

Chapter 7

Bioelectrochemical Systems for Transforming Waste to Energy

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Abstract In recent years, BES has emerged as a new and promising approach for wastewater treatment. BES use microorganisms to convert chemical energy to electric energy and other value added chemicals. Compared to the conventional techniques available, it has evolved as a low energy intensive technology with an approach of integrated management of wastewater and recovering energy. This chapter presents a review on the different types of BESs with a brief discussion of their principle and anodic and cathodic reactions involved. Further, an overview is presented of recent work with different types of wastewater used as substrate, utilising different donors and acceptors of electrons involved and the various kind of electrodes used in various BES setups. BES is still a relevantly new and emerging field that deals with harnessing energy from wastewater with the potential to change the wastewater remediation techniques in future with gross positive energy recovery.

Keywords Bioelectrochemical system • Desalination • Energy generation • Wastewater remediation

Nomenclature

AEM	Anion Exchange Membrane
BES	Bioelectrochemical System
CEM	Cation Exchange Membrane
DCMEC	Dual chambered Microbial Electrolysis Cell
DCMFC	Dual Chambered Microbial Fuel Cell
IEM	Ion Exchange Membrane
MFC	Microbial Fuel Cell
MEC	Microbial Electrolysis Cell

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MDC	Microbial Desalination Cell
MSC	Microbial Solar Cell
PEM	Proton Exchange Membrane
PMFC	Plant Microbial Fuel Cell
SCMEC	Single Chambered Microbial Electrolysis Cell
SCMFC	Single Chambered Microbial Fuel Cell
TEA	Terminal Electron Acceptor

7.1 Introduction

Rapid industrialization and urbanization of the world has increased concerns for more energy demand, clean water supply and fresh and healthy environment for the better sustenance. The maximum portion of this energy comes from the non-renewable sources (e.g. fossil fuels) but the ever decreasing supply and increasing cost of fossil fuels has rendered researchers thinking lately of developing and discovering the sources of energy that are ever sustaining and are not going to end. These sources are the non-renewable sources like sun, water, wind and geothermal energy. The depleting fossil fuel however, is not the only concern. Global warming is also growing as a concern as the climate is changing abruptly that may be damaging to humans and other living forms alike. According to NASA, the global surface temperature has risen dramatically since year 2000 with year 2016 recorded as the warmest year (NASA 2016).

The increasing population and advancement in the lifestyle has lead to an increased development of different types of waste like industrial waste, municipal waste, agricultural and dairy waste. The conventional chemical methods of wastewater treatment such as ozonolysis serve the purpose but are cost intensive and not stable (Robinson et al. 2001). Other methods like chlorination tends to add an additional requirement of removing chlorine before disposing water into water bodies as chlorine affects the aquatic life. The traditional biological methods of water treatment like activated sludge process leads to a lot of sludge production (Wei et al. 2003), disposal of which is again a great issue.

With the rapid development of various sectors and increasing population, the demand for fresh water has increased tremendously. Even though the Earth is 75% water, most of it is saline and unfit for drinking and only 1% is available as fresh water. Most of this fresh water is trapped as glaciers and snowfields. It is estimated that by 2025, the population as high as around 1.8 billion people will be living in water-scarce areas with around 67% of the world's population living in water-stressed regions as a result of excessive usage, over population, and climate change (FAO-WATER 2017). To tackle this global menace, different methods are being employed like wastewater recycling, desalination. However, these methods are highly energy intensive (Al-Karaghoul and Kazmerski 2013). Thus, there is a high need for the development of methods that not only produce fresh water but uses lower energy expenses.

Energy is the driving force of the future global economy. To lift the world out of poverty, enormous energy is required to fulfill the need of the growing population. According to EIA, the energy consumption of the world is expected to increase by 48% by the year 2040 (U.S. Energy Information Administration 2016). To match the need of energy production and also making it more sustainable and environmental friendly, the renewable sources can serve as a better alternative to the non-renewable sources. In recent years, the method of producing energy from waste electrochemically is gaining a lot of focus from the researchers around the world. The electrochemically produced energy can not only alleviates the global energy crisis but at the same time help reducing pollution by treating waste. Unlike the traditional method of water treatment, bioelectrochemical systems (BESs) treats the wastewater with no or minimal expense of energy with the help of microbes.

