10) and treated by mesophilic anaerobic digestion (11). The digested sludge is centrifuged (12) and the sludge liquor is treated in a separate nitritation reactor with NaOH dosing (13) before being fed back into the main treatment stages.

There are two process streams containing dissolved organic matter that potentially could be used as anode feed in BESs. The pre-settled wastewater has COD load of 40144 kg d⁻¹, which represents approximately 198 MWh d⁻¹ assuming an energy content of 17.8 kJ g⁻¹ COD (Heidrich *et al.* 2011). This is four times the current energy consumption at the plant. The other process stream of interest is the sludge liquor which contains 47.1 kg COD d⁻¹ as volatile fatty acids (VFAs). Although VFAs are ideal substrates for BES anodes, this stream only contains an energy content representing less than 0.5% of the total energy consumption at the plant. Therefore, to have a significant impact on the energy-efficiency of the plant, BESs should target the pre-settled wastewater. Currently, 2344 kg COD d⁻¹ in the pre-settled wastewater is used for denitrification of nitrate recycled from the trickling filters and nitrite from the reject water nitritation reactor. This leaves 37800 kg COD d⁻¹ to be oxidized aerobically in the activated sludge at an energy cost of about 0.4 kWh kg⁻¹ COD (Fig. 2, process 3). If 80% of this COD load could instead be utilized in BESs, the electrical energy savings in reduced aeration requirements would be about 12.0 MWh d⁻¹, which represents 24% of the plant's total consumption.

If the COD load currently being oxidized aerobically instead was utilised to generate electrical energy in MFCs at 20% energetic efficiency, 22.3 MWh d⁻¹ could be produced. Together with the savings in reduced aeration of activated sludge tanks, this means a total reduction in electrical energy consumption by 69% at Sjölanda WWTP.

The COD load could also be used to generate H₂ or CH₄. Since Sjölanda, like many other WWTPs, already is capable of valorizing methane gas, it may be advisable to initially focus on producing methane rather than hydrogen. Theoretically, 80% of the available pre-settled COD load could generate over 4 million Nm³ yr⁻¹ of methane gas which would more than double the current production (3.3 million Nm³ yr⁻¹). The biogas presently generated contains about 1,924,000 Nm³ yr⁻¹ of CO₂. Upgrading this to CH₄ in a MEC would only require 38% of the available COD load in the pre-settled wastewater. The electrical energy requirements to power MECs would be substantial. At an operating voltage 0.5 V, the additional electrical energy input required to bioelectrochemically convert 80% of the pre-settled COD load into CH₄ would be 38.7 MWh d⁻¹, which would increase the present energy consumption by 77%.

If MFCs for denitrification were implemented at Sjölanda WWTP, the existing trickling filter could be utilized for nitrification. The activated sludge tanks and the post-denitrification tank (processes 3 and 6 in Fig. 2) could be replaced with a MFC system. To denitrify the total load of nitrate from the trickling filters and nitrite from reject water nitrification reactor, 7633 kg COD d⁻¹ would be required. Since, the total COD load from the pre-settlers is 40,144 kg d⁻¹ aerobic MFCs could be operated in addition to the denitrifying MFC. Over 2,000 ton COD of carbon source currently used for post-denitrification could be saved every year.

