



Science for Environment Policy

FUTURE BRIEF:

Bioelectrochemical systems

Wastewater treatment, bioenergy and
valuable chemicals delivered by bacteria

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Environment

Introduction

Bioelectrochemical systems: Wastewater treatment, bioenergy and valuable chemicals delivered by bacteria

Globally, billions of euros are spent treating trillions of litres of wastewater every year, consuming substantial amounts of energy. However, this wastewater could act as a renewable resource, saving significant quantities of energy and money, as it contains organic pollutants which can be used to produce electricity, hydrogen and high-value chemicals, such as caustic soda. This can be achieved if the organic matter is broken down by electrically-active bacteria in an electrochemical cell, which, at the same time, helps clean up the wastewater. Examples of such 'bioelectrochemical systems' (BES) are microbial fuel cells (MFCs) and microbial electrolysis cells (MECs).

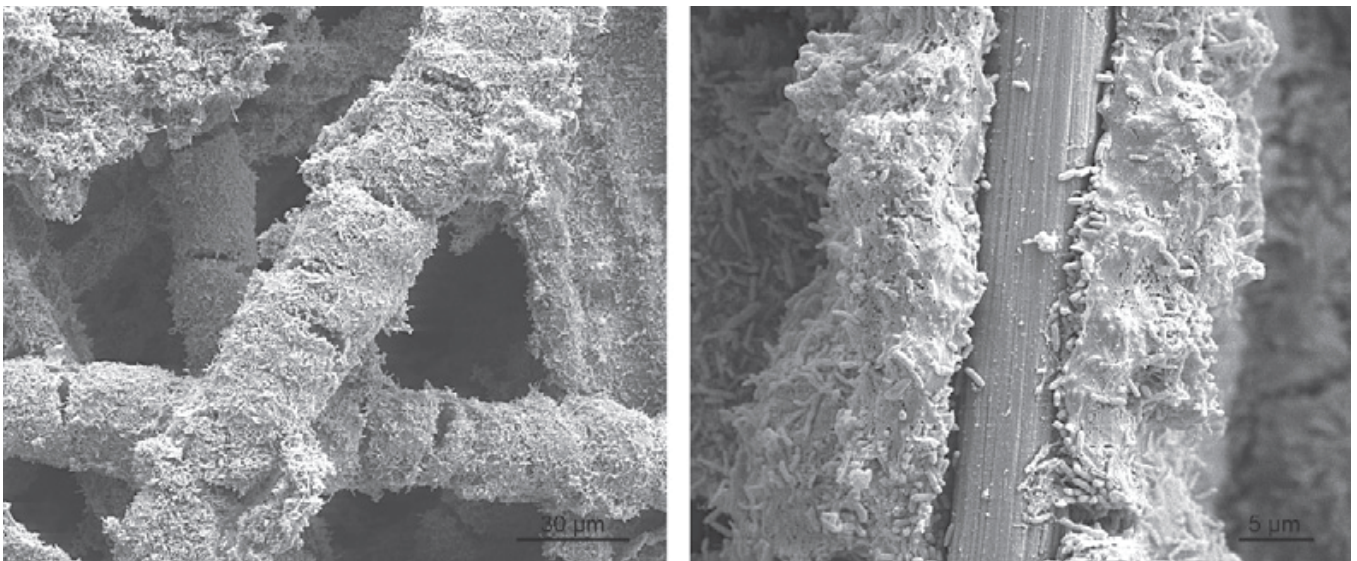


Figure 1. Scanning electron microscopic images of a mixed culture bioelectrocatalytic anodic biofilm derived from wastewater on a carbon fibre electrode, at different magnifications of 5 and 30 µm.

This Future Brief from Science for Environment Policy examines the use of BES to treat wastewater and generate electricity, hydrogen and valuable chemicals.

Although further work is needed to understand important biological and engineering issues that underpin the biotechnology, laboratory experiments have shown BES can work. So far, however, only a few pilot studies have been run in real-world conditions and more pilot studies and scaled-up demonstration projects are needed to prove the reliability of the systems. In addition, costs have to be competitive with other wastewater treatment and chemical production processes before the biotechnology can be adopted on a commercial scale. However, researchers are optimistic that commercial installations could be realised in two to five years' time.

Box 1: Wastewater treatment in Europe

EU Member States are obliged to collect and treat domestic and industrial wastewater from urban areas under the Urban Wastewater Directive¹.

