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Microalgae as a biocathode and feedstock in anode chamber for a self-sustainable microbial fuel cell technology: A review

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A B S T R A C T

Microbial fuel cell (MFC) technology has been investigated for over a decade now and it has been deemed as a preferred technique for energy generation since it is environmentally benign and does not produce toxic by/end products. However, this technology is characterized by low power outputs, poor microbial diversity detection, and the presence of methanogenic microorganisms, poor electrochemically active microorganisms' enrichment techniques, and the type of electrode that is used, amongst others. Furthermore, this technology has relied mostly on refined chemicals for energy production and this practice is not sustainable for long-term application of this technology. This paper reviews the use of a microalgae-assisted MFC for a self-sustainable microbial fuel cell where a microalgae-assisted cathode is established to facilitate the oxidation/reduction reactions (ORR) while recycling the generated algal biomass to the anode compartment as a feedstock for improved energy generation. Furthermore, this review proposes for the utilization of cell disruption techniques to maximize nutrient availability for maximal power generation while also making use of molecular diagnostic tools such as metagenomics and metatranscriptomics to monitor the microbial community structure and function.

1. Introduction

Water, food, and energy are in demand as the world population increases. Consequently, as a result of this growth, the call for the development of alternative energy and water producing techniques are required to satisfy the energy and water demands. Currently, fossil fuels are utilized for the generation of energy and due to the increasing demand of energy, substantial utilization of these resources has over time resulted in their depletion. In addition, the use of these fossil fuels contributes substantially to environmental deterioration due to the produced waste after the combustion and/or gasification processes (Meinshausen et al., 2009; McGlade and Ekins, 2015). In addition, this technology has received widespread criticism due to the environmental burden that is associated with the emission of green-house gases (GHG) which contribute to global warming (McGlade and Ekins, 2015). Due to these shortcomings that are associated with the fossil fuel energy production practices, alternative processes that can produce energy in an environmentally sustainable manner are in-need. There are existing technologies that serve as alternatives to fossil fuels and these processes include nuclear energy, solar power (photovoltaic panels), biomass generation, geothermal and wind power, and hydro-electric power (Varun et al., 2009; Zhou et al., 2010; Zhang et al., 2013). However, the energy generation from these technologies is incomparable to the energy that is generated from fossil fuels, which is still deemed to contribute almost 80% of the world energy demand by 2040 (USEIA, 2016). The mentioned alternative technologies mainly assist or boost the currently utilized methods and not as a replacement technique.

Research on renewable energy for bioenergy harvesting during wastewater treatment and the conversion to technologies that reduce carbon dioxide emission is becoming a general trend in the world's economy. Bioenergy production via the microbial fuel cell (MFC) technology offers direct energy recovery, cleanliness, recyclability and the production of by-products which are non-hazardous (Lovley, 2006). Significant research is being done in this field to exploit this ability of microalgae and integrate it with Microbial Fuel Cells (MFC). This integration becomes especially favourable considering the fact that the

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phototrophic organisms act as in-situ generators of oxygen that facilitate the reaction in the cathode chamber of the MFC.

1.1. Basic concepts of MFC

An MFC is an bioelectrochemical device that utilizes microorganisms for the conversion of organic or inorganic substrates to energy via the metabolic activity of the microorganisms (Logan et al., 2006). These organisms are referred to as electrogens or electrochemically active microorganisms (EAM): organisms which utilizes the extracellular electron transfer (EET) system for the exchange of electrons with an insoluble material such as electrodes and metal oxides (Doyle and Marsili, 2015). This process is typically comprised of an anaerobic anode and aerobic cathode compartments. The anodic compartment normally contains the facultative or strict anaerobic EAMs while the cathodic compartment typically contains air-sparged water. Electric energy is produced via the electrons that are generated by the EAM through the utilization of organic or inorganic substrates and these electrons flow from the anode to the cathode compartment via the resistor while the protons are transferred to the cathode via the proton exchange membrane (PEM) (Logan and Regan, 2006; Logan, 2009). Although this process in environmentally sustainable, cost-effective and does not produce hazardous products, the energy that is produced from this system is not sufficient to replace the existing technologies and this necessitates further investigations especially on the optimization of this process for improved electricity production.

Improved energy production from MFC technology lies within process optimization and this involves the type of microbial community used, substrate (s) present within the medium, electrode type, mitigation of methanogenic organisms from the microbial community and others. However, the type of substrate used plays a significant role as it dictates the microbial population structure and its subsequent activity. Hence, this review highlighted the recent development of a self-sustainable energy production system where algal organisms would be responsible for the generation of oxygen in the cathode compartment while also relying on the carbon dioxide that is produced from the anodic compartment as the carbon source. In addition, the generated algal biomass from the cathode compartment is proposed to be utilized as a feedstock in the anodic compartment such that a zero carbon balance is achieved while producing electricity.

1.1.1. Advantage of integrating algal harvesting technology in MFC

Algae helps in the generation of biochemical energy through the conversion of solar energy. Biological method of CO_2 sequestration using green algae and cyanobacteria is considered as the most promising method. The use of algae has several advantages e.g. it mitigates CO_2 thus reducing global warming, wastewater treatment, production of biofuels, biofertilizer and other important products like industrial biofilters, food products, pigments etc (Moreno-Garrido, 2008; Cheah et al., 2015; Udaiyappan et al., 2017). In a dual chambered MFC, algae can be utilized at the cathode chamber instead of passive aeration which is energy-intensive. In the anode chamber, algal biomass after pretreatment can be used, since algal biomass is rich in carbohydrates, lipids and vitamins (Goh et al., 2019; Lee et al., 2017; Chew et al., 2017), and the biomass that is considered as a potential substrate or feed for EAM in the anode.

1.1.2. Basic concept on algal biomass production and harvesting

Green algae and cyanobacteria are a vast group of both facultative photoautotrophic and photoheterotrophic microorganisms. Their uniqueness from other microorganisms is the presence of the chlorophyll and having photosynthetic ability in a single algal cell, therefore allowing easy operation for biomass generation, and effective genetic and metabolic research in a much shorter time period than conventional plants. Algae cultivation is carried out in illuminated environments which might be natural or artificial. They grow autotrophically using CO_2 as a carbon source and light as an energy source. Some algae can also substitute CO_2 fixation with available carbon sources in the media, thus showing heterotrophic growth. Also, the two growth modes might be combined in a mixotrophic growth mode, with photosynthesis and respiratory metabolism operating simultaneously. This results in parallel assimilation of CO_2 and organic carbon. The major shortage for use of microalgae is the need for designing specially illuminated autotrophic photobioreactors (PBRs). Heterotrophic growth mode helps in overcoming this bottleneck. Also, some algae under heterotrophic mode have higher biomass, growth rates, ATP production, nitrogen content and lipid content than in autotrophic mode. On the contrary, there is a limited number of heterotrophic microalgal species. Also, energy expenses increase by supplementing an organic substrate, thereby, increasing the chances of growth inhibition by surplus organic substrate and failure to produce light induced metabolites. Moreover, heterotrophic mode of cultivation is more prone to contamination and competition from other microorganisms.