The pre-settled wastewater could also be used to generate alkali or H₂O₂. The value and market for the produced products are difficult to predict because they will probably not have the same purity as commercially available products. However, both alkali and H₂O₂ could be used onsite at WWTPs and thereby replace presently used chemicals. In these BESs, ion exchange membranes would be used to separate the anode and cathode compartments and alkalinity concentration in the wastewater, rather than COD concentration, would limit the amount of chemical product that could be produced. Sjölanda's pre-settled wastewater has an alkalinity load of 593 keq d⁻¹ of which 329 keq d⁻¹ are needed to support nitrification in the trickling filters. This leaves 264 keq d⁻¹, which theoretically could be consumed in the production of concentrated alkali or H₂O₂. Sjölanda WWTP uses 462 ton yr⁻¹ of 100% NaOH to control the pH of the nitrification reactor treating sludge liquor. This could be generated onsite by extraction from the pre-settled wastewater. Only 32 keq d⁻¹, or 12% of the available load, would be needed to support the onsite demand. Another option would be to use onsite generated alkali to strip and recover ammonia from the sludge liquor (e.g. Wu & Modin 2013). H₂O₂ is currently not used at Sjölanda WWTP. However, if the plant was converted to a membrane bioreactor plant, e.g. to meet more stringent effluent requirements in the future, onsite generated H₂O₂ could be used for membrane cleaning. Assuming a daily maintenance backwash with 0.2% H₂O₂ and a backwash water to treated water volume ratio of 0.004 (Modin *et al.* 2010), 832 kg H₂O₂ d⁻¹ would have to be generated. This corresponds to 49 keq d⁻¹ of alkalinity consumption in the pre-settled wastewater, which is 19% of the available load, or 392 kg COD d⁻¹, which is only 1% of the available COD load.

BES-based sensors could be used to provide more information about the state and characteristics of treatment processes at Sjölanda WWTP. BOD sensors could give near real-time measurements of the concentrations of biodegradable organics going into and coming

out from the activated sludge process. BOD sensors could also be applied after the post-denitrification process as an extra warning system for excess carbon dosage. Sensors placed in the anaerobic digester could provide information on the VFA content of the sludge liquor. These sensors could be used as indicators of the digester's response to new feeds, for example if the treatment plant decides to accept new industrial or agricultural organic waste in addition to the sludge. Bioelectrochemical toxicity sensors could be used as warning systems upstream from the treatment plant to show whether wastewater with hostile characteristics, e.g. low pH, is on its way to the plant.

A comparison of the reviewed technologies is shown in Table 3. The magnitudes of the required current for application at Sjölanda give an estimation of the size of the different systems relative to each other. Although the exact size of BESs for full-scale applications are difficult to estimate based on the mostly laboratory-scale studies presented in the literature, it is clear that the MFC, MEC for CH₄, and denitrifying MFC processes will all be large systems. In comparison, BESs operated to fulfil onsite needs of alkali or H₂O₂ would be relatively small. The larger systems would potentially produce large economic savings for the treatment plant by reducing electricity consumption, increasing methane output, or eliminating the need for external carbon source (Table 3). However, the capital costs would also be higher.

The capital costs of BESs are difficult to estimate. However, based on the value of the generated products and savings in electricity and chemical consumption, maximum allowed capital costs per unit ampere to achieve a payback period of less than 10 years were calculated. For example, 3.3 € A⁻¹ for MFCs means that for a MFC system installed at Sjölanda WWTP to have a payback period of less than 10 years, the capital cost may not be larger than 3.3 € per installed unit ampere (assumptions used in these calculations are described in the supplementary materials). The MFC, MEC for CH₄, and denitrifying MFC processes have low allowed capital costs of 1.5-6.0 € A⁻¹. This is because of the low value of the produced products (electricity, methane, or methanol carbon source saved). BESs for alkali or H₂O₂ production have higher allowed capital costs because of the higher value of the products. The calculation was not carried out for bioelectrochemical sensors because they are assumed to have negligible size and cost compared to the other processes. The capital cost per unit ampere of a system would depend on the cost of the materials used and the current density obtained. In MFC systems the current density can be increased by decreasing the internal resistance whereas in MEC systems, the current density can be increased more easily, simply by increasing the applied voltage. Therefore, MEC systems may be closer to practical application (Sleutels *et al.* 2012). However, increased current densities would also increase internal losses and lead to higher operational costs.

It should be noted that more studies with pilot-scale reactors are needed to perform an accurate comparison of the economic and environmental benefits of different bioelectrochemical technologies at a full scale WWTP. However, the analysis in Table 3 suggests that implementing bioelectrochemical sensors or systems for covering onsite chemical needs would represent a smaller capital investment and possibly a shorter payback period. Thus, these systems potentially represent shorter paths of development towards full-scale application at WWTPs. Full-scale application of a bioelectrochemical technology at a WWTP would be an important step in the development of other BESs as well.

