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Algae based microbial fuel cells for wastewater treatment and recovery of value-added products

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ABSTRACT

Microalgae based microbial fuel cells are efficient systems to remove nitrogen, phosphorous and CO_2 from wastewater, to produce bioelectricity and value-added products from microalgal biomass. Microalgae can be used in MFCs as algae assisted cathode systems, microbial carbon capture cells or sediment microbial fuel cells as well as photosynthetic microalgae microbial fuel cell. These MFCs are shown efficient for CO_2 capture with a low risk of carbon emission, N and P removal via symbiotic interactions of microalgae-bacteria consortia in wastewater treatment along with power generation. The oxygen production by microalgae during the light period reduces the need for external oxygen supply for cathodic reactions, which is advantageous for reducing the aeration cost, as otherwise power needs to be supplied for mechanical aeration. Utilization of algal biomass harvested from the cathodic compartment requires a pretreatment in a biorefinery concept. This still remains a major drawback, but current advances towards the choice of a biofilm on the cathode allow for further recovery of value-added products from algal biomass. Alternatively, the algal biomass can be utilized as the sole feedstock in the anodic compartment. This paper reviews the application of algae based microbial fuel cells for bioelectricity production, mainly focusing on the use of algae in the cathodic compartment, microalgae in the anodic compartment and the main interactions between the compartments affecting the bioelectricity production.

1. Introduction

Fossil fuels currently provide for the majority of the global energy demand with 86% of the total energy production in the world, but also contribute to the environmental degradation due to the CO_2 release during their use [1,2]. On the other hand, renewable energy resources such as wind, solar and bioenergy provide carbon-neutral and sustainable technologies, but need more research especially towards lowering installation and operational costs and improving process yields and efficiencies [3]. Hence, it is essential to develop alternative sustainable systems, such as microbial fuel cells (MFCs) and photosynthetic algal microbial fuels (PAMFCs), that neither cause any CO_2 emission, nor need high installation and running costs and have high energy conversion efficiencies [1–5].

MFCs for bio-electricity production are advantageous due to their sustainable long-term power generation [6]. MFC could possibly integrate with wastewater treatment, allowing bio-hydrogen and value-added products production using these small, low-cost electrical devices [6–9]. However, the MFCs performance is currently limited by its aeration costs (50% of the total operating costs) in the cathodic compartment [10,11]. Del Campo et al. [10] observed that PAMFCs can overcome this drawback and the O_2 supply by the algae present in the system improves the power generation, allows simultaneous CO_2 removal and high cathode polarization resistance as well as reduces the aeration costs. Bio-electricity production in PAMFCs is assumed to occur not only during the light period when algae take-up CO_2, ammonium and produce O_2 via photosynthesis but also during the dark period due to the presence of other electron acceptors (viz. nitrate and sulfate) in

Abbreviations: MFC, Microbial fuel cells; PMFC, Photosynthetic microbial fuel cell; PAMFC, Photosynthetic microalgae microbial fuel cell; MCCs, Microbial carbon capture cells; ORR, Oxygen reduction reaction; SMFCs, Sediment microbial fuel cell; LEA, Lipid extracted algae; LED, Light emitting diodes; EPS, Extracellular polymeric substance; DO, Dissolved oxygen; Pt, platinum; CO_2, Carbon dioxide; O_2, Oxygen; CH_4, Methane; OD_{658}, optical density; COD, Chemical oxygen demand; COD_{tot}, total chemical oxygen demand; COD_{sol}, soluble chemical oxygen demand.

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the cathode compartment [10].

Microalgae can act as biocatalyst for pollutant removal, including organic matter, nitrogen and phosphate, from wastewaters in algal bio-electrochemical systems (Table 1). These systems can be a simple microbial fuel cell (MFC) [11], microbial carbon capture cells (MCCs) [18] or sediment-type algae microbial fuel cells (SMFCs) [49] or a photosynthetic algae microbial fuel cell (PAMFC) [5]. In such bio-electrochemical systems, the cost for mechanical aeration can be significantly reduced due to the oxygen produced by algal photosynthesis with simultaneous uptake of CO_2, N and P during the light period for cathodic reactions, and use of fresh algal biomass or pretreated algal biomass for anode compartment as substrate. These algae based MFC technologies have many advantages over conventional MFC such as internally produced oxygen (electron acceptor) by algal photosynthesis for cathodic reactions, direct electron transfer through electro-active protein, in situ carbon dioxide capture and cost-efficient C, N, P removal in SMFC [5,18,49,52]. Other than minimizing process costs, microalgae based MFCs can be used for the production of value added chemicals such as lipids and pigments from the low cost harvesting techniques (biofilm formation) [5,13]. However, there is a serious knowledge gap in this area due to the lack of comprehensive studies on different algae based MFCs and their specific application potential. This review, therefore, overviews the application of algae based MFCs for bioelectricity production along with their potential for producing other valuable products. Power generation by algae based MFCs is often limited by oxygen supply to the cathode compartment. Other factors that need to be considered for improving the economics of the process are: biocatalyst type, MFC configuration and operation, light intensity, nutrient source, membrane type, electrode size, maximum power density and scale up [11,13–15]. Various algae based MFCs available are discussed further in light of factors influencing the process efficiency. Parameters for the design and performance of algae based MFCs are also discussed, and the future research directions in this area are identified.

Table 1
Major applications of algae based MFCs.

Microbial culture	Application	Comment	Reference
Anode: Municipal wastewater from primary treatment stage Cathode: *C. vulgaris* (INETI 58) strain	Value pigments production	Total pigment percentage in the extracts is 0.6% w/w (g pigment/100 g dry microalgal biomass)	[5]
Anode: Facultative anaerobic sludge from wastewater sedimentation tank Cathode: *C. vulgaris*	Production of algal biomass	Biomass yield of 0.44 g L^{-1} day^{-1} or maximum biomass concentration of 4 g/L	[13]
Anode: Activated sludge Cathode: *C. vulgaris*	Wastewater treatment (COD, N and P removal)	At anode compartment: 70% (NH_4^+ removal), 75% (COD removal), and 26% (PO_4^{3-} removal)	[10]
Anode: Activated anaerobic sludge Cathode: Algae based cathode	Algal biomass production in combination with wastewater treatment	Algal biomass is utilized as anodic feedstock	[11]
Anode: Acclimated from domestic wastewater Cathode: *C. vulgaris*	Carbon fixation	94 (±1%) of carbon capture in microbial carbon capture cells (MCCs)	[18]
Anode: Acclimated from domestic wastewater Cathode: *C. vulgaris*	Algal biomass used as the substrate	Algae biomass of 5 g/L lead to the power output of 1.78 W/m^2	[35]
Anode: Electrochemically active bacteria Cathode: *C. vulgaris*	Lipid production	Lipid content of 56.75 (± 0.92)%	[53]