2. Mechanisms of extracellular electron transfer in MFC

Though there has been considerable attention given to MFC technology, there is a limited number of EAMs that have been detected thus far and this might be attributed to the lack and/or inaccuracies in the microbial detection techniques used and these are discussed later. In addition, MFC studies are mostly centered on the bio-conversion of organic substrates which serve as electron donors for subsequent electricity generation via the redox reactions occurring at the anode compartment. Briefly, the organic substrates undergo Glycolysis followed by the Citric Acid Cycle with an aid of nicotinamide adenine dinucleotide (NAD^+) and Flavin adenosine dinucleotide (FAD), which are reduced to NADH and $FADH_2$, resulting in the release of carbon dioxide (CO_2). NADH and $FADH_2$ act as electron carriers to the electron transfer chain to produce the energy currency, adenosine triphosphate (ATP) (Yang et al., 2012). *Shewanella oneidensis* and *Geobacter sulfurreducens* are the most widely studied organisms in MFC technology due to their dominance which can be attributed to their high electrochemical activity. The mechanisms involved in electron transfer were mostly studied from these organisms and to date, three main electron transfer mechanisms have been studied and these include *c*-type cytochromes (CTC), nanowires, and electron shuttles (see Fig. 1).

CTCs are heme-containing proteins which are mostly found in the outer-membrane and periplasm of the studied bacteria and archaea. One of the widely studied organisms that utilizes this mechanism is *G. sulfurreducens*, which has been demonstrated to possess 79 putative CTCs. The genome of *G. sulfurreducens* revealed a variety of c-type cytochromes which contained heme groups on the motifs, exposed to the outer membrane (Leang et al., 2003). The electron transport system using the *c*-type cytochromes is mostly assisted by proteins such as iron-sulfur proteins, quinones and *b*-type cytochromes (Inoue et al., 2011; Leang et al., 2010). On the other hand, *Shewanella oneidensis* has been shown to possess 42 putative CTCs, mostly located on the outer membrane where the cymA tetraheme-CTC is central in EET (Lower et al., 2005). Bacterial nanowires, also known as electro-conductive pili, are a novel electron transport mechanism which were initially detected in *G. sulfurreducens*for metal oxide reduction. Studies observed that the formation of pili in *G. sulfurreducens* were localized on one side of the cell, which was induced during the growth of the organism in fumarate at 25 °C (Reguera et al., 2005). Gorby et al. (2006) demonstrated that pili formation is not exclusively influenced by the ability of the organisms to reduce metal oxides as previously shown by other researchers. In the same study, *S. oneidensis*, phototrophic cyanobacterium *Synechocystis* PCC6803 and fermentative *Pelotomaculum thermopropionicum* were shown to produce electro-conductive wires for effective electron transfer and energy distribution. *Flexistipes sinusarabici* produced current that is comparable to that of *G. sulfurreducens* (wild type) in a study conducted by Walker et al. (2018) using pilin genes from *Flexistipes*

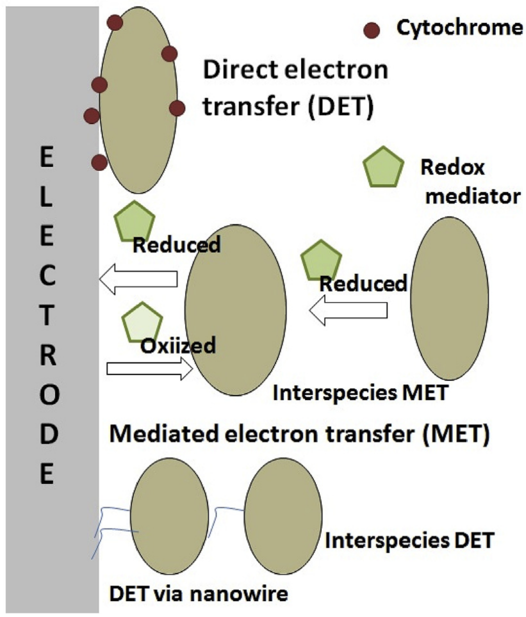

Fig. 1. Different mode of extracellular electron transfer by EAM on anode surface.

sinusarabici that were inserted in *G. sulfurreducens*, thus confirming that *Flexistipes sinusarabici* utilizes the electrically conductive pili for electron transfer. Electron shuttles, which may be supplemented in the medium or produced by the organism for electron transfer, is the third mechanism by which microorganisms can transfer electrons. These are organic molecules of low molecular weight which have the ability to catalyze the oxidation/reduction reactions (Velasquez-Orta et al., 2010). An improvement in power generation (16.6 mW/m^2) in a microbial fuel cell inoculated with an overexpressed *phz*M gene, which codes for pyocyanin in*Pseudomonas aeruginosa,* was witnessed (Yong et al., 2014), while in a separate study, the additions of flavins resulted in a power density of 150 mW/m^2 thus demonstrating the influence that electron shuttles have on electron transfer (Velasquez-Orta et al., 2010). These studies and those that are not mentioned in this review indicate that electron shuttles do contribute to current output, contradicting previous reports which indicated that electron shuttles have minimal impact of current generation (Gorby et al., 2006).

3. Configurations of photosynthetic MFC

Solar energy is one of the major sustainable energy resources. Advanced approaches to convert solar energy into bioelectricity developed with bioelectrochemical systems (BESs) have been made in the last ten years, in which many of these photovoltaic devices have the ability to separate photosynthetic energy and heterotrophic dark electricity production in the absence of artificial mediators. Photosynthetic MFCs are the one which involve an anode or cathode, with a biofilm enclosing photosynthetic microorganisms, in which photosynthesis is carried out and as an outcome they act as electron donors and also as producers of organic metabolites. Removal of carbon dioxide by this integrated PMFC is another additional benefit. Configuration of such PMFCs is the main task in order to increase the power density and obtain long term performance so as to get a cost effective system. Four different configurations of PMFCs are schematized and detailed in the following sections.

3.1. Coupled PMFC

In this concatenated PMFC, bioanodic MFC is connected to a PBR, in which CO_2 is pumped directly from the MFC to the PBR. This configuration functions in the absence of ion exchange membrane which simplifies its structure and makes it cost-effective to scale up. A photosynthetic microbial cathodic half-cell, using the *Chlorella vulgaris* microalgae as the direct electron acceptor, was developed earlier where the half-cell was concatenated to a fermentative yeast anode, creating a complete coupled MFC. This design was tested into an existing bioethanol plant to create coupled MFC with the existing industrial yeast bioreactor acting as anodic half cells. This twin benefit integrated system is used to produce power for the existing bioethanol plant, and simultaneously metabolize CO_2 emissions, from bioethanol production, through photosynthesis by the microalgae growth in the cathodic PBR half-cell. Furthermore, the biodiesel is produced as energy by product during the growth of microalgae. To achieve all these benefits, a synthetic chemical mediator should be supplemented to the anode chamber to allow electron shuttling between yeast cells and the electrode. The cathodic half-cell was aerated with feed-air containing 10 % v/v CO_2 which is sparged directly into the cell culture, and illuminated by sunlight to facilitate photosynthesis by microalgae in the PBR.