Table 3. Comparison of different bioelectrochemical technologies for application at Sjölanda WWTP (assumption used the calculations are described in the supplementary material).

Process	I (kA)	Allowed capital cost for a 10 year payback period (€ A ⁻¹)	Impact on the plant
MFC	4 221	2.4	Reduced electric power consumption by 69%, economic savings of 1001 k€ yr ⁻¹
MEC for CH ₄	4 221	1.5	125% increase in CH ₄ output, 77% increase in electric power, net economic savings of 634 k€ yr ⁻¹
Denitrifying MFC	1 065	6.0	2184 ton COD carbon source saved, economic savings of 634 k€ yr ⁻¹
BES for alkali	35.3	50.3	900 ton of 50% NaOH saved, economic savings of 178 k€ yr ⁻¹
BES for H ₂ O ₂	54.7	60.9	Useful if MBR plant and the H ₂ O ₂ can be utilized onsite for membrane cleaning
Sensors	~0		Better opportunities for monitoring and control of treatment processes

CONCLUSIONS

During the last decade, researchers have developed several bioelectrochemical technologies that potentially could be applied at WWTPs. MFCs and MECs could contribute to the energy efficiency of the plants by producing electric power or energy carriers from the organic content of pre-settled wastewater. Denitrifying MFCs could potentially contribute to energy-efficiency and also eliminate the need to add external carbon sources. BESs could produce alkali and H₂O₂, two useful chemicals at WWTPs, onsite. Bioelectrochemical sensors could improve the opportunities for monitoring and control of treatment processes. Although there are many opportunities for BESs at WWTPs, full-scale applications are still lacking. An analysis of the process flows at Sjölanda WWTP suggests that full-scale applications of bioelectrochemical sensors or BES for covering onsite chemical needs would need to deliver a significantly lower electrical current in comparison with MFCs and MECs for producing energy carriers. The former applications would therefore likely be smaller, have lower capital cost and higher value of produced products, and development of these may therefore represent a shorter path to demonstrate bioelectrochemical technology at full-scale in WWTPs.

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Supplementary material

Opportunities for microbial electrochemistry in municipal wastewater treatment – an overview

Oskar Modin and David J. I. Gustavsson

Integrating BESs into a WWTP: Theoretical calculations using Sjölunda WWTP as an example

MFCs for generation of electric power

Assuming 80% of the pre-settled COD load presently oxidized aerobically is used for current generation.

$$37800 \text{ kgCOD d}^{-1} \times 0.8 \times 0.4 \text{ kWh kg}^{-1}\text{COD} = 11981 \text{ kWh d}^{-1}$$

$$\text{Energy saved by reduced aeration} = 12.0 \text{ MWh d}^{-1}$$

$$37800 \text{ kgCOD d}^{-1} \times 0.8 \times 1000 \text{ g kg}^{-1} \times (8 \text{ gCOD mol}^{-1}\text{e}^{-})^{-1} \times 96485.3 \text{ C mol}^{-1}\text{e}^{-} \times (86400 \text{ s d}^{-1})^{-1} = 4221278 \text{ C/s}$$

$$\text{Current generated by the MFCs} = 4221 \text{ kA}$$

Assuming 1.1 V is the maximum theoretical output of a MFC and that they are operating at 20% energetic efficiency.

$$4221278 \text{ A} \times 1.1 \text{ V} \times 0.2 \times 24 \text{ h d}^{-1} \times (1000 \text{ W kW}^{-1})^{-1} = 22288 \text{ kWh d}^{-1}$$

$$\text{Power generated by the MFCs} = 22.3 \text{ MWh d}^{-1}$$

$$\text{Total electrical energy savings at the plant} = 12.0 + 22.3 = 34.3 \text{ MWh d}^{-1}$$

At present, the electrical energy consumption at the plant is 49.9 MWh d⁻¹.

$$\text{Reduction in electrical energy consumption by introducing MFCs} = 100\% \times 34.3/49.4 = 69\%$$

Assuming the price of electricity is 0.08 € kWh⁻¹ (Eurostat 2013).