2. Algae based MFCs

2.1. Photosynthetic algal microbial fuel cell

Microalgae can be used in the cathode compartment of a MFC to provide the electron acceptor oxygen for the MFC functioning [10,11,13,15–19]. Typical PAMFCs used for oxygen supply are small and consist of two identical cylindrical or cubical compartments (25–50 mL each) divided by an ion exchange membrane [5]. These are usually designed based on dissolved oxygen requirements for the cathode compartment, such as electron acceptor for the cathode as well as DO (dissolved oxygen) for the oxygen reduction reactions. Algae based MFCs, which are not particularly considered to improve microalgal activity, were established by Strik et al. [20] in order to match oxygen production (used as electron acceptor at the cathode) with the simultaneous CO_2 sequestration to biomass.

Algae based MFCs can be single, dual or three chambered built in a tubular, plate and frame, rectangular, circular or H-type configuration made of plexiglass or acrylic material to allow light penetration (Fig. 1). Their volumes range from 200 to 1000 L for pilot-scale applications [21–24]. Under optimal conditions, algae based MFCs can produce power densities up to 153 mW/m^2 (32% higher than mechanical aeration) compared to 116 mW/m^2 with mechanical aeration [14]. PAMFC configurations are limited due to high operational and construction costs [56].

2.2. Microbial carbon capture cells

As indicated by the name microbial carbon capture (MCC) in such bio-electrochemical systems, carbon sequestration is achieved by algae present in the cathodic chamber which is fed with off-gas containing carbon dioxide generated in the other anodic chamber. The sequestered carbon is subsequently used for bioelectricity production. Microbial carbon capture cells (MCCs) offer in situ carbon dioxide capture and better voltage outputs (610 ± 50 mV) than MCCs without aeration, which are similar to those of MCCs (630 ± 30 mV). MCCs are significantly different from PAMFCs with a low risk of carbon dioxide emissions from the anode compartment. MCCs can also utilize CO_2 from the atmosphere or flue gases from fossil fuel combustion and fermentation industries in order to minimize the cost of external CO_2 supply [18,25] and minimize CO_2 emissions by bacteria at the anode compartment and by microalgae at the cathode compartment [11]. MCCs can be scaled up by increasing the cathode specific surface area and electrode spacing [7,24]. They also exhibit higher power densities than MFCs because of the large cathode specific surface area and electrode spacing (reduction in solution resistance) [24,26,27]. Furthermore, a high DO concentration in the cathode compartment up to 7.6 mg/L (DO saturation is 7.6 mg/L at 30 °C) has been attained in MCCs [18]. Voltage produced in MCCs with external aeration is reported to be 630 (± 30) mV, which is comparable with the value reported for MCCs without aeration (610 ± 50 mV) (Wang et al., 2010). Moreover, the maximum production of power density in air cathode MFC (140 mW/m^3) is only slightly higher than the value reported for PMMFC (125 mW/m^3), which indicate that cost due to external aeration can be avoided in algae based MFCs.

2.3. Sediment microbial fuel cells (SMFC)

A sediment microbial fuel cell (SMFC) utilizes sediments like carbon nanotubes and nanoparticles to establish a better contact between the electrode and electrolyte, so as to obtain an efficient electricity generation. Microalgae can also be used in the cathode compartment to provide electron acceptors in algae-based sediment microbial fuel cells (SMFCs) [17,28–30]. Immobilization of *Chlorella vulgaris* on nanotubes used for oxygen supply to the aerobic sediment phase at the cathode has been reported [17]. These algae based SMFCs, which are mainly designed to improve the oxygen consumption rate, were proposed by He