7.2 What Is BES?

BES is a technology that combines the biological and electrochemical processes for waste remediation and side by side generation of value added products like electricity, hydrogen and other useful chemicals (Pant et al. 2012).

The basic principle of BES is the reduction of electron donor at anode by electrochemically active microbes, transferring the generated electrons from anode to cathode thereby generating electrical current (Harnisch and Schröder 2010). The output power efficiency of the BES depends upon the number of electrons recovered and transferred to anode.

7.3 Types of BES

BES is a combination of different types of technologies that involve the same basic principle of waste remediation with the help of microbes. But, the output of different BES technologies can be different. There are four major types of BESs namely Microbial Fuel Cell (MFC) wherein the final product is electricity from wastewater, Microbial Electrolysis Cell (MEC) wherein hydrogen is mainly generated at cathode, Microbial Desalination Cell (MDC) where desalination of saline water can be effectively performed, Microbial Solar Cell (MSC) where solar energy is utilised to produce electricity.

7.3.1 *Microbial Fuel Cell (MFC)*

MFC is a type of BES (Fig. 7.1) where microorganisms catalyse the oxidation of electron donors anaerobically at anode producing electrons and protons. These

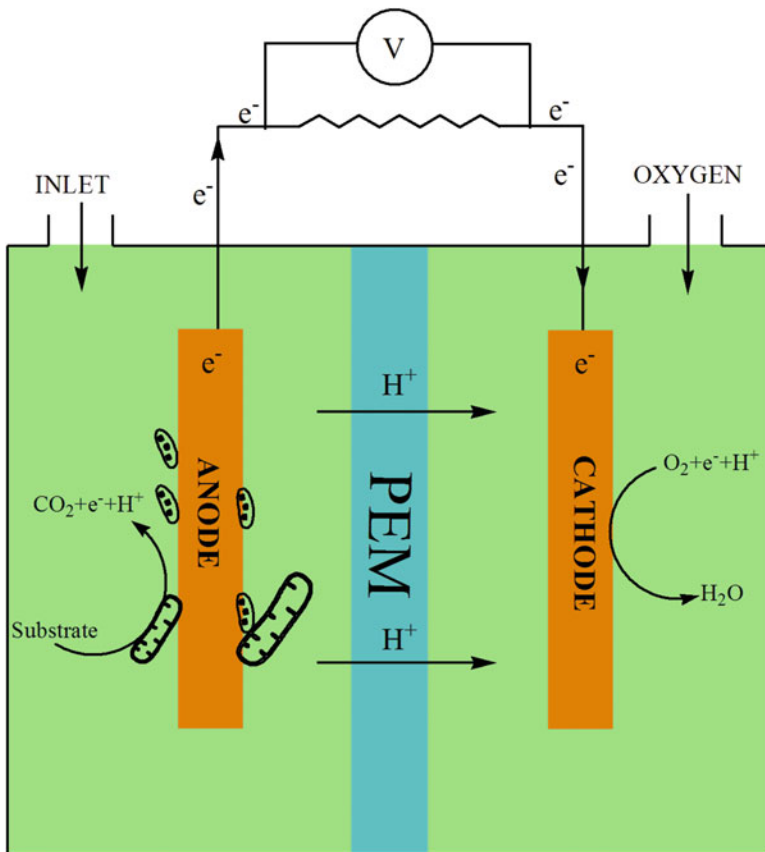


Fig. 7.1 Microbial Fuel Cell (MFC)

electrons flow across the external circuit reaching cathode and thus producing electric current. The electron acceptors in turn accept these electrons at the cathode (Logan et al. 2006; Khan et al. 2017). It has potential to substitute fossil fuels for generating electricity.

7.3.1.1 Components and Configuration of MFC

The main components of MFC include an anaerobic anodic compartment, an aerobic cathodic compartment, electrodes and a proton exchange membrane (PEM) separating the electrodes connected through an external circuit. The materials used as anode and cathode vary widely from graphite rods (Khan et al. 2015), carbon cloths (Elmekawy et al. 2014) to MWCNTs (Mehdinia et al. 2014), and other polymeric electrodes (Yong et al. 2012). However, carbon-based electrodes

are most common. The most commonly used PEMs are NAFION, ULTREX and ZIRFON (Elmekawy et al. 2014; Khan et al. 2015).