$$34.3 \text{ MWh d}^{-1} \times 365 \text{ d yr}^{-1} \times 1000 \text{ kW MW}^{-1} \times 0.08 \text{ € kWh}^{-1} = 1000659 \text{ € yr}^{-1}$$

$$\text{Economic savings} = 1000.7 \text{ k€ yr}^{-1}$$

Assuming zero interest rate in the calculation of payback period.

$$1000659 \text{ € yr}^{-1} \times 10 \text{ yr} \times (4221278 \text{ A})^{-1} = 2.37 \text{ € A}^{-1}$$

$$\text{Maximum allowed capital cost for 10-year payback period} = 2.37 \text{ € A}^{-1}$$

MEC for methane production

Again, assuming 80% of the pre-settled COD is used for current generation.

$$\text{Energy saved by reduced aeration} = 12.0 \text{ MWh d}^{-1}$$

$$\text{Current generated by the MECs} = 4221 \text{ kA}$$

Assuming voltage input to the MECs is 0.5 V.

$$0.5 \text{ V} \times 4221278 \text{ A} \times 24 \text{ h d}^{-1} \times (1000 \text{ W kW}^{-1})^{-1} = 50655 \text{ kWh d}^{-1}$$

$$\text{Power consumption to drive MECs} = 50.7 \text{ MWh d}^{-1}$$

Overall increase in electric power consumption = 50.7 – 12.0 = 38.7 MWh d⁻¹
Percentage increase = 100% x 38.7/49.9 = 77%

Assuming methane is produced from current at 100% efficiency.
 $4221278 \text{ C s}^{-1} \times 86400 \text{ s d}^{-1} \times (96485.3 \text{ C mol}^{-1} \text{e}^{-})^{-1} \times (8 \text{ mol e}^{-} \text{ mol}^{-1} \text{CH}_4)^{-1} = 472505 \text{ molCH}_4 \text{ d}^{-1}$
 $472505 \times 23.6 \text{ L mol}^{-1} \times 365 \text{ d yr}^{-1} \times (1000 \text{ L m}^{-3})^{-1} = 4078671 \text{ m}^3 \text{ CH}_4 \text{ yr}^{-1}$
Amount methane produced by MECs = 4078671 m³ CH₄ yr⁻¹
Increase in plant's methane output = 100% x 4078671/3276000 = 125%

Assuming the value of methane is 0.046 € kWh⁻¹ (Eurostat 2013) and the energy content of methane is 0.2222 kWh mol⁻¹.
 $(472505 \text{ molCH}_4 \text{ d}^{-1} \times 0.2222 \text{ kWh mol}^{-1} \times 0.046 \text{ € kWh}^{-1} - 38700 \text{ kWh d}^{-1} \times 0.08 \text{ € kWh}^{-1})$
 $\times 365 \text{ d yr}^{-1} = 633673 \text{ € yr}^{-1}$
Economic savings = 633.6 k€yr⁻¹

Assuming zero interest rate in the calculation of payback period.
 $633673 \text{ € yr}^{-1} \times 10 \text{ yr} \times (4221278 \text{ A})^{-1} = 1.50 \text{ € A}^{-1}$
Maximum allowed capital cost for 10-year payback period = 1.50 €A⁻¹

MFC for denitrification

Assuming 100% utilization of the produced current for denitrification.
 $(2301 \text{ kgNO}_3\text{-N d}^{-1} \times 5 \text{ mol e}^{-} \text{ mol}^{-1} \text{NO}_3^{-} + 617 \text{ kgNO}_2\text{-N d}^{-1} \times 3 \text{ mol e}^{-} \text{ mol}^{-1} \text{NO}_2^{-}) \times (86400 \text{ s d}^{-1})^{-1} \times$
 $96485.3 \text{ C mol}^{-1} \text{e}^{-} \times 1000 \text{ g kg}^{-1} \times (14 \text{ g mol}^{-1} \text{N})^{-1} = 1065481 \text{ C s}^{-1}$
Current required to denitrify total NO₂⁻ and NO₃⁻ loads = 1065 kA