Similar concept was demonstrated by joining a glass PBR to MFC to form the PMFC. The illuminated PBR was used for the preliminary start-up of algal growth. A sparger was used to pump air inside the reactor, whilst the MFC has dual electrodes separated by a cation exchange membrane. Jiang et al. proposed a design in which upflow MFC and PBR coupled system for bioelectricity generation and waste water treatment (Fig. 2) (Jiang et al., 2012). The upflow MFC mainly comprised of a plastic cylinder with carbon fiber brush electrodes, and glasswool/bead layers separator between anode and cathode compartments. An external column PBR was coupled with the upflow MFC, in which the effluent from the cathode compartment of the up flow MFC was continuously pumped into the column PBR. Continuous illumination was provided to the microalgal culture and a purge of CO_2 (effluent of MFC) and air mixture gas, to help it grow.

3.2. Single chamber PMFC

S. platensis has the ability to directly shuttle electrons to the electrode, without the requirement of mediators. A membrane-less single chamber PMFC design was employed with photosynthetic bioanode. In this design, there's a simple scheme that allows the direct attachment of microalgae to the anode and it was suggested to construct an electrical power generator. Some blue–green microalgae were used as a biocatalyst for electricity production. The required electro potential can be created by anodic biofilm, where the respiration reaction in the dark and the photosynthetic reaction in light can generate current.

Mixed culture of bacterial and microalgal cells can be used to improve the efficiency of PMFC as a synergistic approach (Nishio et al.,

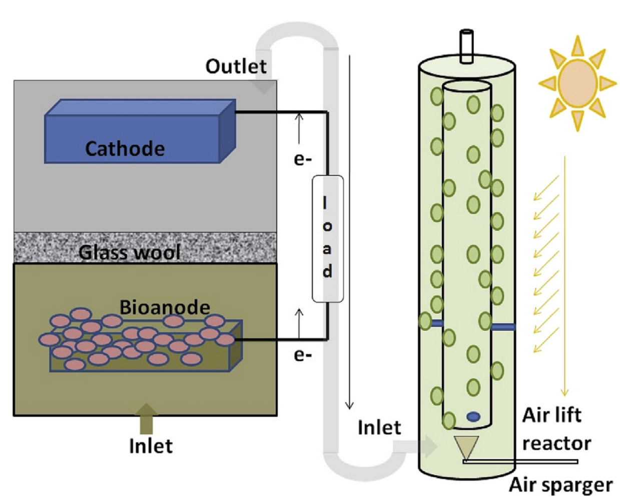

Fig. 2. Schematic diagram of upflow type MFC integrated with PBR.

2013) in which the microalgal cells have the potential to use organic materials like acetate, which is assimilated by the bacterial cells as a substrate for electricity generation. This design can be used as a MFC and portable bio-battery, with the main application of in both light and dark conditions as the photosynthetic reaction is activated by illumination which is considered as a reversible process for recharging the MFC to operate for longer times.

Another type of the single chamber PMFC is photo-biological fuel cell in which a PEM is sandwiched between anode and cathode. Microalgae was used to form anodic biofilm with atmospheric CO_2 as a carbon source in mixotrophic nutritional mode which increases the practicality of the association between autotrophic and heterotrophic metabolism in the same system by facilitating the conditions in which all types of CO_2 (atmospheric and organic) could be consumed.

3.3. Dual chambers PMFC

The algal photosynthesis is used as the source of oxygen in the cathodic chamber using a dual chambered PMFC. This setup is consists of two chambers separated by an ion exchange membrane (IEM). Usually, the inoculum for the anodic compartment, is the activated sludge from a wastewater treatment plant, which is covered during operation to exclude light and thus to avoid the growth of algae, whereas, the cathode compartment contains a culture of microalgae, which is illuminated for 12 h a day. The anodophilic bacteria produce CO_2, which is transferred to the cathode compartment in some of these configurations so that it can be utilized by the microalgae through the photosynthesis process. This can be achieved by creating a vent at the top of each chamber which is connected by a tube with a funnel shaped gas collector placed in the anode side in order to simplify the piping of the produced CO_2 into the cathode for microalgal biomass production via photosynthesis (Wang et al., 2010).

An alternate method is the utilization of microalgae as a bioanodic catalyst within a dual chamber PMFC separated by PEM with a chemical cathodic catalyst. Overall, the dual chamber setup can be efficiently started up by a direct three-stage process involving the separate production of bacteria and microalgae cultures, subsequently the substitution of the mechanical aeration system by the microalgae culture and finally a shift in the light dosage from the continuous input to the dynamic light/dark regime.

3.4. Photosynthetic sediment MFC (PSMFC)

Energy can be produced through the naturally existing differences in potential by using a configuration in which an anode is buried in sediment and a cathode submerged in the water laying on top of the sediment. Such configuration is called sediment microbial fuel cell (SMFC) or benthic MFC. This energy is exploited through the reducing power of microorganisms in the sediment, directly created by the oxidation of organic molecules or the redox reactions of inorganic reduced complexes i.e. sulfur and the cathodic reaction of the SMFC includes the reduction of electron acceptors like the dissolved oxygen in water (Fig. 3).

A configuration which incorporates microalgae in SMFC was proposed, in which biogenic compartment was added, replacing the cathodic compartment. The CO_2 produced by anodic bacterial activity is consumed by algal cells, and the O_2 produced by the algae is consumed by the PSMFC's cathode compartment for current generation. This PSMFC generally consists of an anode placed in the middle of a sediment layer which is covered with sand and a cathode compartment which is filled with microalgal culture medium. The PSMFC is normally operated in the presence of a light source for photosynthesis to take place.

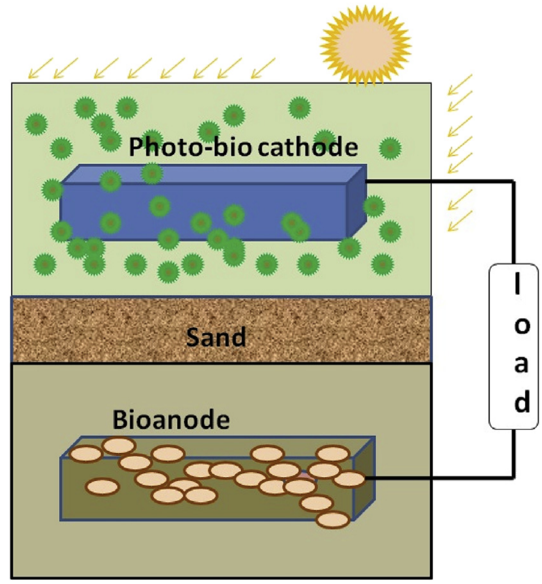

Fig. 3. Schematic configuration of photosynthetic sediment MFC (PSMFC).