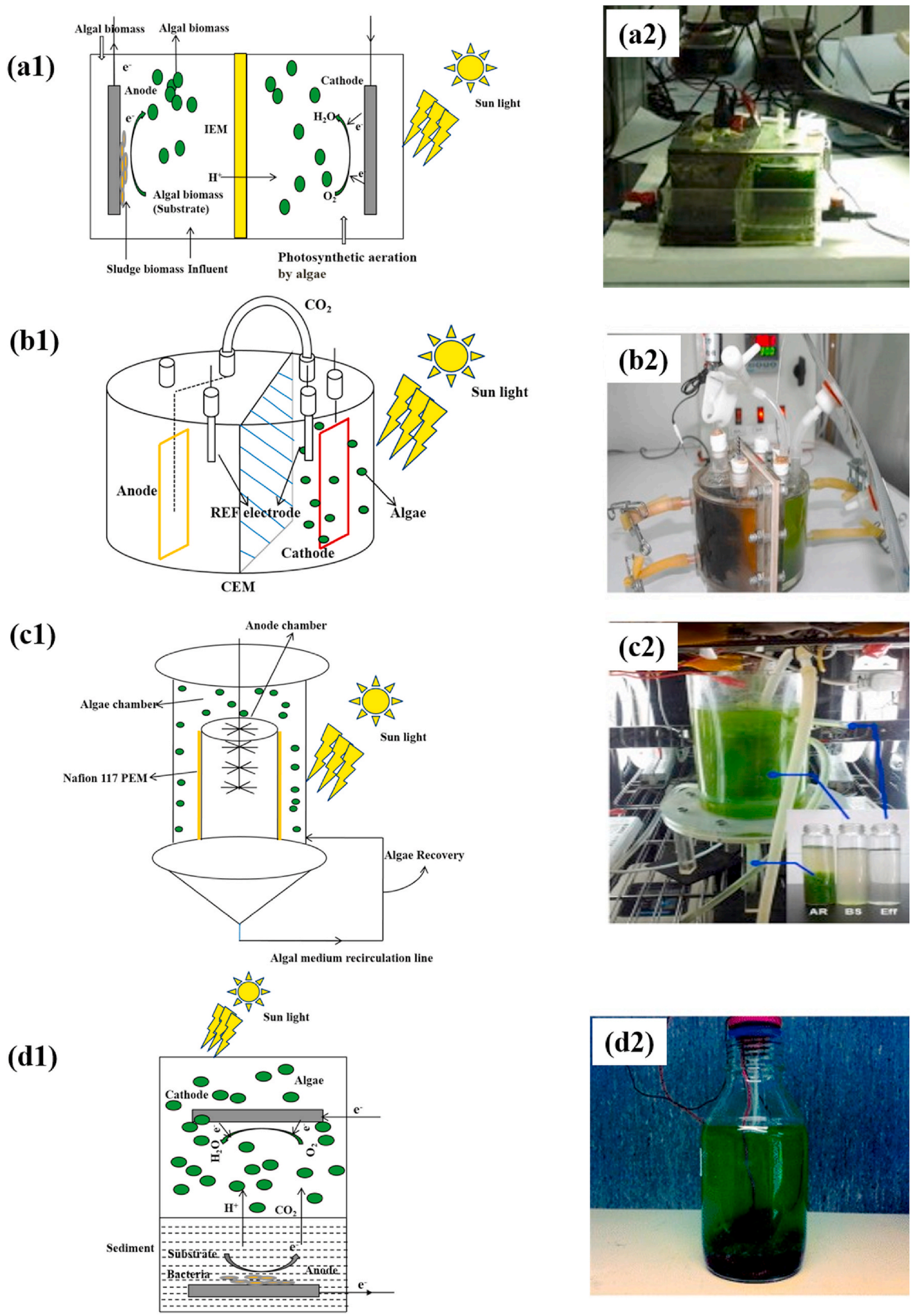

Fig. 1. Schematic representation of (a1) flat plate MFC, (b1) MCCs with CO_2 exchange from the anode compartment, (c1) tubular PMFC and (d1) sediment type PMFC. Image of (a2) flat plate MFC (reused with permission from Del Campo et al. Copyright (2015) Fuel), (b2) MCCs with CO_2 exchange from the anode compartment (reused with permission from Wang et al. Copyright (2010) Biosensors and Bioelectronics), (c2) tubular PMFC (reused with permission from Ma et al. Copyright (2017) Water Research) and (d2) sediment type PMFC (reused with permission from Zhang et al. Copyright (2011) Energy and Environmental science.

et al. [31] who designed a rotating cathode in a river SMFC in order to match the increased oxygen availability with a high-power generation of 48 mW/m^2 compared to algae assisted SMFC (38 mW/m^2). These algae based cathodes in SMFCs were made of Plexiglas, acrylic, or glass material to support light penetration in the cathode made from graphite felt multi-walled carbon nanotubes coated with *C. vulgaris*, solely graphite felt multi-walled carbon nanotubes and graphite felt coated with *C. vulgaris*. In order to improve the oxygen reduction rate, graphite felt of different types have been used at lab-scale with a maximum working volume of 240 L [17,32–34]. Under optimal conditions, algae based SMFCs can produce power up to 21 mW/m^2, which can be further improved to 38 mW/m^2 with addition of carbon nanotubes (multi--walled carbon nanotubes-*C. vulgaris)* in the cathode compartment [17]. An increase (2.4 times) in the power produced in the cathode compartment due to carbon nanotube addition is supported by the reduction in oxygen produced by the algal biomass present. Algae based MFC for treating N and P rich wastewater and CO_2 sequestration consists of either the flat panel or tubular configuration. Both these configurations offer efficient light utilization and good scalability for industrial wastewater treatment. However, the tubular configuration is reported to outperform the flat panel and sediment type algal microbial fuel cells [47,55,56]. This type of configuration (open type) is more preferable than tubular, plate and frame due to low operational and construction costs [56].

3. Use of algae in MFCs

3.1. MFCs with algae-assisted cathodic compartment

Mechanical aeration in MFCs accounts for approximately 50% of the total operating cost [10]. Therefore, microalgae based MFCs can be more energy efficient due to algal photosynthesis in the cathodic compartment, which can provide O_2 for the cathodic reactions (Fig. 2 and Fig. 3). This symbiotic relationship can also be used for sustainable development of MFCs by using excess algal biomass as electron donor in the anodic compartment and CO_2 from the anodic compartment as