Every year, wastewater is dealt with in plants across the EU with the collective treatment capacity equivalent to around 550 Million 'population equivalents' (European Commission, 2011). Population equivalent is a concept used in the wastewater sector, and is the theoretical measure of the organic pollutant load generated by a human being, and includes both domestic and industrial wastewater flow.

1. http://ec.europa.eu/environment/water/water-urbanwastel/index_en.html

1. Bioelectrochemical Systems: how they work

Microbial fuel cells (MFCs) and **microbial electrolysis cells (MECs)** are two examples of a rapidly developing biotechnology, generally known as **bioelectrochemical systems (BES)**, that combine biological and electrochemical processes to generate electricity, hydrogen or other useful chemicals.

MFCs and MECs are both types of electrochemical cells (batteries are another example). Electrochemical cells consist of two electrodes, an anode and a cathode, which are joined by an external wire to complete an electrical circuit.

MFCs are designed to produce electricity and MECs use electricity to drive chemical reactions at the cathode to produce hydrogen and/or other chemicals (see Figure 2). Both MFCs and MECs can achieve this by using wastewater and, in the process, can remove organic matter from the wastewater.

In an MFC and an MEC, special types of microorganisms (see Box 2), typically bacteria, break down organic material, as found in wastewater, at the anode under anaerobic (without oxygen) conditions. When breaking down the organic material, the bacteria release electrons (negatively charged particles), protons (positively charged hydrogen ions) and carbon dioxide into solution. The anode collects the electrons, which then travel to the cathode via an external circuit (i.e. an electric current can flow). The protons travel through the solution in the cell to the cathode. The carbon dioxide can be captured and reused.

In an MFC, electricity is produced by extracting it from the electron-carrying external circuit. The electrons arriving at the cathode under aerobic conditions, i.e. in the presence of oxygen, combine with the protons and oxygen, typically from the air, to form water.

An MEC is a modified MFC. If oxygen is excluded from the cathode, electrons released by the bacteria when breaking down the organic

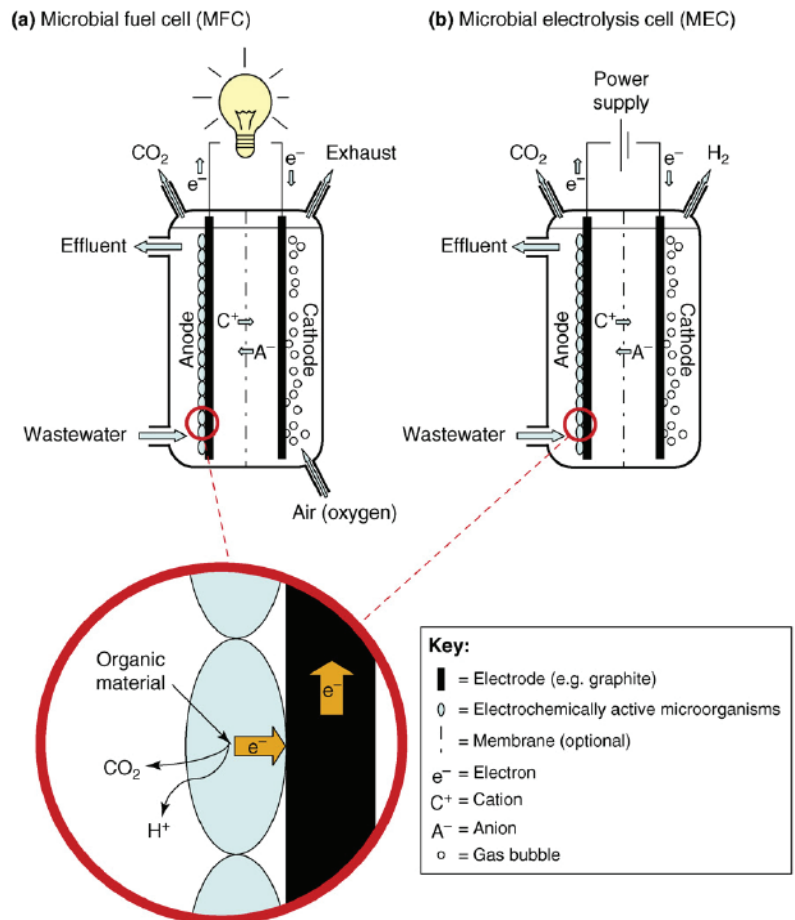


Figure 2. Bioelectrochemical systems using wastewater treatment as an example. Schematic representation of a typical configuration of the two most common bioelectrochemical wastewater treatment systems: (a.) the microbial fuel cell (MFC) (b) the microbial electrolysis cell (MEC) for hydrogen production.

matter that arrive at the cathode can combine with the protons to produce hydrogen. This reaction does not occur spontaneously and a small amount of external energy (in addition to that generated by the bacteria) needs to be added to the system (to drive this process). MECs can also be set up so that other, ideally high value, products such as caustic soda can be produced.