There are two main configurations of MFC viz. Single Chambered Microbial Fuel Cell (SCMFC) and Dual Chambered Microbial Fuel Cell (DCMFC).

SCMFC

In a SCMFC, anode is contained in an anaerobic compartment and cathode is directly in contact with the air either with or without a PEM. The anaerobic microbes release electrons and protons as they oxidise the substrate in the anodic chamber. The flow of these electrons through the circuit generates current.

DCMFC

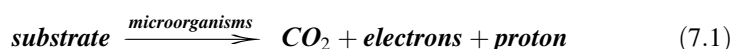
DCMFC consists of an anaerobic chamber for oxidation of the substrate and an aerobic chamber where reduction of electron acceptors takes place. PEM separates the two chambers. Microbes oxidise the substrate at anode releasing electrons and protons. The movement of these released electrons across the circuit generates current. The charge balance is maintained by protons diffusing through PEM to cathode where they are accepted by terminal electron acceptors (TEA) like ferri-cyanide (Rabaey et al. 2005). DCMFC has the advantage of simultaneous treatment of two different waste streams (ter Heijne et al. 2010).

7.3.1.2 Different Types of Anolyte and Catholyte in MFC

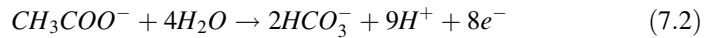
Various types of substrates can be utilised in MFC both as anolyte and catholyte. Anolyte may vary from glucose (Khater et al. 2015), acetate (Liu et al. 2005), cellulose (Rezaei et al. 2009), to phenol (Luo et al. 2009), synthetic and real wastewater (Elmekawy et al. 2014). However only oxygen can act as catholyte in case of SCMFC but in case of DCMFC, many different types of electron acceptors can be utilised as catholyte like copper (ter Heijne et al. 2010), chromium (Tandukar et al. 2009; Gupta et al. 2017), dyes (Han et al. 2015) and sulphate (Zhao et al. 2008) etc.

7.3.1.3 Anodic and Cathodic Mechanism Involved in MFC

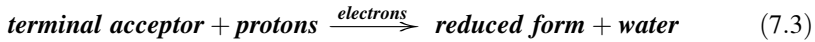
Since MFC is a BES, its mechanism simply involves redox reaction taking place at anode and cathode. Microorganisms under anaerobic conditions provided in the anodic chamber of both single and dual chambered MFC catalyse the reduction of substrate added to release electrons and protons. This can be represented as:



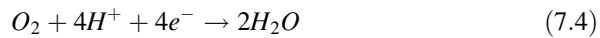
E.g. If acetate is present as electron donor,



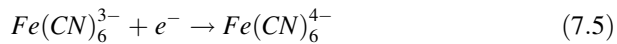
At cathode, reduction of oxygen or TEA takes place. This can be represented as:



E.g. If oxygen is TEA:



If ferricyanide is taken as TEA:



7.3.2 Microbial Electrolysis Cell (MEC)

Hydrogen is considered as a source of green energy with zero pollution. Hydrogen is basically obtained by three main methods: from fossil fuels by thermochemical processes, by water electrolysis and by biological process like dark fermentation. However the energy recovery from dark fermentation is rather low while the other two processes are costly. MEC is considered an advanced version of MFC and can serve as an alternative to cleaner hydrogen production.

MEC (Fig. 7.2) can be defined as a technique that utilises wastewater and produce hydrogen by the catalytic action of microorganisms in the presence of external power and fully anoxic conditions. The microbes oxidise the substrate at anode releasing protons which undergo reduction to release hydrogen at cathode. Cucu et al. suggested there can be two modes of hydrogen production in MEC by either applying negative polarisation on anoxic cathode or by applying negative polarisation on microbial biofilm at anode (Cucu et al. 2013). An external voltage of over 0.14 V is ideally required for hydrogen production (Rozendal et al. 2006).