4. Power generation by PMFC

Normally, microalgae can be cultivated in the anode or cathode compartments of the PMFC. Anodic microalgae have the ability to assimilate substrate, generating electrons and transferring these electrons directly to the anode without the aid of a shuttling mediator, hence they can be used to generate current directly. The role of cathodic microalgae is different, where they are used as biological oxygenators instead of the mechanical ones which add up to the total cost of generated energy of MFC. A number of trials were performed in order to obtain the maximum benefits of microalgal MFC either in anode or cathode compartments.

4.1. PMFC with anode catalyzed microalgae

Microalgae can develop a biofilm on the anode electrode of the PMFC while assimilating a substrate for electron generation, which are then transported to the cathode either directly or via a mediator.

4.1.1. Photosynthetic bacteria at the anode with mediators

During the period 1995–2005, extensive e research was carried out in the field of mediator based PMFCs. Electrons cannot be transferred from the normal microbial electron transport systems to the electrode due to the non-conductive nature of the cell surface structures. Mediators are typically redox molecules (e.g. ubiquinones, dyes and metal complexes) that can form reversible redox couples, are stable in both oxidised and reduced form, are not biologically degraded and are not toxic towards the microbial consortium. Electrochemical mediators are, therefore, employed to render electron transfer from the microbial cells to the electrode. It may be noted that the overall efficiency of the electron transfer mediators also depends on many other parameters, and in particular on the electrochemical rate constant of the mediator re-oxidation, which depends on the electrode material (Fig. 4).

Cyanobacteria species such as *Anabaena* and *Synechocystis* were identified to function as biocatalysts with HNQ (2-Hydroxy-1,4-napthaquinone) as a mediator. The artificial redox mediator helped in shuttling electrons from the microalgae to the anode. Power generation increases in the dark phase during which oxidation of intracellular carbon sources (glycogen) occurs, and electrons are recovered with BES. On the other hand, power production was limited by oxygen production during light phase reaction. The bottleneck for these early PMFCs was that the mediators used were unsustainable and not

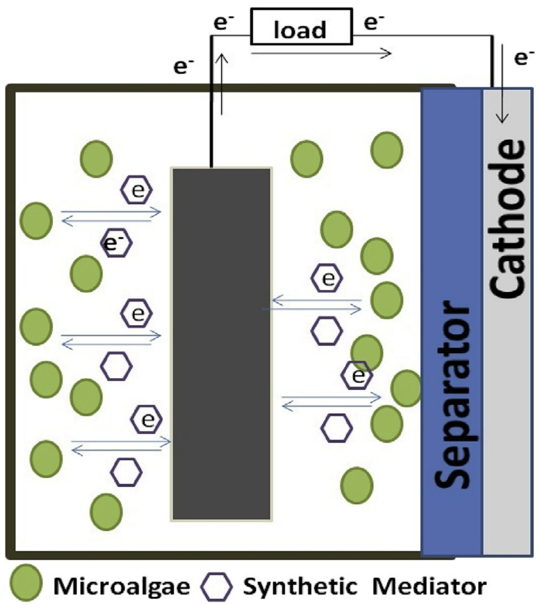

Fig. 4. Schematic configuration of PSMFC with chemical mediator in anode chamber.

environment-friendly. Hence, their popularity has drastically reduced, and is hardly in use now a days.

4.1.2. *Hydrogen generating photosynthetic bacteria with an electrocatalytic anode*

The general idea of using hydrogen-generating photosynthetic bacteria along with catalyst loaded anode is biohydrogen production photosynthetic bacteria followed by *in situ* oxidation of hydrogen on the electrocatalytic surface of anode. A direct biophotolysis of H_2 production is a biological process which utilizes solar and photosynthetic systems similar to plants which convert water into chemical energy. With hydrogen gas recovery, it is advantageous to generate electric power from bio-hydrogen (Fig. 5).

To reap the advantages of maintaining a very low partial pressure of hydrogen, the photosynthetic hydrogen gas production units are coupled with *in situ* hydrogen oxidation by an electro catalytic conversion step. In this process, originally tested in 1964, H_2/H^+ serves as a natural electron mediator between the microbial metabolism and the

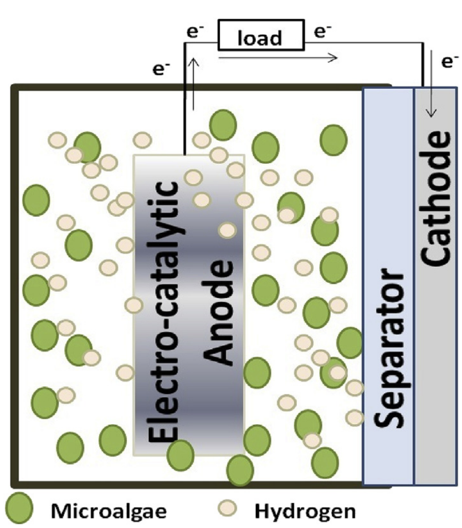

Fig. 5. Schematic diagram of PBR (for biohydrogen generation) with electro-catalytic anode (for *in situ* current production).

anode. It was found that only after a period of dark followed by illumination, microalgae acquire ability to produce H_2 because dark period creates anaerobic environment. In a recent study involving the green alga *Chlamydomonas reinhardtii*, it was found that *in situ* hydrogen removal (keeping partial pressure of hydrogen very low) is beneficial for increasing hydrogen production. Sulfur deprivation on green algae, *C. reinhardtii,* was found to create anaerobic conditions and hydrogen evolution by biophotolysis under light using photosynthetic pathway (Melis, 2002). Studies have also been done on anoxygenic photosynthetic bacteria, producing H_2 in a photo fermentation process, coupled with electro catalytic electrodes for immediate removal of hydrogen. Further, direct dependence of power production on photosynthetic activity has been determined using *Rhodobactre sphaeroides* ($3\,W/m^3$ in light vs. $0.008\,W/m^3$ in dark). Hydrogen was produced by splitting of water, which can sustain for longer period of time. Hydrogen production in a sulfur deprived condition is the result of two different electrons transfer pathways: the residual photosynthesis (PSII-dependent pathway, resulting from water photolysis) and simultaneously with a PSII-independent pathway that uses catabolism of endogenous starch reserves as an additional source of electrons. A combined process of H_2 generation and *in situ* oxidation of the hydrogen to produce electricity could be a cheaper process than a two stage process of hydrogen collection followed by the oxidation of hydrogen. Nevertheless, the hydrogen yield and rate of hydrogen production are very low, process is complex, and complicated. The most important requirement for an electro catalytic PMFC is an electro catalyst that is stable and cost efficient. Typical H_2/H^+ exchange membrane fuel cell catalysts are prone to poisoning and inactivation under dirty microbial conditions. Though the platinum catalyst typically used can be protected using conductive polymers, cheaper non-noble metal electro catalysts, like tungsten carbide (WC), can be more a promising substitute. However, even with these catalysts, stability issues should be overcome before it becomes possible to use them practically on a large scale.