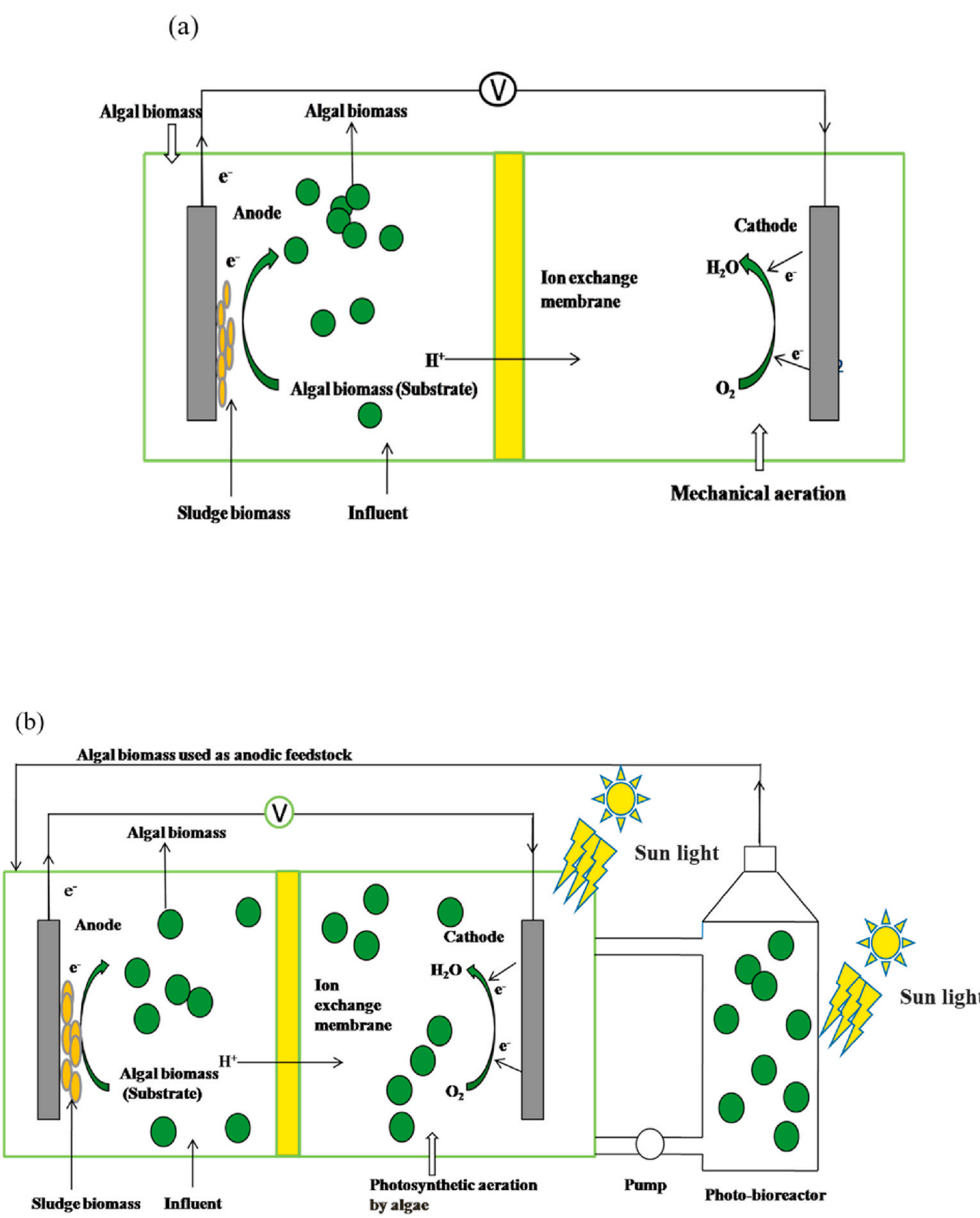

Fig. 2. Algae based MFCs with (a) direct utilization of algal biomass as anodic substrate and (b) harvested biomass from cathodic compartment used as feedstock for anodic compartment.

inorganic carbon source for algal growth, which is advantageous in terms of simultaneous CO_2 capture and electricity production. Fig. 4 shows the different mechanisms of electron transfer between algae and electrode in the cathodic compartment. Fig. 4a shows the direct transfer of electrons using CO_2 as the acceptor from the cathode to the algae. In some cases, self-supported mediators, e.g. c-type cytochromes found in the outer membrane of algal cells, support extracellular electron transfer as portrayed in Fig. 4b, whereas Fig. 4c depicts the reduction of O_2 produced during algal photosynthesis [17,18,52]. Some previous studies reported successful use of algae in the cathodic compartment for power generation using MFCs (Table 3). For example, an algae assisted cathode was successfully utilized for power production in MFCs with a maximum power density of 21 mW/m^2, which was further improved to 38 mW/m^2 with modification (carbon nanotube coating) of the cathode [17]. Similarly, the growth of algae on the surface of the cathode supported oxygen production by algae via photosynthesis without any external aeration and with the addition of sodium carbonate as inorganic carbon source [14]. Wang et al. [18] analyzed different algal concentrations of 0.21 and 0.85 with optical densities (OD_{658}) at 658 nm for the removal of CO_2 in algal based MFCs and compared the electricity production values. Oxygen produced by algal photosynthesis was efficiently consumed (DO concentration decreased from 7.6 to 0.9 mg/L), showing that the produced O_2 during the light period was used as electron acceptor for the cathodic reaction with an excess of inorganic carbon source. Simultaneous use of algae in both the anode (lipid extracted algal biomass used as electron donor) and cathode (oxygen produced by algal photosynthesis used as electron acceptor for the cathodic reaction) compartment in algae based MFCs yielded a maximum power density of 2.7 W/m^3 [18].

3.2. Algal biomass as substrate for the anodic compartment

Algal biomass can be considered as a complex organic substrate for the anode half-cell in MFCs [11,35], which can be efficiently utilized to produce bioelectricity without any pretreatment (Table 4). The mechanisms involved in algal fed MFCs for bioelectricity production from

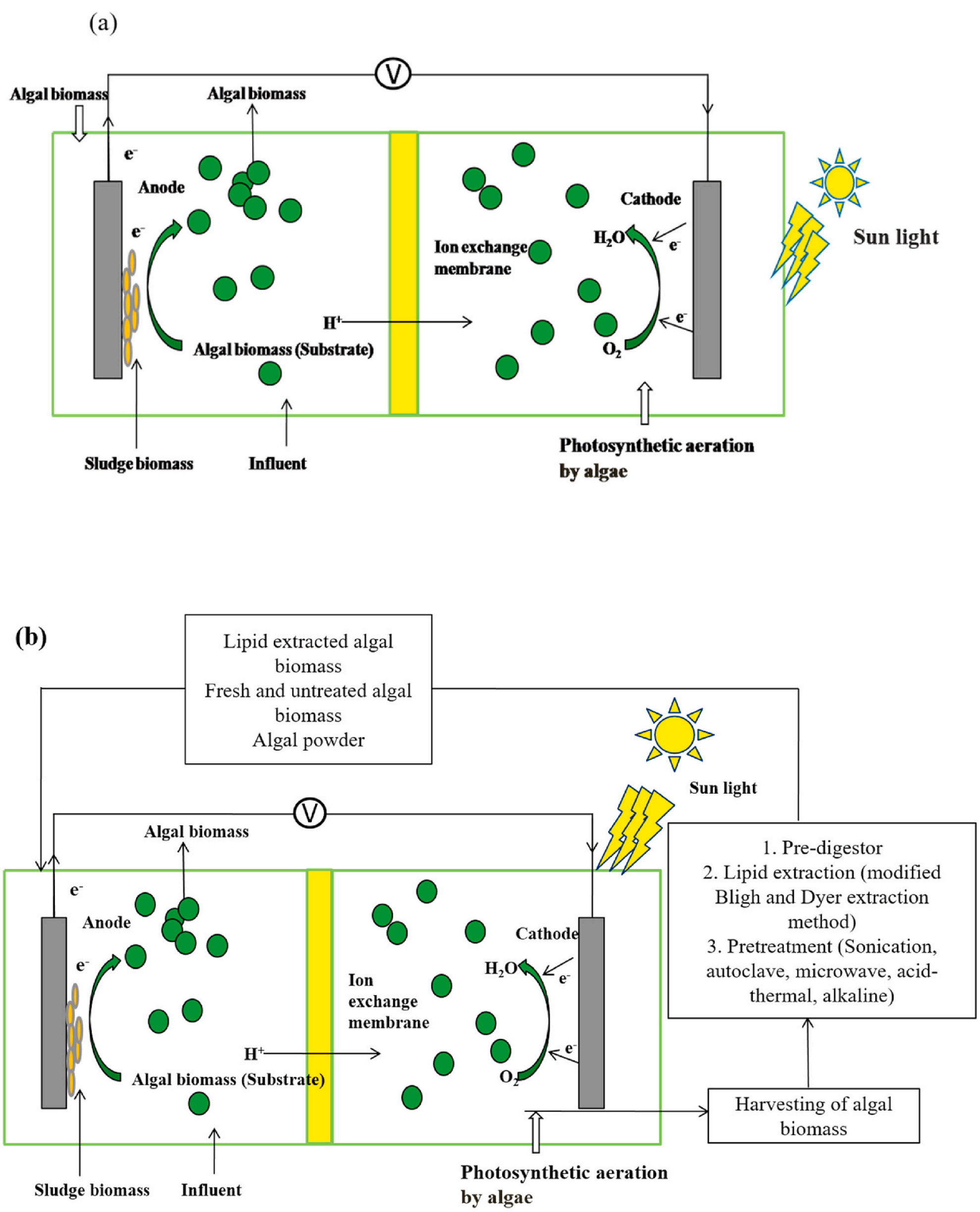

Fig. 3. Algae based MFCs: (a) direct use of algae as electron acceptor for cathodic reaction biomass and (b) harvested biomass from cathodic compartment followed by different pretreatment techniques used as feedstock for anodic compartment (electron donor).