7.3.2.1 Composition and Configuration of MEC

MEC, just like MFC is composed of two chambers but unlike MFC, here both chambers are maintained under anaerobic conditions. It also contains an anode, a cathode, a PEM separating the two chambers. The electrodes used can be graphite felt (Escapa et al. 2012b), graphite granules (Batlle-Vilanovaa et al. 2014), graphite brushes (Cheng and Logan 2011) beside many others.

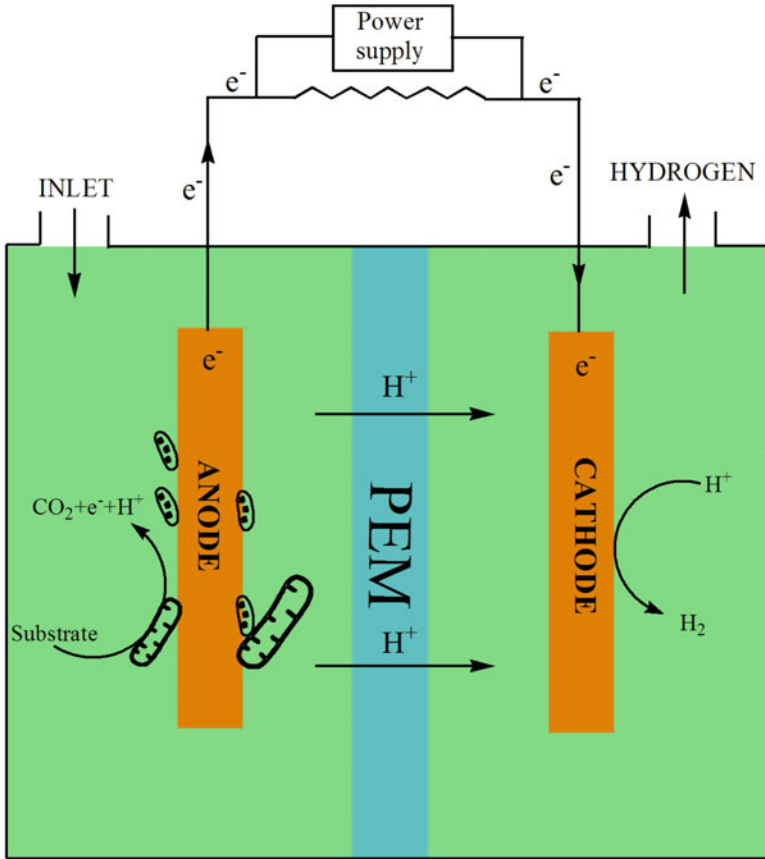


Fig. 7.2 Microbial Electrolysis Cell (MEC)

Just like MFC, the two main configurations of MEC are:

SCMEC

In this type of setup, a single chamber lacking a membrane encloses both anode and cathode under anaerobic conditions. The microbes act on substrate producing protons and electrons at anode. These generated protons are reduced to hydrogen at cathode by the application of external potential over it.

DCMEC

DCMEC is composed of separate anodic and cathodic chambers connected through PEM, both under the anaerobic conditions. The microbes in the anodic chamber act on substrate liberating electron and protons at anode. The released protons are diffused to cathodic chamber via PEM and electrons through external circuit where protons get reduced to hydrogen.

Both SCMEC and DCMEC can utilise variety of substrate to produce hydrogen but SCMEC is considered more economical for high hydrogen production rates as suggested by Call and Logan (Call and Logan 2008).

7.3.2.2 Different Types of Anolyte and Catholyte in MEC

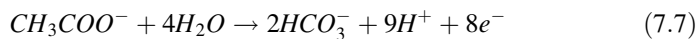
Variety of substrates can be utilised in MEC as anolyte like acetate (Cheng and Logan 2011), glycerol (Escapa et al. 2009), domestic wastewater (Escapa et al. 2012b) etc. Unlike MFC, MEC contains anaerobic cathode where catholyte can be abiotic with only hydrogen being produced by reduction of proton in the presence of metal catalyst like platinum on cathode or it can be biotic where substrate like sulphate (Luo et al. 2014a), sodium bicarbonate (Jeremiase et al. 2010) and metal ions like Cd (II) (Chen et al. 2016) can be reduced along with hydrogen production.