2. Recovering energy from wastewater

MECs and other types of BES have the potential to play a major role in developing sustainable urban wastewater systems that do not consume large amounts of energy, whilst simultaneously generating useful products, such as electricity and hydrogen (Rozendal *et al.*, 2008).

Substantial amounts of wastewater are also generated from industrial and agricultural sources and require treatment to remove organic matter before being released to the environment or being reused.

In the future, the cost of energy is expected to rise as a growing global population demands more energy. At the same time, the volume of wastewater from all sources will increase and the cost of wastewater treatment will also rise. In Europe, it is estimated that the market for municipal water and wastewater treatment is growing at a compound rate of 4.1% per year reaching a value of US\$3.09 billion in 2010 (Di Lorenzo *et al.*, 2009). Globally, wastewater treatment is estimated to be growing by 7% per year.

Box 2

Extracellular electron transfer: how microorganisms drive bioelectrochemical systems

One of the big challenges for researchers to overcome, before BES can be used commercially, is to improve the performance of the bacteria and the electrodes so that 'electron transfer' can be enhanced. This would lead to greater production of electricity, hydrogen or other chemicals.

Particular species of microorganisms (e.g. bacteria) that are able to release electrons from inside their cells to an electrode are at the heart of a BES. The way in which these electrically-active bacteria do this is called 'extracellular electron transfer' (EET) (Rozendal *et al.*, 2008; Harnisch *et al.*, 2011).

So far, two main methods of electron transfer have been identified: direct electron transfer from bacteria physically attached to an electrode, and indirect electron transfer from bacteria that are not physically attached to an electrode.

1) **Direct electron transfer** between the bacteria and the electrode can occur in two ways:

- a) when there is physical contact between outer membrane structures of the microbial cell and the surface of the electrode. These outer structures are also linked to inner structures of the microorganism, allowing electrons to be transported from inside the microbial cell, through the membrane wall and directly on to the electrode.
- b) when electrons are transferred between the microorganism and the electrode through tiny projections (called pili or nanowires) that extend from the outer membrane of the microorganism and attach themselves to the electrode. As nanowires can reach across tens of microns, microorganisms that are further away from the electrode can still maintain direct contact with the electrode.

2) **Indirect transfer of electrons** from the bacteria to an electrode occurs via long-range electron shuttle compounds (Velasquez-Orta *et al.*, 2010) that may be naturally present (in wastewater, for example), or may be produced by the bacteria themselves. Electrons are first transported to the bacterial cell surface and the shuttle compounds collect them and then transport them to the electrode.

By using one or more of these mechanisms to transfer electrons to the electrode, microorganisms are able to grow around the electrode, building up multi-layered films, called biofilms (see Figure 1). The larger the surface area of the electrode, the more possibility there is for bacterial films to develop. This in turn implies there is more possibility for electron generation, which in turn means a greater amount of electricity, hydrogen or other chemicals can be produced.

Organic waste in wastewater contains more internal energy than the amount of energy required to treat the wastewater. If that energy could be released, little or no extra energy would be needed during the treatment process. One study (Heidrich *et al.*, 2011) has conservatively estimated the amount of energy that could be contained in waste excreted by the world's population. For 6.8 billion people, there would be $2.2\text{--}4.4 \times 10^{18}$ joules of energy available each year, which could continuously supply 70-140 gigawatts of energy: this is equivalent to burning 52-104 million tonnes of oil in a modern power station, or 12-24,000 of the largest wind turbines working continuously. Although the composition of different wastewaters would vary, the same study estimated that the energy value of domestic wastewater could be 7.6 kJ per litre (kJ/L) and mixed industrial and domestic wastewater could be 16.8 kJ/L.

MECs would require little energy to treat wastewater and would simultaneously produce hydrogen or other chemical products. For wastewater treatment plants, the largest energy savings may come from reducing costs for aeration. In addition, as MECs operate under anaerobic conditions (without air), the production of sludge could be significantly reduced compared with the activated sludge process, which generates large amounts of sludge that has to be disposed of. MECs would thus considerably reduce costs associated with handling

and treating sludge waste. MECs also have other advantages: the biotechnology is suitable for treating low concentrations of organic matter in wastewater and can operate at temperatures below 20°C, where other methods to anaerobically decompose organic matter generally fail (Pham *et al.*, 2006).