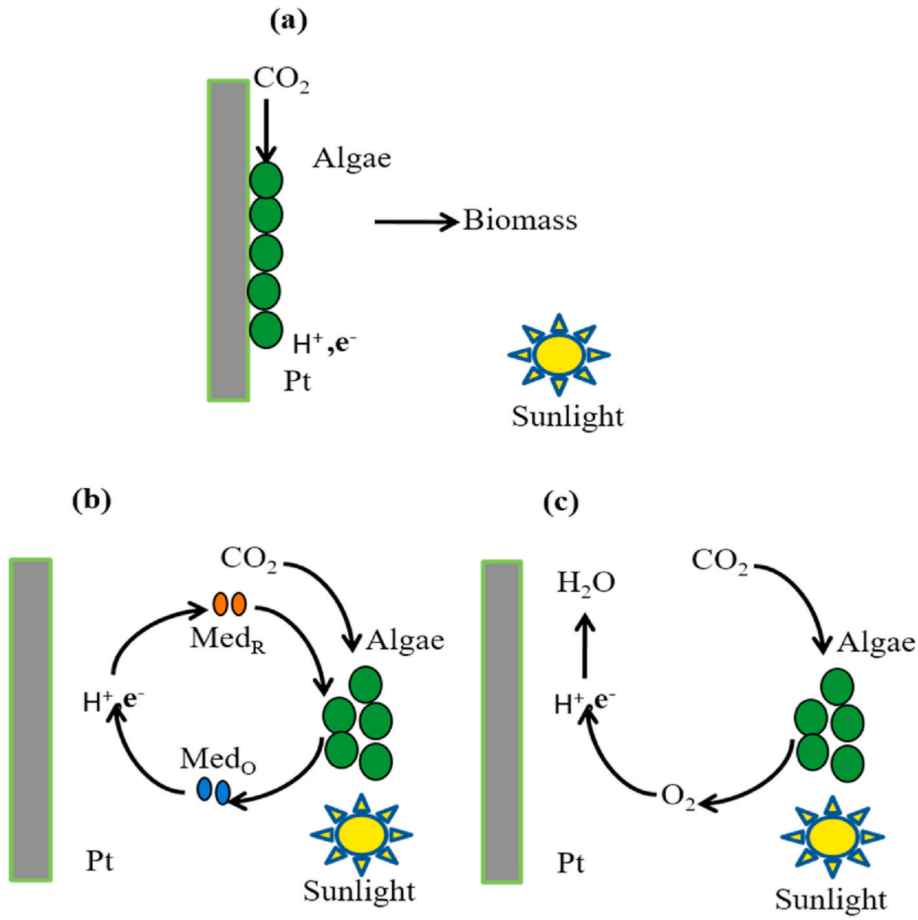

Fig. 4. Possible mechanisms of cathode reaction in PAMFCs: (a) direct transfer of electrons (CO_2 as the acceptor) from cathode to algae, (b) mediator supported electron transfer and (c) Reduction of O_2 produced by algal photosynthesis (reused with permission from Wang et al. Copyright (2010) Biosensors and Bioelectronics).

Table 2
Comparison of different types of algae based MFCs using an algae assisted cathode.

Types of MFC	Effective volume of the cathode or wet sediment	Microalgae in the cathode	Maximum power density or current	Maximum DO concentration (mg/L)	Reference
PAMFC	140 mL	*Chlorella vulgaris*	126 mW/m^3	9.5	[13]
Two identical double-chamber MCCs	220 mL	*Chlorella vulgaris*	5.6 W/m^3	7.6	[18]
Two identical chamber of an H-type MFCs	125 mL	*Scenedismus obliquus*	153 mW/m^2	15.7	[14]
SMFC	650 mL or 700 g	*Chlorella vulgaris*	38 mW/m^2	5.8	[17]
PAMFC	2 L	Algae	110 mW/m^2	6.0	[20]
PAMFC	1 L	*S. platensis*	10 mW/m^2	NA	[12]
PAMFC	171 cm^2 for cathode Compartment	*Chlorella*	200 mA/m^2	NA	[47]
PAMFC	100 mL	*Chlorella vulgaris*	62.7 mW/m^2	NA	[5]
Fully biotic MFC	50 mL	Fresh pond water	128 μW	NA	[11]
SCMFC	125 mL	*Chlorella vulgaris*	123.2 (±27.5) mW/m^3	NA	[48]

*PAMFC; photosynthetic algal microbial fuel cells; MCCs; microbial carbon capture cells; MFCs; microbial fuel cells; SMFC; sediment-type algae microbial fuel cells; SCMFC; Single chamber microbial fuel cell.

wastewater are analogous to the use of wastewater as the substrate for the anodic compartment in MFCs (Figs. 2b and 3). A maximum power output of 1.78 W/m^2, 0.85 W/m^2 and 0.56 W/m^2 has been reported using 5 g/L, 2 g/L and 1 g/L of dry algal biomass, respectively, thereby confirming that the algal fed MFC process is feasible and produces bioelectricity comparable to that with other organic substrates, e.g. acetate which generates a maximum power density of 0.661 W/m^2 [36].

Velasquez et al. [37] utilized two algae species, *C. vulgaris* and *Ulva lactuca*, in dry powder form as the feed in the anodic compartment of MFCs. The *C. vulgaris* MFC produced 2.5 kW h/kg dry weight compared to 2.0 kW h/kg dry weight with the *U. lactuca* MFC that had a maximum power density of 0.98 W/m^2. Gajda et al. [11] fed different concentrations of algal biomass (0.25, 0.39, 0.56 and 0.72 g/L) in MFCs, which yielded power production values of, respectively, 10, 17, 11 and 17 μW.

Algal biomass can still be out-competed by acetate in the anodic half-cell in MFCs because microalgae biomass is a complex substrate with slow release of the electrons. Walter et al. [38] compared the use of fresh algal biomass in a cascade of 9 MFCs with a maximum output of 42

Table 3
Use of O_2 produced by algae as electron acceptor for the cathode.