7.3.2.3 Anodic and Cathodic Mechanism Taking Place in MEC

At anode, oxidation of electron donor takes place. This step is similar as MFC.



E.g. If acetate is present as electron donor:



At cathode, under anoxic conditions reduction of protons generated at anode takes place.



7.3.3 Microbial Desalination Cell (MDC)

With the growing population and industrialisation, the demand for fresh water has increased drastically and this calls for the need to desalinate the sea water or brackish water. The techniques available for desalination e.g. reverse osmosis, electrodialysis and distillation are highly energy exhaustive. A new method has evolved from the so called BESs, which is popularly known as Microbial Desalination Cell (MDC) as shown in Fig. 7.3.

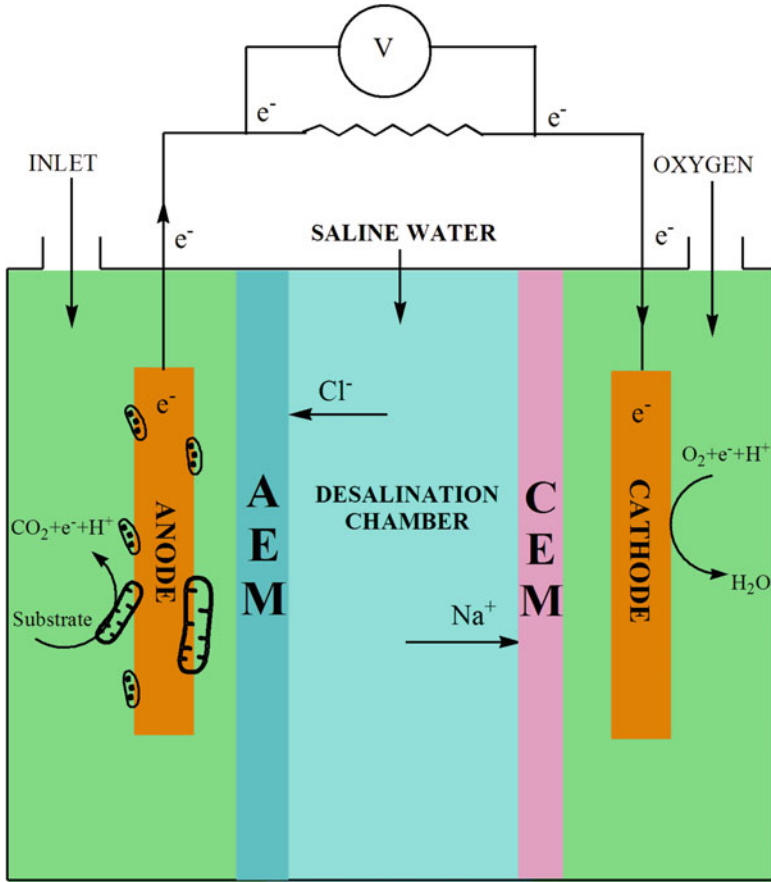


Fig. 7.3 Microbial Desalination Cell (MDC)

MDC is a modification of MFC. It is an electrochemical technique of desalination where microbes act on the organic matter generating electric potential which drives the ion transport through ion exchange membranes (IEMs) thereby removing dissolved salts present in saline water (Cao et al. 2009).

MDC involves the basic principle of creating across the electrodes a sufficient electric gradient. This gradient drives the anions towards anode and cations towards cathode thus desalinating the water in the middle chamber (Kim and Logan 2013). MDC serves three main goals viz decomposition of organic waste, energy generation and desalination.

7.3.3.1 Components and Configuration of MDC

Since MDC is the modification of MFC, the basic components are similar consisting of anodic and cathodic chambers. The cathodic chamber can be kept under both anaerobic and aerobic conditions thereby reducing either protons to release hydrogen gas at cathode or oxygen to form water. It also contains anode, cathode, anion exchange membrane (AEM) and cation exchange membrane (CEM) (Cao et al. 2009).

The two basic configurations of MDC are three chambered MDC and Stacked MDC.

3-CHAMBERED MDC

This is the most basic configuration of MDC first designed by Cao and coworkers in the year 2009 (Cao et al. 2009). It consists of three separate chambers linked together through IEMs. The three chambers are anodic chamber, cathodic chamber and a middle desalinating chamber. On the anodic side, AEM separates the middle chamber while the middle and the cathodic chamber are connected through the CEM. As the electric potential is generated between anodic and cathodic chamber the desalination of the saline water in the middle chamber takes place (Brastad and He 2013).