A recent theoretical life cycle assessment (Foley *et al.*, 2010) has compared the environmental impact of three treatment options of industrial wastewaters: MFCs producing electricity for use onsite; MECs producing hydrogen peroxide e.g. as a bleach or disinfectant for use onsite; and the conventional anaerobic treatment with biogas produced as a by-product. Provided that the efficient industrial-scale development of BES can be realised, MECs offer the most environmental benefits of all three approaches, primarily through replacing the traditional production of hydrogen peroxide, which is a more energy-intensive process.

Other environmental benefits of using MECs to produce hydrogen peroxide come from reduced emissions of greenhouse gases and other pollutants, such as aromatic hydrocarbons, compared with the traditional production of hydrogen peroxide.

CASE STUDY 1

The goal: treating wastewater without using extra energy

A pilot plant MEC¹ is being used to treat mainly domestic wastewater and has been running in the UK for over 12 months, including the cold winter period, at the site of a commercial water utilities company.

The reactor is 100 litres in size and produces around 1 litre of almost pure hydrogen (under standard ambient conditions) every day.

Principally designed to determine if MEC technology is feasible at a larger-scale and in real-world conditions, the demonstration reactor was engineered to allow the electrically-active bacteria to cope with a variety of natural conditions.

This demonstration reactor has managed to recover 70% of the electrical energy put into it, in the form of hydrogen gas. With an improved design, it should be able to recover all of the input electrical energy, plus some of the energy from the sewage itself – making it ‘energy positive’.

The continued operation of the reactor over 12 months shows that the system can regulate itself and that the bacteria are able to cope with a variety of natural conditions. The growth of the electrically-active bacteria around the anode has formed a biofilm that is barely visible to the naked eye, demonstrating that there is almost no solid matter produced by the process. In comparison, conventional aerobic digestion produces large quantities of sludge and sludge disposal is an energetically expensive process. In addition, the electrically-active bacteria only use a small amount of the energy in wastewater for their growth.

Operating Conditions

For practical reasons, the hydrogen gas has been captured in plastic tubes, which then go into gas bags. As hydrogen is able to permeate through plastics, it is quite likely that up to 40% of the hydrogen being produced in the reactor has been lost through leakage. If some of the technology used by the hydrogen industry (e.g. for gas capture) was used, and if the system was fully sealed, it is likely that most of the hydrogen produced by the reactor would be collected.

Temperature

Although energy recovery dropped during the cold winter months, the system has demonstrated that wastewater can be treated at low as well as higher temperatures, within the range of 2°C up to 21°C. This saves energy as the wastewater does not require heating during treatment in the reactor.

Continuous flow

Wastewater flows continuously through the pilot reactor, just as in conventional wastewater treatment. This means that the treatment rate of the organic waste can be adjusted.

Retrofitting existing wastewater treatment plants

One of the potential advantages of this biotechnology is that it would be able to exploit the existing concrete structure of wastewater treatment plants. Wastewater infrastructure is expensive to build and is designed to last 50 years or more.

An MEC reactor could be retrofitted into the same size tank currently used in the activated sludge treatment process in an existing wastewater treatment plant and treat the wastewater effectively at the same rate.

Costs

The reactor has an energy cost of treatment of 2.3 kJ of energy per gram of COD (Chemical Oxygen Demand – an indicator of the amount of organic material in wastewater), compared with 2.5-7.5 kJ/g COD of energy required using the process of activated sludge. The energy cost of the reactor takes into account the 70% energy recovery in the form of hydrogen gas.

The pilot plant removes 0.14 kg COD/m³/day compared with 0.2-2 kg COD/m³/day removed by the current activated sludge technology. The organic waste removal efficiencies of the pilot would need to be increased for it to reach the constant levels needed in commercial plants, but this should be a matter of improved engineering. Building the reactor cost the equivalent of £2300/m³ (€2800/m³), but only 2% of this cost was for the cathode and membrane, typically the most expensive parts of the cell. The most costly element was the anode, followed by the plastic components. To keep costs down, the cheapest available materials have been used. Earlier work had suggested that any improved performance using more expensive cathode and membrane materials was not warranted for this reactor trial.