COD oxidation at anode
 $= 1065481 \times 86400 \text{ s d}^{-1} \times (96485.3 \text{ C mol}^{-1} \text{e}^{-})^{-1} \times 8 \text{ gCOD mol}^{-1} \text{e}^{-} \times (1000 \text{ g kg}^{-1})^{-1} =$
7633 kgCOD d⁻¹
Energy saved by reduced aeration = 0.40 x 7633 = 3024 kWh d⁻¹

Assuming the cost of methanol is 0.25 € kg⁻¹COD and that the amount of methanol carbon source saved at the plant would be 2184 tonCOD yr⁻¹.
 $2184 \times 1000 \times 0.25 + 3024 \text{ kWh d}^{-1} \times 365 \text{ d yr}^{-1} \times 0.08 \text{ € kWh}^{-1} = 634302 \text{ € yr}^{-1}$
Economic savings = 634.3 k€yr⁻¹

Assuming zero interest rate in the calculation of payback period.
 $634302 \text{ € yr}^{-1} \times 10 \text{ yr} \times (1065481 \text{ A})^{-1} = 5.95 \text{ € A}^{-1}$
Maximum allowed capital cost for 10-year payback period = 5.95 €A⁻¹

MEC for producing alkali

Assuming 462 ton yr⁻¹ of 100% NaOH is needed at the plant and that alkalinity can be produced at the cathode of a MEC with 100% current efficiency.
 $462 \text{ tonNaOH yr}^{-1} \times 1000000 \text{ g ton}^{-1} \times (40 \text{ g mol}^{-1})^{-1} \times 1 \text{ eq mol}^{-1}$
 $\times (365 \text{ d yr}^{-1} \times 86400 \text{ s d}^{-1})^{-1} \times 96485.3 \text{ C mol}^{-1} \text{e}^{-} = 35338 \text{ C s}^{-1}$
Current needed to be generated in the MECs = 35.3 kA

Alkalinity consumption at the anode = $462000 \text{ kgNaOH yr}^{-1} \times (40 \text{ g mol}^{-1} \times 365 \text{ d yr}^{-1})^{-1} = 31.6 \text{ keq d}^{-1}$
Fraction of wastewater alkalinity load consumed = 100% x 31.6/264 = 12.0%

COD oxidation at the anode
 $= 35338 \times 86400 \text{ s d}^{-1} \times (96485.3 \text{ C mol}^{-1} \text{e}^{-})^{-1} \times 8 \text{ gCOD mol}^{-1} \text{e}^{-} \times (1000 \text{ g kg}^{-1})^{-1} =$
253 kgCOD d⁻¹
Energy saved by reduced aeration = 0.40 x 253 = 100 kWh d⁻¹

Assuming 1 V input voltage to the MECs and that hydrogen is generated, which is subsequently converted to methane gas in the anaerobic digester at the plant.

$$1.0 \text{ V} \times 35338 \text{ A} \times 24 \text{ h d}^{-1} (1000 \text{ W kW}^{-1})^{-1} = 848 \text{ kWh d}^{-1}$$

$$\text{Power consumption to drive MECs} = 848 \text{ kWh d}^{-1}$$

$$\text{Overall increase in electric power consumption} = 848 - 100 = 748 \text{ kWh d}^{-1}$$

$$\text{Percentage increase} = 100\% \times 0.748/49.9 = 1.5\%$$

$$35338 \text{ C s}^{-1} \times 86400 \text{ s d}^{-1} \times (96485.3 \text{ C mol}^{-1}\text{e}^{-})^{-1} \times (8 \text{ mol e}^{-} \text{ mol}^{-1}\text{CH}_4)^{-1}$$

$$\text{Produced methane} = 3955 \text{ molCH}_4 \text{ d}^{-1}$$

Assuming value of NaOH is 0.4 € kg⁻¹NaOH.