Algae	Cathode name	Power generation	Reference
Algae from fresh pond water	Algal water, Algae, Algae string, Algae cellulose, Algae wire	Maximum power production of 128 μW; algae water 81 μW, algae string 74 μW, algae wire 67 μW and algae cellulose 61 μW	[11]
C. vulgaris	Algae assisted cathode	Maximum power production of 21 mW/m^2, which further increased to 38 mW/m^2 with modification on the cathode (carbon nanotube coating)	[17]
C. vulgaris	Algae assisted cathode	13.5 mW/m^2 at steady state conditions.	[10]
Scenedismus obliquus	Attach on the surface of a cathode electrode	Maximum power density of 153 mW/m^2	[14]
C. vulgaris	Algal cathode	Maximum power density of 5.6 W/m^3	[18]
C. vulgaris	Algal cathode	Power density of 68 ± 5 mW/m^2	[49]
C. vulgaris	Algal cathode	Power density of 2.7 mW/m^2	[15]
C. vulgaris	Algal cathode	Maximum power density of 62.7 mW/m^2	[5]
C. vulgaris	Algal cathode	Maximum power density of 67.07 mW/m^2.	[16]
C. vulgaris	Algal cathode	The maximum volumetric power density of 123.2 ± 27.5 mW/m^3	[48]
Chlamydomonas reinhardtii and *Pseudokirchneriella subcapitata*	Algal cathode	The maximum power density of 2.2 W/m^3	[26]
Chlorella and *Phormidium*	Algal cathode	Maximum power density of 18 and 26 W for 6 and 12 W power of light.	[50]
Chlorella vulgaris	Algal cathode	The maximum power density of 126 mW/m^3	[13]
Chlorella	Algal cathode	The maximum current density 200 mA/m^2	[47]

W/m^3 of fresh algal culture (6 × 10^5 cells/mL). Wang et al. [9] utilized *C. vulgaris* and *Microcystis aeruginosa* from an algal bloom in an aquatic environment and reported maximum volumetric power densities of 3.70 W/m^3 (*C. vulgaris*) and 4.14 W/m^3 (*M. aeruginosa*). Lipid extracted algae (LEA) harvested from the cathode compartment can serve as well as a substrate for the anodic half-cell with a maximum power density of 67.07 mW/m^2 [16].

Algal biomass contains a strong cell wall, which often hinders its effective utilization by microorganisms such as bacteria in the anode chamber of MFCs. This can be solved by pretreatment of the algal biomass by various techniques such as sonication [35], thermal treatment [19] or microwave treatment [39]. For example, a maximum power density of 1.78 W/m^2 was produced with 5 g/L of dry algal biomass pretreated with thermal and sonication techniques [35]. Gadhamshetty et al. [39] pretreated *Laminaria* brown algae biomass by autoclaving and microwave irradiation before using it as the substrate in the anodic compartment of MFCs. The autoclave-based pretreatment produced more power density energy (218 mW/m^2) compared to microwave irradiation (118 mW/m^2) or without any pretreatment (86 mW/m^2) [39]. These studies show the potential of different pretreatment techniques in enhancing the utilization of algal biomass in MFCs.

Table 4
Use of algal biomass as the substrate (electron donor) in the anode compartment in MFCs for power production.

Anode culture	Pre-treatment method followed	Power production and biomass concentration	Reference
Mixed culture of activated sludge and *Scenedesmus*	Nil	1.78 W/m^2 0.85 W/m^2 and 0.56 W/m^2 at 5 g/L, 2 g/L and 1 g/L	[35]
	Pre-treated algal biomass -Sonication	Maximum voltage of 0.604 V (untreated algae biomass) and 0.290 V (pre-treated mixture)	
Laminaria	Nil Autoclave Microwave irradiation	86 mW/m^2 218 mW/m^2 118 mW/m^2	[39]
Synechococcus leopoliensis	Fresh and pretreated algal biomass –pre digester	42 W/m^3 of fresh culture (6×10^5 cells mL^{-1}).	[38]
Microcystis aeruginosa and *Chlorella vulgaris*	Nil	3.70 (±0.02) W/m^3 and 4.14 (±0.05) W/m^3	[51]
Algae water	Nil	10, 17, 11, 17 μW at 0.25, 0.39, 0.56 and 0.72 g/L concentration	[11]
C. vulgaris and *Ulva lactuca*	Pre-treatment of *U. lactuca*- drying in a hot-drum (93% loss of total water) *C. vulgaris*- spray drying	Maximum power density of 0.98 W/m^2	[37]
Algae sludge from domestic wastewater treatment	Nil	MFCs by raw algal sludge a current density of 0.6 A/m^2	[51]
	Alkaline pretreatment	311 mW/m^2 for MFCs at a current density of 0.86 A/m^2	
Lipid extracted algae	Lipid extraction by modified Bligh and Dyer extraction method	Maximum power density of 67.07 mW/m^2	[16]
Scenedesmus obliquus	Pretreatment-acid-thermal	Maximum power density of 102 mW/m^2 (951 mW/m^3)	[19]

4. Design considerations for algae based MFCs

4.1. Algae biomass concentration in the cathodic compartment

The microalgae biomass concentration influences the light utilization efficiency in PAMFCs [13]. It also controls oxygen production and power generation in algae based MFCs. Bazdar et al. [13], for example, reported a decrease of 53.4% in coulombic efficiency when the biomass concentration in the cathodic compartment was increased from 3.6 (5000 lux) to 4.0 g/L (10,000 lux) in a PAMFC. However, the coulombic efficiency increased with 24% when the biomass concentration increased from 3.25 to 3.6 g/L. When the biomass concentration reaches a maximum value, all the light supplied to the MFCs is utilized for photosynthesis and the dissolved oxygen concentration increases to a maximum. Any further increase in biomass concentration causes back diffusion of oxygen to the cathode compartment [24,40], which reduces the power density in the MFCs. Nevertheless, at high light intensities, PAMFC can be utilized as biological reactors for microalgal growth which helps in maximizing the photosynthetic activity [13]. In general, the higher the light intensity, the higher should be the biomass concentration, and the use of high amounts of algal biomass with high light/dark frequencies thus produces a maximum power density (126 mW/m^3 at 24/00 light/dark regime). Estimating the best biomass concentration under sunlight is also difficult as onsite availability of light differs very much with time and geographic condition.