Exceeded expectations

The breakeven point for the reactor would be where the same amount of energy (electricity) that is put into the system is gained back from the energy carried in the hydrogen. Then the stage would be reached where the wastewater is treated ‘for free’, in terms of energy put into the system. For this reactor, around 70% of energy is recovered.

The nature of the technology potentially means that it is possible to recover all of the electrical energy and some of the wastewater energy that is put in, resulting in a net profit of energy.

1. *Personal communication with Professor T. Curtis and Dr. Heidrich*

Box 3

European Routes project

A European Union funded project, Routes¹, is investigating innovative ways to treat sewage wastewater and sludge. One of the options is to use MECs to optimally manage and minimise the production of sludge in municipal wastewater treatment plants.

The research aims to:

1. Explore the use of MECs as novel bioreactors for the treatment of low-strength wastewater (i.e. wastewater with a low concentration of organic material (<1 kg COD/m³) which makes the wastewater unsuitable for anaerobic digestion), in addition to minimising the amount of bacterial growth and subsequent production of sludge. It is not necessary for MEC technology to outcompete anaerobic digestion in terms of net energy recovery, rather that the net energy requirement and sludge production will be less than traditional technologies for treatment of low-strength wastewater (e.g. the activated sludge process).
2. MECs designed to produce methane could be used to refine the liquid and gaseous effluents of a conventional anaerobic digestion system (Villano *et al.*, 2012; Villano *et al.*, 2011). The liquid anaerobic digestion effluents mostly consist of diluted organic acids which are ideal foods for electro-active bacteria. In addition, continuously bubbling the biogas produced from anaerobic digestion through the MEC cathode will supply carbon dioxide for methane formation, which could be a strategy to refine biogas by increasing its methane content and so its energetic and economic value. Hence, coupling anaerobic digestion and MECs in the sludge line of a wastewater treatment plant will also contribute to a decrease in net sludge production while increasing the energy recovery.

The project started in May 2011 and will run until April 2014.

1. Routes: Novel processing routes for effective sewage sludge management (FP7- ENV- 2010) See: www.eu-routes.org

3. Hydrogen production from wastewater

MECs also offer a promising means of producing hydrogen fuel. Hydrogen is an energy carrier and is seen as an attractive source of renewable energy. When hydrogen is burnt, only heat and water are released. Hydrogen powered cars, for example, produce only water. Using hydrogen as a fuel source in a hydrogen economy is environmentally-friendly, providing the hydrogen is produced sustainably from renewable sources.

Currently, there are a number of ways to produce hydrogen. The majority of large-scale processes use fossil fuels and consume large amounts of energy. Water can be split to generate hydrogen and oxygen, but this is an expensive process which also requires large amounts of energy.

Hydrogen can also be produced by the bacterial fermentation of carbohydrates. However, the amount of hydrogen that can be produced is limited by the ability of the bacteria to completely breakdown the carbohydrate sources.

MECs can potentially produce large volumes of hydrogen from any organic waste material (Wrana *et al.*, 2010). Compared with

conventional fermentation processes, the electrically-active bacteria in MECs can produce four times more hydrogen (Liu *et al.*, 2005).

However, a small amount of extra energy needs to be added to an MEC to drive the production of hydrogen (Logan *et al.*, 2008) (see Section 1 'Bioelectrochemical Systems: how they work'), but the final energy balance of the process is positive, i.e. the energy contained in the obtained hydrogen offsets the energy initially needed to activate the process. If, in addition, the extra input energy to activate hydrogen production comes from clean and renewable sources, MECs could be a viable source of renewable hydrogen.

Wastewaters from a variety of sources, such as food processing industries, are suitable as feedstocks for MECs. When used in this way, treating wastewater may no longer be seen as a problem. Instead, with the help of these electrically-active bacteria, wastewater can be cleaned (provided, for example, that the removal efficiency of the organic waste is at the required level) and the organic matter in wastewater can be transformed into a source of hydrogen. (See Section 2 'Recovering energy from wastewater').

4. Cost-effective production of useful chemicals

In addition to producing hydrogen, an MEC can also produce other useful chemicals, such as sodium hydroxide, commonly known as caustic soda. Caustic soda is a key ingredient in many industrial processes. Large amounts are used, for example, in the pulp and paper industry

and to clean processing equipment in the brewery and dairy industries. It is currently produced by passing an electric current through a salt solution, an industrial process that uses large amounts of energy.

CASE STUDY 2

Producing hydrogen from winery wastewater

The first pilot-scale study (Cusick *et al.*, 2011) of an MEC using actual wastewater to produce hydrogen gas was carried out at a winery in California in late 2009.