STACKED MDC

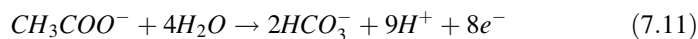
Stacked MDC also consist of separate anodic and cathodic compartment linked through a series of IEM pairs forming multiple cell pairs with concentrate and desalinates chambers. As the number of IEMs increases, the magnitude of filtration also increases. However, the system's internal resistance is also increased. Therefore it is necessary to monitor the resistance and apply the appropriate number of membrane to improve the performance of the system (Chen et al. 2011).

7.3.3.2 Anodic and Cathodic Mechanism Taking Place in MDC

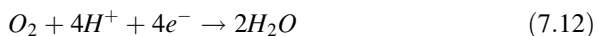
At anode, oxidation of organic substrate takes place

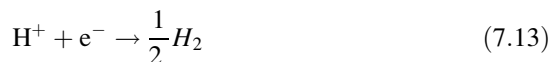


The most common substrate taken in MDC is acetate



At cathode, reduction of either oxygen or proton takes place to form water or hydrogen





In middle chamber, the ions present in the saline water move towards anode and cathode under the effect of electric potential gradient. As the electrons and protons are generated at anode, AEM prevents the positively charged species from escaping the anodic chamber causing the negative charge carriers from the middle chamber to move into the anodic chamber to maintain the charge balance. At the same time the consumption of protons in the cathodic chamber lead to the movement of positive ions towards the cathodic chamber thereby causing desalination in the middle chamber.

7.3.4 Microbial Solar Cell (MSC)

MSC (Fig. 7.4) is a collection of biotechnologies that integrates the photosynthetic and electrochemical activity of microbes to harvest electricity directly from solar

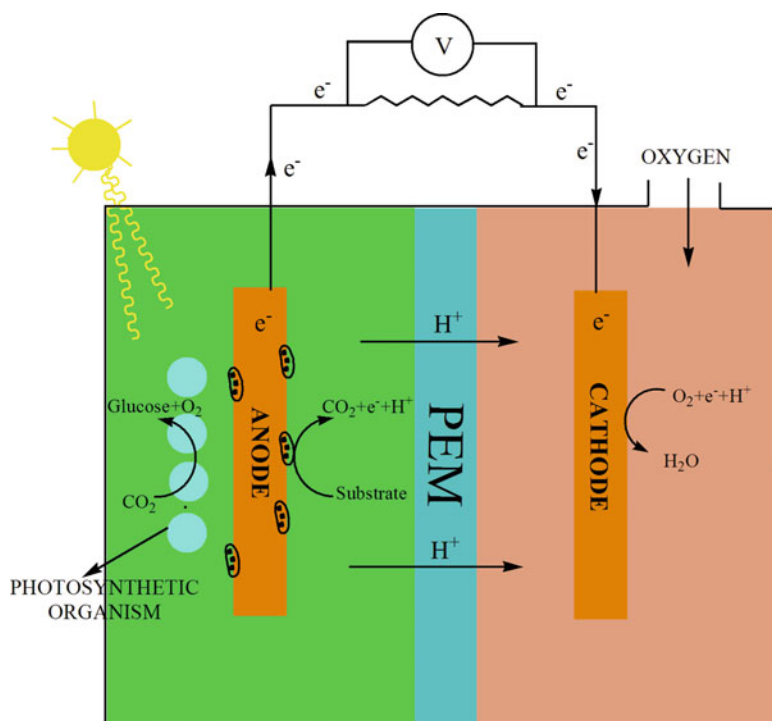


Fig. 7.4 Microbial Solar Cell (MSC)

energy. The technology establishes a synergic relationship between photosynthetic organisms and electrochemically active microbes (Kadier et al. 2016).

MSC works on the basic principle of oxidation of organic substrate transferred to anode that is produced by photosynthesis and thus producing electricity by flow of electrons to the cathode for the reduction of electron acceptor usually oxygen (Strik et al. 2011)

7.3.4.1 Component and Configuration of MSC

The basic components of MSC are same as MFC composing of an anode, a cathode and an IEM. However, MSC are different from typical MFC in the involvement of photosynthetic organisms either at anode or cathode.