4.1.3. *Direct electron transfer between photosynthetic bacteria and electrodes*

The transfer of electrons from the microorganism to the anode without the presence of any artificial redox mediators, electro catalytic electrodes or heterophillic bacteria is known as Direct Electron Transfer (DET). It still remains unclear whether this process actually takes place in nature. Till date, publications which identified DET at the anode also included the use of electro catalysts, like Pt or polyaniline, which are catalytically active towards H_2 generated by the photosynthetic algae. Again, independent from the BES, potentially conductive microbial nano-wires have been discovered for some cyanobacteria like *Synechocystis* sp. PCC 6803, which suggest that DET might be possible in nature. Synechocystis PCC-6803 was used as exoelectrogen to generate anode potential (Fig. 3). Electrically conductive nano-wires were observed in these cyanobacteria at anode chamber under excess light and CO_2 limiting condition. More interestingly, even bicarbonate reduction using light in a photo-bio-cathode was shown as a DET process since the autotrophic microbes, in the absence of any organic matter, did not produce oxygen, neither were any electro catalysts present, nor did flushing the cathode to wash away soluble redox mediators disrupt the current (Gorby et al., 2006). This anoxygenic photosynthetic process would use CO_2 as the e^- acceptor with the cathode as the e^- donor, mimicking iron (II) - mineral oxidation as described for photo-autotrophic bacteria. However, for this process, an unidentified mixed culture was used as inoculum, which indicates presence of other autotrophic bacteria that might have played a role. Further research is, therefore, required to confirm DET process occurrence in pure bacterial cultures.

Some microalgal species have the ability to shuttle electrons directly to the anode without the need of mediator, e.g. *S. platensis* and based on this ability, it was examined by several authors for current generation

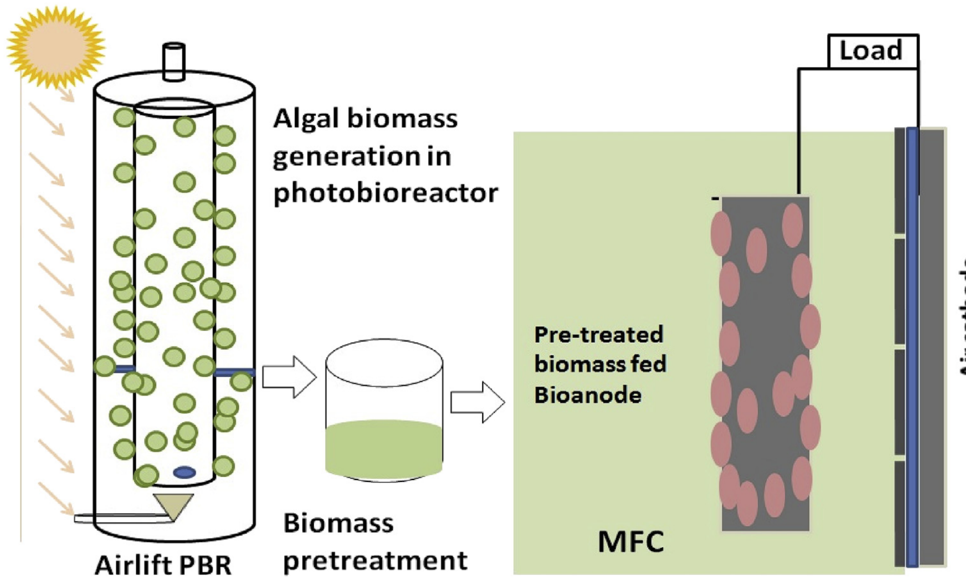

Fig. 6. Flow chart of algal biomass generation in airlift PBR followed by pre-treatment and its utilization in MFC as substrate.

using a single chamber membrane-less and mediator-free PMFC. Different electrode types were used in these studies, i.e., gold and platinum (Fu et al., 2009). Fu et al. observed power density of 1.64 mW/m, which was amplified by Lin et al. to reach10 mW/m^2. The amplification was probably due to the usage of gold anode and graphite cathode. In this type of PMFC, *S. platensis* is carrying out the photosynthesis reaction to produce oxygen as a by-product while exposed to light. Then at acts as an oxidant and possibly inhibits anodic oxidation reactions, reducing the generated electrical power. The PMFC's electricity generation gets influenced by the chlorophyll content of microalgal film where lower voltage is obtained in light conditions as compared to dark conditions. This negative influence of light on the voltage is reversed with other PMFC configurations in which light intensity increases the output voltage.

In order to achieve a sustainable system which is able to sustain on CO_2 and concurrently obtain a value added biomass in a biorefinery concept, membrane was included in the same PMFC configuration and operated with the mixed culture of microalgae inoculated in the anode side. Low power density was obtained (0.004 mW/m^2), almost certainly because of the presence of different strains in the mixed culture with different abilities toward direct electron shuttling to the anode. The reason could also be the mixotrophic mode that was applied using both the atmospheric CO_2 and wastewater as carbon sources. Dissolved oxygen produced during the photosynthesis process was found to be the major restrictive factor toward dropping performance. In addition, electrons installed at the electrode in light condition were higher as compared to that installed in dark condition under oxygenic environment. Light source and intensity also plays a major role in chlorophyll development, stomata opening and photosynthesis in phototrophic cells (here microalgae). Lan et al. studied the influence of light on the PMFC power density in terms of light source and intensity, as they can significantly affect the chlorophyll development, stomata opening and photosynthesis process in microalgal cells. So, the *Chlamydomonas reinhardtii* was used as a bioanode catalyst in PMFC and was illuminated with monochromatic red and blue lights with different intensities. The observed PMFC power density was directly proportional to light intensity, with the superiority of red light to blue one, with maximum value of 13 mW/m^2. In another study, the same microalgal strain was used to optimize the electrode distance within two chambers PMFC with graphite electrodes and the application of dynamic light/dark regime. Maximum power density of 0.82 mW/m^2 was achieved at electrode distance of 14.7 cm, with a substantial reduction in the internal resistance.

4.1.4. Synergism between phototrophic microorganisms and mixed heterotrophic bacteria in sediments

Photosynthetic processes help in accumulating organic matter which subsequently undergo oxidation by heterotrophic microbial catalysts and consequently electricity is produced by the PMFCs. Photosynthetic producers and heterotrophic consumers form various synergistic relationships in the eco system, often along with diverse anode-respiring bacterial species. In recent years, researchers investigated CO_2 fixation by photosynthesis combined with heterotrophic electricity generation with three types of systems.