4.2. Electrode spacing and separator

Electrode spacing and the use of a separator in the MFCs is critical to its performance [24,40]. Narrow electrode spacing (anode placed too close to the cathode) limits the production of power density and oxygen crossover via the cation exchange membrane affects the anode bacteria [24,40]. Electrode spacing used for MFCs should be selected properly to produce improved power density based on solution resistance and electrochemistry. Cheng et al. [40] reported an increase in power intensity from 720 to 1210 mW/m^2 in MFCs when the anode was separated from the air cathode at 4 and 2 cm, respectively. Conversely, separating the anode within 1 cm of the cathode reduced the power density in the MFCs. A cloth separator is, therefore, often used to decrease the level of oxygen transfer between the anode and cathode and to improve the power production. Cheng et al. [40] reported an increase in power density with a maximum electrode spacing of 11 mm for a solution containing high acetate concentrations and a spacing of 1.7 mm for domestic wastewater. Hence, the optimum spacing depends on the design configuration, type of substrate and oxygen permeability of the membrane.

4.3. Cathode specific surface area

A critical design factor of MFC systems is the cathode specific surface area that determines the maximum power density when scaling up MFCs. For lab-scale MFCs, a relatively low liquid per cathode surface area and small electrode spacing are most important for achieving a maximum power density production due to their low oxygen transfer crossover [40]. However, the cathode specific surface area should be optimum from the point of economics, high power output and easy operation as well.

A high cathode specific surface area generally means high cost owing to the materials used (Pt or other metal catalyst) and aeration in particular for large scale MFCs. For this purpose, algae based MFCs are recommended for large scale applications [16,18] as the expenses for aeration cost and metal catalyst are taken care of by algae. Information on large scale power generation related to the cathode specific surface area achieved in algae based MFCs is, however, thus far not reported in the literature.

5. Influence of operational parameters on PAMFC performance

5.1. Dissolved oxygen concentration in the cathode compartment

High dissolved oxygen concentrations can cause back diffusion of oxygen into the anode compartment and therefore decrease the power density [24,40]. For example, Bazdar et al. [13] reported a 53.4% decrease in power density when the dissolved oxygen concentration inside the cathode compartment increased from 7.8 to 9.5 mg/L. Light saturation or photoinhibition severely reduced the power density in a PAMFC planned for mass algal cultivation that can reach up to 4 g/L (biomass concentration).

High DO concentrations do not pose serious problems in power generation due to the continuous decrease of the O_2 concentration in the cathode compartment. For example, the dissolved oxygen concentration was always low ($\approx$0.9 mg/L) during the cathode reaction in MCCs [18]. However, it also rapidly decreased after maximum power was produced [18]. Low dissolved oxygen concentrations are thus a good evidence of maximum power generation in PAMFCs with oxygen as the electron acceptor. Further research is warranted to understand if the DO concentrations can be utilized for process control to enhance, for example, the power generation in PAMFCs.

5.2. Light intensity at the cathode compartment

Variation in light intensity greatly affects the performance of algae MFCs. The algal biomass concentration increases with light intensity up to 3500 lux–10000 lux, where the PAMFC becomes saturated [13,41]. Photoinhibition has been observed with light irradiance up to 10,000 lux [13], and it is likely to occur at low light intensity in the range of 3500–5000 lux (light limitation). Careful selection of the optimum light intensity in algae based MFCs is, therefore, required to avoid photo-inhibition of algae. Increasing the light intensity beyond light saturation reduces power generation and microalgal activity in PAMFCs [13,41].

The dark period does not allow photosynthesis, which generally leads to low or no power generation in PAMFCs. However, photosynthesis and power generation usually restart when light is accessible again. PAMFCs are thus designed to operate under different light and dark regimes, for example, 24/00, 16/8, 12/12 h of light/dark regimes, with increased electricity production of, respectively, 126, 112 and 72 mW/m^3 [13]. Maintaining a dark period is also important for algae respiration and oxygen consumption. In a PAMFC with *C. vulgaris*, power generation dropped when the illumination period was reduced from 16/8 h to 12/12 h (72%–57% coulombic efficiency).

5.3. Use of artificial light sources

Artificial light using e.g. light emitting diodes (LED) can significantly improve algal growth, which usually enhances the performance of MFCs [42]. The performance and efficiency of MFCs were enhanced when LED was used as the source of light as compared to conventional light sources such as compact fluorescent lamps [43].

Power density increases with increase in light intensity (100–900 lux) which was operated under both blue (0.156–4.741 mW/m^2) and red (1.525–12.947 mW/m^2) light [42]. Enhanced electron movement from the algal cell via the electrolyte to the electrode was reported when using red LED light, which occurs due to the high absorption of light energy by the photosynthetic system of algae at this wavelength. Selection of the light wavelength (white, red, yellow, blue and green) in PAMFCs is hence required to achieve maximum power density [42,43]. Blue light affects photosynthesis (lower absorption of light energy), which leads to lower power generation in PAMFCs [42]. However, photosynthesis and power density are affected when light of different wavelengths is used [43]. PAMFCs are thus designed to operate under different light wavelengths, for example, red LED produced a maximum power density of 12.947 mW/m^2. In a PAMFC with *Chlamydomonas reinhardtii*, power generation increased when red LED light (12.947 mW/m^2) was replaced with blue LED light (4.741 mW/m^2).

5.4. Carbon dioxide mass transfer rate

The carbon dioxide mass transfer rate can affect the growth rate of algae in the cathode compartment, thereby decreasing the oxygen production by algae and thus the power density [15,44]. For example, Powell et al. [15] reported an increase in growth rate of algae from 1 to 3.6 mg/L·h when the carbon dioxide concentration was increased from 0.037% to 10% by volume and a further increase in carbon dioxide concentration decreased the growth rate from 3.5 to 0.25 mg/L·h. However, carbon dioxide generated from the anode compartment for organic substrate degradation does not pose serious problems in power generation due to the continuous decrease of the carbon dioxide concentration in the cathode compartment by algae. A maximum power density of 5.6 W/m^3 was observed during exchange of carbon dioxide from the anode compartment to the cathode compartment in MCCs due to its utilization by algae in the cathode compartment. However, the increase in voltage produced was only 60 mV when pure CO_2 was supplied in the cathode which was attributed to a pH change of the solution [18]. Thus, a low CO_2 concentration is preferred for maximum power generation in MFCs with oxygen (produced by algal photosynthesis) as the electron acceptor. Further research is required to establish if CO_2 released from the anode compartment can be used for achieving maximum power density in algae based MFCs. Besides, environmental factors, in particular pH and temperature, also affect algal growth, which are well-reported in the literature [58].