Overall, the energy content of the gas produced by the MEC (which was in this case a mixture of hydrogen and methane) was greater than the electrical energy input to the system necessary to drive the production of the gas, despite the level of hydrogen recovery not being as high as anticipated. About 62% of the organic matter in the wastewater was removed by the electrically-active bacteria. If the technical and biological issues identified in this study can be resolved, the MEC technology could potentially become an important method for cleaning wastewater whilst simultaneously recovering energy in the form of hydrogen.

For the pilot, a 1000 litre reactor containing 144 pairs of anodes and cathodes was purpose-built to receive a continuous flow of winery wastewater.

Over a 100-day period, the current generated and the amount of gas produced was monitored and conditions were altered in response to the performance of the reactor.

Running the reactor at the winery has revealed a number of challenges that need to be overcome when scaling-up MEC technology from laboratory experiments.

Initially, the reactor was slow to start-up, taking 60 days to reach the state where gas production at the cathode was significantly increased. A number of factors probably contributed to this problem:

- conditions must be right for the electrically-active

bacteria to become acclimatised and established at the anode.

- in the real-world, the composition of the winery wastewater changed according to the different winery processes, which means the bacteria have to adapt to the changing conditions.
- continual operation of the reactor changed the acidity of the wastewater, creating less agreeable conditions for the electrically-active bacteria, which need near neutral conditions.
- keeping the temperature of the wastewater constant at about 31°C was essential to starting the reactor. However, once working, the system continued to operate (although at a lower level), even with a fall in temperature. Subsequent studies (Cheng *et al.*, 2011) have shown that power is produced in proportion to the operating temperature, once the biofilms have been formed (see Box 2).

In the pilot-scale reactor at the winery, about 86% of the gas collected at the end of the operation was methane. This compares with laboratory tests (Cusick *et al.*, 2010) using winery wastewater in an MEC operated over six days, where the composition of the collected gas was about 70% hydrogen, 26% carbon dioxide and 4.3% methane. The high methane content in the gas collected from the reactor could have been caused by the competing growth of methanogenic bacteria that are naturally present in the wastewater. Methanogenic bacteria reduce the yield of hydrogen by using the hydrogen to form methane.

In addition to the waste organic material, wastewater from the brewing and many other processing industries often contains high concentrations of sodium ions e.g. from using caustic soda in the equipment cleaning process.

The sodium ions migrate from the anode to the cathode during the

operation of an MEC. At the cathode, the electrons that have travelled through the external circuit reduce the water in the cathode to produce hydrogen and a weak sodium hydroxide (caustic soda) solution, which can be flushed out by flowing water through the cathode (Rabaey *et al.*, 2010b).

5. Challenges to scaling-up the technology

Experiments in the laboratory, often under controlled and ideal conditions, are the first step to understanding and improving new technologies. Proving that a new technology works reliably at a larger scale and for sustained periods of time in real-world conditions can be far more challenging, but is essential if commercialisation of the technology is to be realised. (Clauwaert *et al.*, 2008; Logan, 2010).

- Capitalising on the potential of these new technologies requires demonstration projects to scale them up from small projects to

commercial-sized pilots. Support is also needed for research into applications using real waste. At least one commercial installation would prove useful in demonstrating that the technology will work at a large enough scale.

- The size of the market should be assessed to complete the picture. To this end, a comprehensive study into the scale of the resource of wastewater across Europe could be useful.

Box 4

The European Union's Fuel Cells and Hydrogen Joint Undertaking (FCH JU)¹

In line with Europe's longer term objectives for a low-carbon economy² for 2020 and 2050, including decarbonisation of the transport sector, the mid-term target for hydrogen production is supplying up to 50% of the anticipated hydrogen energy demand (expected to come mainly from transport and early market applications) from renewable energy sources by 2020.

The MEC technology, when at a commercial scale, could potentially help achieve this objective.

In the future, several processes and feedstocks will be used to produce hydrogen. This will be either in centralised (large-scale) plants, which provide economies of scale or distributed (small-scale) plants that take advantage of locally available primary energy sources and feedstocks, with the benefit of generally improved sustainability and lower distribution infrastructure costs.

Here, the MEC technology would fall under the second category – small-scale plants. In addition, if successful, this technology could generally contribute towards an increased security of energy supply and independence of fossil fuels in the long-term.