In saline and freshwater sediments, algae and some bacteria, like cyanobacteria, are capable of supplying organic matter (e.g. excreted polysaccharides) to heterophillic bacteria through photosynthesis, hence maintaining synergistic communities in ecosystems like microbial mats. The same synergistic relationship was examined in freshwater sediment-type PMFC for generating electricity. The PMFC when containing microbial community under illumination produced current continuously. Similar to early studies, electricity generation in this case also showed inverse relationship with illumination. The magnitude of current increased in the absence of light and decreased when light was provided. Current production decreases under continuous illumination possibly due to accumulation of oxygen. Studies were also conducted using marine micro biota a sediment-type PMFCs with microbial anode and cathode. Photosynthetic microorganisms here in the overlaying water produced O_2, for reduction by the cathode, and organic matter, which is used as a carbon source in the anode in the anaerobic sediment. This forms a self-maintaining synergistic BES, consuming light and producing electricity. Other than in the previous studies, light dependent current generation was observed in this work, because the system depended on O_2 production at the cathode.

4.1.5. Ex situ photosynthesis coupled with mixed heterotrophic bacteria at a dark anode

Externally generated biomass formed by photosynthesis can also be added to heterotrophic MFCs to generate electricity (Fig. 6).

Algae can be used as anodic fuel to generate electricity in these *ex situ* PMFCs. The energy value of algal biomass comes about because its carbon molecules contain high-energy electrons. Biofuels from algae are the “third generation” of biofuel feedstock as they can potentially address most of the concerns about first- and second-generation fuels.

Algal biomass is rich in carbohydrates, protein and lipids though its concentration varies depending upon strain to strain and on various physico-chemical parameters influencing the metabolic pathway. One of the most attractive features of microalgal biomass production is the potential to fix CO_2 from atmosphere. Between 1.6 and 2 g of CO_2 is captured for every gram of microalgae biomass produced. The microalgal cell wall contain significant amount of the cellulose and hemicelluloses for which pre-treatment is required to break down cell structure and disrupt crystalline structure of cellulose for the accessibility of the cellulose prior to its use as substrate for biofuel generation. This pretreated substrate can be converted into anaerobic production of electricity. Electro active bacteria (EAB) can channel the electrons and their energy to generate bioelectricity in MFCs, society's most widely useful energy form—directly without combustion. These systems require separate PBRs for optimal algal growth (no shading by electrode) and less complicated dark MFC system for optimal generation of electricity. In the first study, dried algae powder was added to the MFC and desirable results were obtained. In the second study, the MFC and PBR were connected in series. At this point it is of special interest to note that there are limitations of feeding complex organic matter (like algae cells) to a mixed heterotrophic bacterial community in a MFC. This limitation arises in the form of very low columbic efficiencies, of only about 2.8%. *Chlorella vulgaris* (2500 mg COD/L), a phytoplankton containing more than 50% protein and *Ulva lactuca* (2500 mg COD/L), *a macrophyte* containing about 60% carbohydrates, was used in MFCs to produce electricity and their performance was compared. Maximum power densities obtained was 980 mW/m^2 for C. *vulgaris* and 760 mW/m^2 for *U. lactuca* (Velasquez-Orta et al., 2009).

A better modified system would be a PBR along with immobilized cyanobacteria, to generate easily degradable metabolic products, in series with a dark MFC to increase the columbic efficiency of the system, since higher efficiency levels are reached by carboxylic acids than complex materials.

4.2. PMFC with microalgae at the cathode

It is possible to generate O_2 by photosynthesis both *in situ* and *ex situ*, by recirculating the solution from the PBR to the PMFC cathode. The aim of this is to provide the terminal e^- acceptor oxygen without aeration (Logan, 2009). The concept had evolved during the very early development of BES. In the study, the PMFC was provided with O_2 at the cathode by marine algae. In more recent research work, the alga *Chlorella vulgaris* was grown at the cathode and it was claimed that there was mediated electron transfer with the cathode since an artificial mediator was added. However, it is also believed that the oxygen also played a very important role in the transfer process. The artificial redox mediator used might have transferred electrons directly from the non-catalytic cathode to the O_2 produced by photosynthesis activity of the algae. In another recent study, *in situ* O_2 generation in a PMFC using an undefined mixed culture was used to reverse the anode and cathode during the dark and light phases respectively. It might be strategic to have small amounts of O_2 at the anode since it would provide advantageous energetic profiles under micro-aerobic conditions. Also, as mentioned earlier, photosynthetic O_2 generated by bacteria at the cathode on top of the anaerobic sediment, during the light phase, might be advantageous with regards to current generation in sediment type PMFCs.

4.3. Microbial carbon capture cell (MCC)

Carbon dioxide (CO_2) was also demonstrated as the major gaseous end products when either glucose or acetate was used as substrate and in an MFC with real wastewater. In MCC, with light illumination, the microalgae in the cathode chamber can utilize CO_2 from the anode as carbon source for photosynthesis and produce oxygen, which as electron acceptor for electricity generation. Further, CO_2 in exhausted gas from different industries can be converted to useful biomass with photosynthetic creature, achieving simultaneous electricity generation, CO_2 sequestration, wastewater treatment and biomass production. Flue gas which contains large amounts of CO_2 could provide suitable buffering capacity and high NOx-containing flue gas could be used for power augmentation since nitrate can act as potential electron acceptor.