The organisms involved in the fixing solar energy into electricity are higher plants, photosynthetic bacteria and algae on basis of which MSC can be divided into 3 categories of plant MSC, algal MSC, MSC with phototrophic biofilm.

Plant MFC

PMFC is the most commonly investigated MSC. In PMFC, plants perform photosynthesis to synthesis organic matter that is excreted by the roots of the plants in form of rhizodepositions onto the anode where exoelectrogens oxidise the matter to release electrons thereby generating electricity (Timmers et al. 2010). The proof of concept for PMFC was demonstrated by Striks and co-workers in 2008 (Strik et al. 2008a).

Algal MSC

Algal MSC is a growing field of harvesting energy from algae either by growing algae in the anodic chamber and allowing the exoelectrogenic oxidation of the organic matter synthesised (Xu et al. 2015) or by utilising the photosynthetic nature of algae to produce oxygen insitu for reduction at cathode (Kakarla and Min 2014). The biomass produced can either be directly fed as substrate in the anode of MFC or it can be utilized to synthesise other value added products (Gouveia et al. 2014). Cui et al. fed anode with dead algae and grew live algae at cathode and harvested current (Cui et al. 2014). A photosynthetic algal MFC was developed by Strik et al. by integrating photobioreactor with the anode of MFC to derive electricity by the direct feeding of living algae (Strik et al. 2008b).

MSC with Phototrophic Biofilm

An autotrophic biofilm can be generated at anode to fix solar energy into substrate that can be further oxidised to release electrons leading to the flow of electric current (Pisciotta et al. 2010).

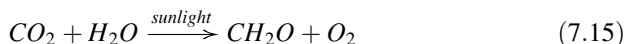
7.3.4.2 Anodic and Cathodic Mechanism Taking Place in MSC

(a) when photosynthetic organisms are present in the anodic chamber

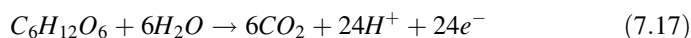
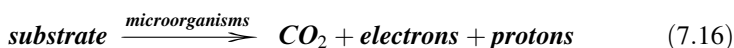
- (i) solar energy fixed to form organic substrate



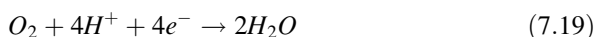
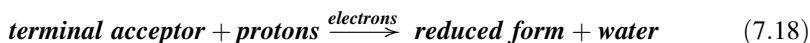
e.g.



- (ii) At anode,

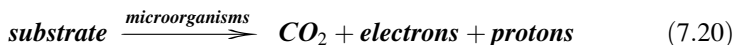


- (iii) At cathode

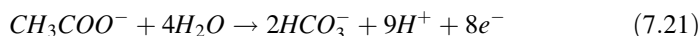


- (b) when photosynthetic organisms are present in the cathodic chamber

- (i) At anode,



e.g. If acetate is present as electron donor:



At cathode, algae consume carbon dioxide to produce organic matter and oxygen. The organic matter can be further utilised to produce value added products while oxygen is utilised as TEA.

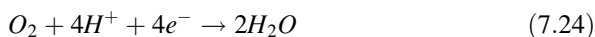
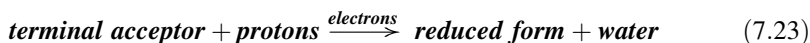
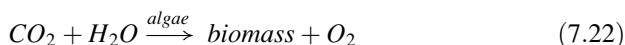


Table 7.1 presents the summary of the work done in recent years on different bioelectrochemical systems.