1. See: FUEL CELLS AND HYDROGEN JOINT UNDERTAKING (FCH JU) Multi - Annual Implementation Plan 2008-2013 www.fch-ju.eu/page/documents
2. See: EU Energy Roadmap: http://ec.europa.eu/clima/policies/roadmap/index_en.htm. The EU Energy Policy to 2050 aims to reduce greenhouse gas emissions (by 80-95%, compared with 1995 levels, over the next 40 years), increase energy efficiency and the share of renewables in Europe's energy mix, whilst ensuring security of energy supply and economic growth and prosperity.

CASE STUDY 3

Caustic soda production using brewery wastewater

An Australian study (Rabaey *et al.*, 2010b) has been the first to demonstrate the use of MEC technology to produce caustic soda using actual brewery wastewater onsite at a local brewery.

Laboratory conditions

A one litre reactor was first operated in the laboratory using sodium acetate as the synthetic feed for the bacteria. This resulted in an overall yield for the conversion of acetate into caustic soda of 52%; with the bacteria consuming some of the acetate for their own growth.

Operation onsite at a brewery

After successfully demonstrating that the reactor could produce caustic soda under laboratory conditions, the same reactor was taken to a brewery and fed with a mixture of different wastewaters produced from various brewery operations, including cleaning of the processing equipment.

Under these real conditions, the organic pollutants in the wastewaters fluctuated during the course of a week as a result of different operational cycles in the brewery, which

meant that the bacteria had to significantly adjust to the variable feed conditions. This pilot plant one litre reactor successfully produced caustic soda.

Costs

Operated under laboratory conditions and including the input of energy to the system, the reactor produced low strength caustic soda at a cost of about US\$0.1 (€0.072) (2009 conversion rate) per kg of caustic soda.

At the time of the study in 2009, the market price of caustic soda was above US\$0.5 (€0.36) per kilogram. If capital costs are sufficiently low, this is potentially a cost-effective method of producing caustic soda, especially given that the caustic soda can be reused as a cleaning agent onsite.

An additional benefit is that the caustic soda recovered from the MEC is already diluted. Ordinarily, the pulp and paper industry, for example, buys concentrated caustic soda which needs to be further diluted before use. The process of dilution provides a risk to workers, for whom caustic soda burns are a leading cause of accidents.

- Wider studies on the full economic and life cycle costs of implementing the required changes to the wastewater industry would equally be useful, including feasibility studies. Ideally, this research should take place alongside scaling-up tests, finding new materials and investigations to improve our understanding of the bacteria's biology.
- Potential vehicles for technology testing by water utility companies could include two European Commission initiatives:
 - 1) **The European Innovation Partnership (EIP)** on water has the overall objective of supporting and facilitating '*the development of innovative solutions to deal with the many water related challenges Europe and the world are facing*', whilst also supporting economic growth by bringing these solutions to the market. See: http://ec.europa.eu/environment/water/innovationpartnership/index_en.htm
 - 2) Third-party verification such as **Environmental Technology Verification (ETV)** could help reduce the risks perceived by utilities. ETV has been developed '*to help innovative environmental technologies reach the market. It consists in the validation of the performance claims put forward by technology manufacturers, on a voluntary basis, by qualified third parties*'. This tool is designed to '*help manufacturers prove the reliability of their claims, and help technology purchasers identify innovations that suit their needs*'. See: <http://ec.europa.eu/environment/etv/index.htm>
- One of the challenges for the research community in the field of BES is to bring together researchers with a background in electrochemistry and electrochemical engineering with researchers with a background in biology and environmental engineering.

To summarise the main challenges of scaling-up the technology:

Capital costs are a big barrier. There are three ways to overcome this:

- Undertake cost engineering, i.e. make the system cheaper.
- Increase the density of current generated by the electrically-active bacteria. This would mean more electrons produced per cubic metre of reactor, which generates more product per cubic metre of reactor, and therefore results in more revenue per cubic metre.
- Change to a more valuable product. At the moment, the value of electricity produced in an MFC is less valuable than the value of hydrogen, which in turn is less valuable than some chemicals (e.g. caustic soda) which can be produced in an MEC.

Scaling-up requires:

- Better and cheaper materials
- A better understanding of the biological processes

6. The outlook

Development of MFCs to generate electricity has been the gateway for further applications of BES that could transform the way wastewater is treated and many chemicals, such as caustic soda, hydrogen peroxide and bioplastics, are produced.