$$462000 \text{ kgNaOH yr}^{-1} \times 0.4 \text{ € kg}^{-1} + 3955 \text{ molCH}_4 \text{ d}^{-1} \times 365 \text{ d yr}^{-1} \times 0.2222 \text{ kWh mol}^{-1} \times 0.046 \text{ € kWh}^{-1} \\ - 748 \text{ kWh d}^{-1} \times 365 \text{ d yr}^{-1} \times 0.08 \text{ € kWh}^{-1} = 177722 \text{ € yr}^{-1}$$

$$\text{Economic savings} = 177.7 \text{ k€yr}^{-1}$$

Assuming zero interest rate in the calculation of payback period.

$$177722 \text{ € yr}^{-1} \times 10 \text{ yr} \times (35338 \text{ A})^{-1} = 50.3 \text{ € A}^{-1}$$

$$\text{Maximum allowed capital cost for 10-year payback period} = 50.3 \text{ € A}^{-1}$$

MEC for producing H₂O₂

Assuming Sjölanda WWTP were to be converted to an MBR plant and the a daily backwash with 0.2% H₂O₂ solution was necessary for maintenance cleaning. The ratio between filtrate and backwash flows is 0.004.

$$104000 \text{ m}^3 \text{ d}^{-1} \times 0.004 \times 2000 \text{ gH}_2\text{O}_2 \text{ m}^{-3} = 832000 \text{ gH}_2\text{O}_2 \text{ d}^{-1}$$

$$\text{Amount H}_2\text{O}_2 \text{ that must be generated at the plant} = 832 \text{ kgH}_2\text{O}_2 \text{ d}^{-1}$$

Assuming H₂O₂ generation at cathode with 100% current efficiency

$$832000 \times (34 \text{ g mol}^{-1})^{-1} \times 2 \text{ mol e}^{-} \text{ mol}^{-1} \times (86400 \text{ s d}^{-1})^{-1} \times 96485.3 \text{ C mol}^{-1}\text{e}^{-} = 54654 \text{ C s}^{-1}$$

$$\text{Current needed} = 54.7 \text{ kA}$$

Assuming alkalinity is consumed at anode because an ion exchange membrane is used.

$$54654 \times 86400 \text{ s d}^{-1} \times (96485.3 \text{ C mol}^{-1}\text{e}^{-})^{-1} = 48941 \text{ eq d}^{-1}$$

$$\text{Fraction of wastewater alkalinity load consumed} = 100\% \times 48.9/264 = 18.5\%$$

$$\text{COD consumption at anode} = 48941 \text{ eq d}^{-1} \times 8 \text{ g eq}^{-1} \times (1000 \text{ g kg}^{-1})^{-1} = 392 \text{ kgCOD d}^{-1}$$

$$\text{Energy saved by reduced aeration} = 0.40 \times 392 = 157 \text{ kWh d}^{-1}$$

Assuming voltage input of 0.5 V needed to drive MECs.

$$0.5 \text{ V} \times 54654 \text{ A} \times 24 \text{ h d}^{-1} (1000 \text{ W kW}^{-1})^{-1} = 656 \text{ kWh d}^{-1}$$

$$\text{Power consumption to drive MECs} = 656 \text{ kWh d}^{-1}$$

$$\text{Overall increase in electric power consumption} = 656 - 157 = 499 \text{ kWh d}^{-1}$$

$$\text{Percentage increase} = 100\% \times 0.499/49.9 = 1.0\%$$

Assuming value of H₂O₂ is 1.14 € kg⁻¹ (US Peroxide 2013).

$$832 \text{ kg d}^{-1} \times 365 \text{ d yr}^{-1} \times 1.14 \text{ € kg}^{-1} - 462 \text{ kWh d}^{-1} \times 365 \text{ d yr}^{-1} \times 0.08 \text{ € kWh}^{-1} = 331534 \text{ € yr}^{-1}$$

$$\text{Economic savings} = 331.5 \text{ k€yr}^{-1}$$

Assuming zero interest rate in the calculation of payback period.

$$331534 \text{ € yr}^{-1} \times 10 \text{ yr} \times (54654 \text{ A})^{-1} = 60.7 \text{ € A}^{-1}$$

$$\text{Maximum allowed capital cost for 10-year payback period} = 60.9 \text{ € A}^{-1}$$

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