Table 7.1 Summary of work done on different types of BES

Type of BES	Anode/cathode	Electron donor/acceptor	Output	References
Plant MFC	Graphite anode/graphite felt cathode	<i>A.anomala</i> , <i>S. anglica</i> , <i>A. donax</i> grown in graphite felt	Electricity+ biomass	Helder et al. (2010)
Plant MFC	Graphite granule anode/carbon felt cathode	Ryegrass grown at anode/Cr(IV)	Electricity + Cr (IV) removal	Habibul et al. (2016)
Biofilm MFC	Gold electrode/graphite carbon cloth	Algal biofilm grown at anode	Electricity	Lin et al. (2013)
Algal MFC	Carbon fibre brush/Pt coated carbon cloth	Dead microalgae biomass/live algae	Biomass + electricity	Cui et al. (2014)
Algal MFC	Carbon fibre veil electrodes	Acetate/algal feed from bioreactor	Biomass + electricity	Gajda et al. (2015)
Algal MFC	Graphite rods	Live algae/ferricyanide	Electricity	Xu et al. (2015)
Stacked MDC	Carbon felt/Pt coated carbon cloth	Sodium acetate/phosphate buffer with NaCl solution in middle chamber	Desalination + electricity	Chen et al. (2011)
Photosynthetic MDC	Graphite paper electrodes	Glucose/microalgal biocathode with NaCl in desalination chamber	Electricity + biomass	Kokabian and Gude (2013)
Tubular MDC	Carbon fibre brush/Pt coated carbon cloth	Sodium acetate/tap water with NaCl and boric acid in desalination chamber	Simultaneous desalination and boron removal + electricity	Ping et al. (2015)
MDC	Carbon graphite electrodes	Municipal wastewater/tap water with Ni, Pb containing water in desalination chamber	Removal of heavy metal + electricity	Mirzaienia et al. (2016)
SCMEC	Graphite brush/Pt coated carbon cloth	Sodium acetate/proton	Hydrogen	Call and Logan (2008)
Continuous flow MEC	Graphite/Ni based GDE	Domestic wastewater + proton	Hydrogen	Escapa et al. (2012a)
DCMEC	Graphite brush electrodes	Sodium acetate/sulphate and proton	Sulphate removal + hydrogen	Luo et al. (2014b)

(continued)

Table 7.1 (continued)

Type of BES	Anode/cathode	Electron donor/acceptor	Output	References
DCMEC	High density carbon fibre/ stainless steel	Dilute sugarbeet juice/ proton	Hydrogen	Ranjan et al. (2015)
SCMEC	Graphite brush/Ni foam based graphene	Acetate/proton	Hydrogen	Cai et al. (2016)
DCMFC	Carbon paper electrodes	Rice straw/ferricyanide	Electricity	Hassan et al. (2014)
SCMFC	Carbon paper/Pt coated carbon paper	Cadmium chloride and zinc sulphate with sodium acetate /oxygen	Electricity + heavy metal removal	Abourached et al. (2014)
DCMFC	Graphite rod electrodes	Dyes/oxygen	Electricity + dye removal	Khan et al. (2015)
DCMFC	Carbon felt/ stainless steel	Sodium acetate/sodium bromate	Bromate removal + electricity	Dai et al. (2016)
DCMFC	Graphite electrode	Soak liquor/ferricyanide	Electricity	Rajeswari et al. (2016)

7.4 Merits of BES:

1. BES is an energy efficient technology that does not require heavy external power to operate.
2. Wastewater can be treated efficiently including toxic chemicals and recalcitrant xenobiotic compounds.
3. In BES, the recovery of energy can be in the form of electricity, hydrogen, potable water (through desalination) and other value added chemicals.
4. The technology has the potential to decrease the pre-treatment cost of the conventional treatment of solid waste.
5. Very low secondary pollution in form of sludge and harmful gases is an added advantage.

7.5 Conclusion

BES is a novel technology of harvesting energy from waste without any external assistance. BES has broad application of pollutant removal, energy generation and desalination. BES is one of the few technologies that combine the applications of catalysts of different nature like chemical, microbial and enzymatic origin. It can

treat recalcitrant pollutants and toxic chemicals present in wastewater as suggested by reports with synthetic and real substrates. It has a unique ability to not only treat toxic pollutants but also at the same time generate electric power that makes it a potent future technology. The results of extensive ongoing research and studies in this field suggests that the technology still lags in power generation especially with real waste stream as compared to synthetic waste stream. It is crucial to shift the focus of research to treat real wastewater for generating power. It is also necessary to work in the direction of upscaling the technology for better power production with large volume and heavy loadings of waste for real time assessment of performance on large scale.

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