- Initially, the technology is likely to evolve as a way of treating sewage, industrial or agricultural wastewater, not only lowering the amount of energy needed, but, at the same time, producing electricity, hydrogen or other chemicals of high value. Wastewater, when used in this way, provides both energy-saving benefits and high value products, and can be regarded as a resource rather than a problem requiring costly treatment.
- Given that the value of electricity is relatively low compared with the value of other forms of energy, such as hydrogen, and of chemicals that are expensive to produce, electricity production might not be the main aim of BES in the future (Harnisch *et al.*, 2011).
- For industrial wastewater treatment, individual industries do not necessarily need to invest in the hardware. On industrial estates, it would be feasible to establish a plant to process the wastewater from surrounding industries and sell the caustic soda or hydrogen peroxide, for example, back to the providers of the wastewater.
- BES are promising candidates not only for the production of

electricity, hydrogen and chemicals such as caustic soda, but also for the microbial production (bioproduction) of other fuels and chemicals, e.g. (Rabaey and Rozendal, 2010a):

Starting from carbon dioxide to produce organic compounds:

- methane (for fuel)
- bioplastics (e.g. poly- β -hydroxybutyrate)

Starting from organic compounds commonly found in industrial wastewaters:

- ethanol (used e.g. as a biofuel) from acetate
- butanol (used e.g. as a biofuel) from butyrate

- The efficiencies and yields of these processes, however, would need to be improved before they would be considered attractive enough to replace existing production methods.
- MFCs are also being explored as sustainable power supplies for robots ('gastro-bots') using biomass to generate electricity in artificial stomachs (Ieropoulos *et al.*, 2008). The goal is to develop autonomous robots that can produce their own energy from material collected from the environment, which is then processed in MFCs. In addition, MFCs are being used to power remote biosensors, such as tools for monitoring water quality. Sensors can be put in position and the collected data transmitted wirelessly. Batteries that have traditionally been used to power the sensors and data transmissions can be replaced with self-sustaining MFCs (Shantaram *et al.*, 2005).

- Recently, researchers in America have modified an MEC so that the extra power that is needed to drive the production of hydrogen at the cathode is self-generated. The reactor design uses alternative stacks of seawater and river water to take advantage of the small amount of voltage that is produced as atoms move from the seawater to the river water, driven by the difference in salt levels. This is sufficient to power the MEC, in theory, enabling a 'limitless' supply of hydrogen to be generated. However, there are a number of biotechnological barriers that first have to be overcome before this application would be feasible at the commercial level (Kim and Logan, 2011).
- The recent development of biocathodes (Rosenbaum *et al.*, 2011) (which have electrically active bacteria that accept electrons) has made development of BES for use in bioremediation a possibility. Bioremediation could take place at contaminated sites to clean up chlorinated hydrocarbons (used as industrial solvents and degreasing agents) that have contaminated soil or groundwater, nitrate pollution (mainly from agricultural fertilisers) in groundwater, and uranium pollution in soils and groundwater from nuclear energy production, weapons testing and mining (Harnisch *et al.*, 2011).

Overview

BES can produce energy from waste, by converting biodegradable organic matter directly into electricity, hydrogen or other valuable products. It is the bacteria's special ability to transfer electrons out of their cells to the anode that is at the heart of an MEC and an MFC. There is a huge range of organic wastes in wastewater, including human waste, agricultural waste and waste from food production, which can potentially be used in BES.

BES technology, particularly in the area of biological research, is changing very quickly, but many challenges remain and it could be two to five years before first generation technologies are available commercially. So far, nothing controversial with this technology has been identified and commercial uptake is expected to be driven by cost and reliability.

Currently, electricity is not valuable enough as an end-product to justify the costs of producing it using a BES system, i.e. the costs of the wires

and collectors outweigh the value of electricity produced. However, chemicals, such as caustic soda, are more valuable and the economic case for chemical production is stronger, especially if such products are produced and used locally.

The development and use of this technology for treating wastewater could be useful to help implement the EU regulatory framework on water (in particular the Urban Waste Water Treatment Directive¹, but also the Water Framework Directive²).

1. Council Directive 91/271/EEC of 21 May 1991 concerning urban wastewater treatment See: http://ec.europa.eu/environment/water/water-urbanwastel/index_en.html
2. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. See: http://ec.europa.eu/environment/water/water-framework/index_en.html

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Figure 2. Rozendal, R.A., Hamelers, H.V.M., Rabaey, K. *et al.* (2008) Towards practical implementation of bioelectrochemical wastewater treatment. *Trends in Biotechnology*. 26: 450-459

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