Using microalgae as bio-cathodes in PMFCs help in replacing the mechanical aeration methods. This reduced the cost of the process and is hence more sustainable as well as economic. The algae cultivated in the cathode can also reduce the CO_2 generated from bacterial metabolism and respiration. CO_2 could be used as electron acceptor in cathode. It is already reported that the use of bicarbonate buffer resulted in decrease in the internal resistance and an increased power density and continuous addition of CO_2 to cathodes maintained sustainable catholyte pH and improved the anolyte pH, alkalinity and conductivity. Studies have been conducted with *C. vulgaris* to study CO_2 capture in the cathodic chamber. At 10 %v/v CO_2 concentration, the maximum cell growth of 3.6 $mg\,l^{-1}\,h^{-1}$ was obtained which generated a power density of 2.7 mW/m^2. Use of algae in MFCs help to convert them into complete microbial systems, reducing the need for mechanical energy and hence reducing the net cost of the process. This configuration consists of anodic and cathodic chambers separated by a PEM, and wastewater as an anolyte. The cathode can be illuminated by different light regimes, for 12–24 h, and the importance of light for the working process can be determined. The cell voltage as well as the DO decreases in the dark phase reaction, the acclamation phase power density becoming around 13.5 mW/m^2. Wang et al. developed another configuration of the PMFCs called the microbial carbon capture cell (MCC), which employs the ability of the algae *C. vulgaris* to reduce CO_2 emissions. The CO_2 generated in the anode was removed by the microalgae, while the soluble inorganic carbon was transformed into algal biomass. The output voltage of the MCC (610 mV) was comparable to that of an MFC (630 mV), generating a maximum power density of 5.6 W/m^3 (Wang et al., 2010). From these values it was confirmed that the algae are capable of producing enough oxygen for optimum operation of the MFCs. However, the electricity generated was not constant due to fluctuations in the dissolved oxygen concentration, which is dependent on the illumination in the chamber. It was also discovered that the cathode polarization resistance is higher than that of the anode due to which the cathodic reaction is the limiting factor in this configuration. To reduce this resistance, immobilized *C. vulgaris* is used in the cathode in MCC, the configuration simultaneously generating electricity, treating wastewater and producing biodiesel. 85% COD removal was achieved with a power density of 2485.35 mW/m^3. Compared to suspended cells, the immobilized cells had about 58% more columbic efficiency. Cao demonstrated that in the presence of light, biocathode could be used to directly reduce bicarbonate. When the biocathode was used in an MFC, the maximum power density obtained was 15-fold larger than that produced using a plain carbon cathode. This indicated the possibility of direct electron transfer between a cathode and microorganisms for fixation of carbon dioxide in biomass, while at the same time allowing the generation of electricity from biodegradable organic matter. Pandit et al. investigated the performance of the MCC with *Anabaena* sparged with CO_2–air mixture was compared with that of a conventional cathode sparged with air only. The power densities achieved were 33.3% higher for *Anabaena* sparged with a CO_2–air mixture, as compared to air sparging only. The experimental results suggested that flue gas which contains large amounts of CO_2 might provide suitable buffering capacity and high NOx-containing flue gas could be used for power augmentation since nitrate can act as potential electron acceptor. Power generation in a MCC depends on both light and bicarbonate utilization.

To determine the applicability of *C. vulgaris* for PMFC operation without an oxidant, studies were conducted with organic rich sediments in the anode. The CO_2 generation increase is independent of the generated current and this in turn inhibits CH_4 production. This reflects the

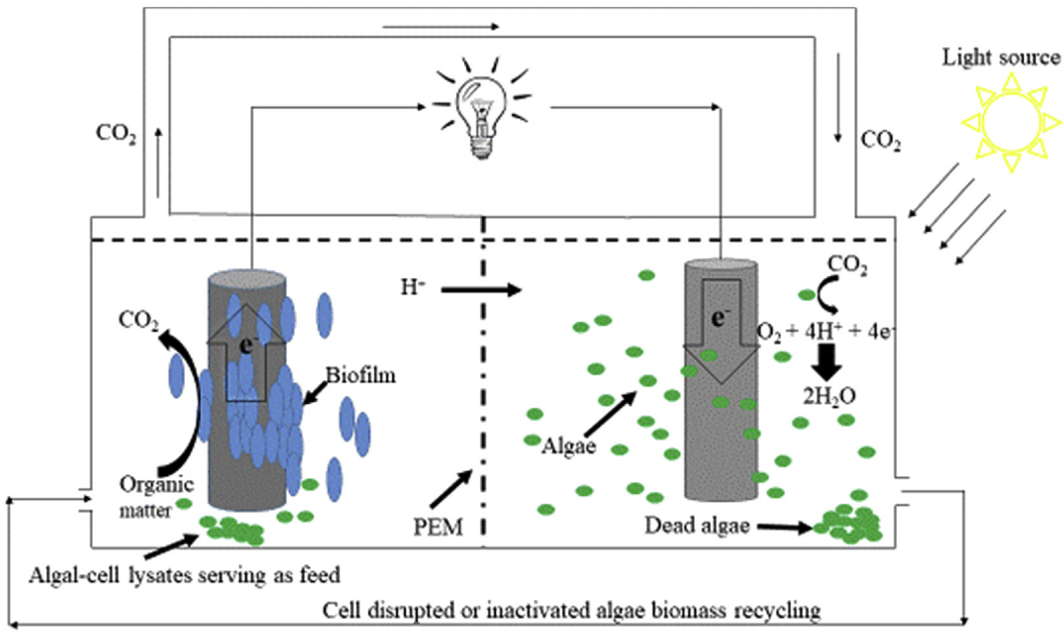

Fig. 7. A schematic representation of an algae-supported microbial fuel cell.

PSMFC capability to provide microalgae biomass producing method by the oxidation of organics based on current generation. A mixed culture of *Chlorella* and *Phormidium* can be used to study the effect of current intensity on power generation by PMFCs (Jiang et al., 2012). High light power should be avoided if oxygen in the cathodic chamber is produced by algal photosynthesis. Syntrophic interactions between the bacteria and the algae were employed to make a photo-solar cell, using mixed cultures of *C. reinhardtii* and the iron reducing bacteria *Geobacter sulferreducens*. The maximum power density was 41 mW/m^2 (Nishio et al., 2013). The algae produced formate in the absence of light, which was oxidised by the bacteria to generate current.

4.4. PMFC with integrated PBR

Another possible configuration, as already mentioned, is formed by connecting a membrane-less up-flow MFC to a PBR containing the microalgae. This can be used for treating wastewater as well as for generating electrical energy. Wastewater is fed into the MFC to reduce COD, phosphorous, and nitrogen and to produce electricity. The effluent leaving the cathode then enters the PBR to reduce the remaining phosphorous and nitrogen by the microalgae. The maximum power density obtained in this case was 481 mW/m^2, along with 78% COD removal. A modified configuration, with a polytetrafluoroethylene membrane introduced, was capable of producing electricity regularly for 100 d with a maximum power density of 110 mW/m^2 (Jiang et al., 2012). This MFC can continuously produce electricity and algal biomass along with treatment of wastewater.

4.5. Proposition of a self-sustainable MFC

The aforementioned studies in this review relied exclusively on the external supply of an energy source either as wastewater or refined organic or inorganic source. A number of studies have been done on the use of algal organisms as electrogens or as feedstock for anaerobic microbial communities for current generation. When used as electrogens, algae convert solar energy to chemical energy, which is then converted to electrical energy via the electron transport chain. For example, a study was undertaken to assess the interaction of photosynthetic microorganisms and heterotrophic bacteria in a phototrophic MFC (PMFC) where He et al. (2009) observed a synergistic relationship between the two microbial groups. Further, the authors observed that current generation increased during the dark cycle while it decreased during the light cycle, whereas current generation with the initial inoculum (one month old) was contradictory. This observation was in agreement with a study where illumination decreased the voltage of a *Spirulina platensis*-driven PMFC while the voltage increased during the dark cycle, producing a maximum power density of 1.64 mW/m^2 (Fu et al., 2009). It is hypothesized that the increase in current generation is due to the utilization of the carbohydrates produced during the light phase (via Equation (1)) and that current decrease during the light phase was due to the oxygen accumulation which is produced by the photosynthetic microorganisms (Ho et al., 2012), which acted as an electron acceptor (Equation (2)) in place of the anode electrode.

$$CO_2 + H_2O + 8\,photons \rightarrow CH_2O + O_2 \quad (1)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

These studies and others which have not been mentioned in this review highlight the use of algal organisms as electrogens and their efficiency in current production. However, these organisms could be utilized as a feedstock to already known or new electrochemically active anaerobic microorganisms for power generation. In a typical double-chambered MFC setup, an electron acceptor is normally an air-cathode (Feng et al., 2008), bubbled O_2, ferricyanide (Oh and Logan, 2006) and permanganate, among others. However, recent studies have demonstrated the capability of algal species such as *Scenedesmus obliquus*, to produce oxygen in the biocathode which resulted in higher power generation compared to that with mechanical aeration (Kakarla and Min, 2014) with another study confirming this observation (del Campo et al., 2013). Furthermore, MFCs produce CO_2 in the anodic chamber which is mostly allowed to escape the chambers unused. However, algal species are known for CO_2 sequestration and could be used as a biocathode to capture the produced $CO_2$and this has been successfully demonstrated in microbial carbon capture cells (Wang et al., 2010). At this stage, the sustainability of the process is still not solved since the anode compartment is still operating using the previously mentioned substrates which add to the costs of the process. To solve this shortcoming, this review proposes for a self-sustainable microbial fuel cell system where the cathode compartment would be inoculated with algal species for oxygen production (facilitates the ORR) and the produced algal biomass would be recycled to the anode compartment as a feedstock for the anaerobic electrogenic microbial community. The resultant CO_2 production from algal biomass degradation would be transferred to the cathode compartment to serve as a carbon source for the algal organisms, thereby creating a closed-loop system which is carbon-neutral (see Fig. 7).

This proposition has been witnessed in studies undertaken by Velasquez-Orta et al. (2009) where a comparative study between powdered micro- (*Chlorella vulgaris*) and macroalgal (*Ulva lactuca*) species produced maximum power densities of 980 and 760 mW/m^2 respectively. Also, activated sludge was fed with algal biomass at the anode, which resulted in the maximum power density of 1780 mW/m^2 (Rashid et al., 2013). Emerging studies are now focusing on the algal pre-treatment strategies for enhanced nutrient bioavailability for energy generation and these range fromalkaline pretreatment to ultrasonic techniques (Wang et al., 2015). Acid thermal-pretreatment of harvested *S. obliquus*slurry in 3% sulfuric acid followed by autoclavation at 120°Cwas undertaken and the authors witnessed a maximum power density of 102 mW/m^2 whereas Wang et al. (2012) obtained a maximum power density of 311 mW/m^2 using an alkaline pretreated mixed algae sludge. Further, Liu et al. (2016)acid-treated *Enteromorphaprolifera* biomass and used this as a substrate in alkaline MFC, obtaining maximum power densities of 3810 mW/m^2. Ultrasonic techniques, which this review recommends, have been observed to be more effective in micoralgal cell disruption for nutrient recovery and this has been confirmed by Prabakaran and Ravindran (2011). Recently, a lipid-extracted *C. vulgaris* culture which was achieved using the chloroform-methanol technique, was harvested in the cathode compartment, was used as a substrate in a pre-acclimatized cow manure inoculum and obtained a maximum power density of 67 mW/m^2 compared to the 28.47 mW/m^2 obtained in a fruit pulp-fed MFC (Khandelwal et al., 2018). This study demonstrated the importance of pre-acclimatization such that electrochemically active microorganisms may be enriched for successful and optimal power generation. This observation was suggested by Doyle and Marsili (2015) where a streamlined approach was proposed for EAM enrichment using a potentiostat-controlled three-electrode set-up. The authors suggested 5 steps, which include (i) inoculum source, which should be sourced from sediments, soil and extreme environments, (ii) medium with multiple carbon sources with solid and soluble electron acceptors, (iii) long-term potentiostatic enrichment, (iv) frequent electrochemical analysis, (v) community profiling using metagenomics and metatranscriptomics, which should result in the discovery of new EAMs.

However, one aspect that is mostly ignored or overlooked in MFC work is how to deal with methanogens and fermentative organisms within the inoculum. The presence of methanogenic and fermentative organisms in the inoculum would compete with the EAMs, thus producing lower power output. 2-Bromoethanesulfonate was used in a microbial electrolysis cell (MEC) to suppress the methanogens and was observed to be successful over 10 batch cycles after the inhibition stage, without adding 2-bromoethanesulfonate (Chae et al., 2010a, 2010b), while in a different study, hexadecatrienoic acid produced by the algae *Chaetoceros* suppressed methanogens and improved power generation (Rajesh et al., 2015). 1.1 mM neomycin sulfate inhibited both methane and hydrogen production in an MEC while 2-chloroethane sulfonate (20 mM), 2-bromoethane sulfonate (20 mM), and 8-aza-hypoxanthine (3.6 mM) inhibited methane generation coupled with an increase in hydrogen production (Catal et al., 2015). Also, *Bacillus cereus* has been shown to possess antimethanogenic properties where 54% reduction in methane production was witnessed when co-cultured with an anaerobic sludge inoculum (Islam et al., 2017). However, it has been demonstrated that natural inhibition of methanogens is possible, but this would require long term enrichment ($\geq$90 days) of the inoculum which would progressively eliminate the presence of methanogens (Rismani-Yazdi et al., 2013). These strategies are paramount to the success of an algae-fed MFC which is proposed in this review for improved current generation.

5. Conclusion

The currently utilized substrates such as acetate, glucose and others, for energy power generation in microbial fuel cell technology add to the already expensive material of construction that is associated with this technology. Although these substrates result in high power generation, their non-renewability hampers the long-term sustainability of this process. Hence, this review proposes for the utilization of algal biomass as a feedstock for power generation in MFC while also serving as a biocathode for the production of oxygen, which facilitates the oxidation-reduction reactions. The biocathode produced biomass would be recycled to the anode compartment as feed while the CO_2 produced from the anode would be transferred to the cathode compartment as a carbon source for the growth of algae. This proposition ensures a carbon-neutral energy generation system which is self-sustainable and can be operated on a long-term basis. However, the effectiveness of this process should be improved by utilizing potentiostatically controlled microorganisms ($\geq$90 days enrichment) such that electrochemically active microorganisms are selected prior to the commencement of the experimental undertakings. This review also proposes for the utilization of cell disruption techniques such ultrasonication to allow for maximal bioavailability of nutrients for the EAMs. In addition, techniques such as metagenomics and metatranscriptomics, among others, should be used to study the community structure and function within these systems such that new or dominant organisms and their resultant gene expression patterns can be elucidated. Although these undertakings can be cumbersome, it is however the authors' belief that these interventions would improve the process performance of an algae-fed MFC for improved power generation.

Declaration of competing interest

The authors declare that there is no conflict of interest that is associated with this work.

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