5.5. Challenges of algae based MFC design and operation

Microalgal cathode-assisted MFCs are an attractive technology for power generation, value added chemical production and wastewater treatment. However, there are many challenges to become commercially successful. For example, although microalgae can be used as the substrate for the anodic compartment, pretreatment of the algal biomass using techniques such as thermal, sonication, alkaline and acid treatment complicates the direct use of algal biomass in MFCs [9,11,35,37,38]. Moreover, algae based MFCs with lipid extracted algae (used as the substrate) can affect the growth of anodic microorganisms due to the presence of toxic chemicals or the solvents used for the lipid extraction [35].

Electricity production is influenced by the thickness of the cathodic biofilm as it limits oxygen diffusion and CO_2 mass transfer [11,45]. Also, changing the cathode electrode to biocathodes is challenging for efficient application of this process in terms of biofilm formation on the electrode surface [11]. Change in cathode type can alter the surface structures of microalgal cells within the biofilm, i.e. hydrophobicity, cell morphology, net electrostatic charge, biofilm thickness and biofilm structure, which in turn affect the bioelectricity generation [11]. In spite of the requirement of utilizing a buffer system to maintain the pH in the biocathode compartment, it has emerged to be one of the main problems for MFCs with a biocathode, since sustainable MFCs have to operate at high rates; and thus high chemical (buffer agents) usage. The performance with CO_2 is an additional main concern, as CO_2 limited conditions in the biocathode influence the power generation [15,18].

Oxygen diffusion is key to achieving high performance of biocathode MFCs, as it is essential for an efficient diffusion of oxygen (biofilm) to the electrode. This crossover can decrease the cathode or anode potential and change its surface features leading to inhibition of the catalytic agent or the anode microorganisms, which adversely affects the system performance and coulombic efficiency [24,40]. As compared with the conventional wastewater treatment systems, algae based MFCs require a large land area for efficient light utilization by the algal biomass, which escalates the cost of such algal based treatment systems [57]. Besides, fluctuation in light intensity during various seasons of a year negatively impacts oxygen production and eventually bioelectricity production in algae based MFCs [57].

6. Wastewater treatment and production of value-added chemicals using algae based MFCs

6.1. Nitrogen and phosphorous removal using MFCs with algae assisted cathode

Microalgae have gained interest as attractive organisms for application in nitrogen and phosphorous removal bioprocesses [5,10,18,26]. They are highly suited for removal of N, P and COD from wastewater, and at the same time produce oxygen which can be used as electron acceptor in algae assisted cathodes. Xiao et al. [26] reported a decrease in nitrogen (98% N as ammonium) and phosphorus (82% P as phosphate) from municipal wastewater by *Chlamydomonas reinhardtii* and *Pseudokirchneriella subcapitata* using an integrated photobiochemical system (MFC inside an algal reactor). The authors suggested that the N and P removal occurred in both the anode and cathode compartments, where 55% phosphate removal was due to algal activity in the cathode chamber and 27% removal by bacterial activity in the anode compartment. In another study, Del Campo et al. [10] clearly established the high potential of using an integrated system consisting of a photo-bioreactor and an upflow membrane-less microbial fuel cell for the removal of N (58.7% ammonium) and P (99% phosphate). It has been successfully used for treating digestate from anaerobic digestion of food waste containing a low COD/N ratio and fixing CO_2 from flue gas generated during processes, such as fermentation and fossil fuel combustion [53,54].

6.2. COD removal (algal biomass) in algae based MFC

Algae based MFCs can utilize various forms of algal biomass produced from the cathode compartment, including fresh and untreated algal biomass, lipid extracted algal biomass, pretreated algal biomass, algal powder and pre-digested algal biomass (Table 2). Previous studies examined the performance of algae based MFCs with different biomass concentrations (1–5 g COD/L) to understand the feasibility of using algal biomass as chemical oxygen demand (COD) in the anode compartment for enhancing the bioelectricity production and COD removal efficiencies [35]. Both current and power density depended on the algal biomass concentration. Recent studies focused on using pre-treated algal biomass of *Scenedesmus obliquus* in terms of total (COD_{tot}) and soluble (COD_{sol}) chemical oxygen demand to determine the applicability of algal biomass as the substrate for the anode in MFCs. The composition of raw algal biomass is different from pretreated algal biomass, which is readily degradable and yielded maximum COD_{tot} and COD_{sol} removal efficiencies of 59.2% and 66.4%, respectively [19]. Similarly, Khandelwal et al. [16] reported a maximum COD removal efficiency of 70.8% and 62.3% for microbial fuel cells fed with lipid extracted algal biomass and fruit pulp waste, respectively. The COD removal rates were 0.29 ($\pm$0.11) and 0.28 ($\pm$0.04) $kg/m^3 \cdot d$ for lipid extracted algal biomass and fruit pulp waste, respectively.

6.3. CO_2 removal using MFCs with algae assisted cathode

Microalgae are capable of utilizing CO_2 for autotrophic growth, which in turn is useful to capture CO_2 from the anode compartment in the presence of light and produce oxygen to be used for the cathodic reaction. The net CO_2 removal in these systems depends on the release of CO_2 in the anode chamber and the CO_2 assimilation by microalgae in the cathode chamber. Wang et al. [18] reported that CO_2 released in the anodic chamber was totally removed by the catholyte in microbial carbon capture cells (MCCs) with a maximum power density of 5.6 W/m^3. The authors suggested that the method could be used for simultaneous power generation, biodiesel production and carbon capture through wastewater treatment without mechanical aeration. Cao et al. [46] used a biocathode for CO_2 removal in the presence of light using a completely anoxic MFC with a theoretical average CO_2 reduction of 0.28 ($\pm$0.02) moles bicarbonate/mole electron.

6.4. Recovery of value-added chemicals from algae based MFCs

6.4.1. Photosynthetic biofilm formation on the cathode electrode

An alternative method for minimizing the biomass harvesting costs in PAMFCs is to produce a biofilm on the surface of the cathode electrodes (algae cellulose, algae wire or algae string), from which algae may be recovered from the culture medium simply by scraping [11]. In this method, biofilm attachment on the electrode surface affects oxygen diffusion, MFC performance, corrosion and light limitation. Up to a certain thickness of the biofilm on the electrode surface, the algae mediate direct oxygen transfer to the electrode in algae based MFCs (Fig. 4). Photosynthetic algal biofilms on cellulose can provide important information about the extracellular polymeric substance (EPS) matrix produced onto the electrode surface [11]. The biofilm formation on the cathode electrodes (better attachment) varied considerably with respect to the cathode types (surface texture, roughness or porous) and material type. Algal biomass growth was lower on algae wire surfaces due to stainless steel corrosion compared with that on algae string and algae cellulose surfaces [11]. All three electrodes supported algal growth on the surface of the cathode electrodes for power generation.

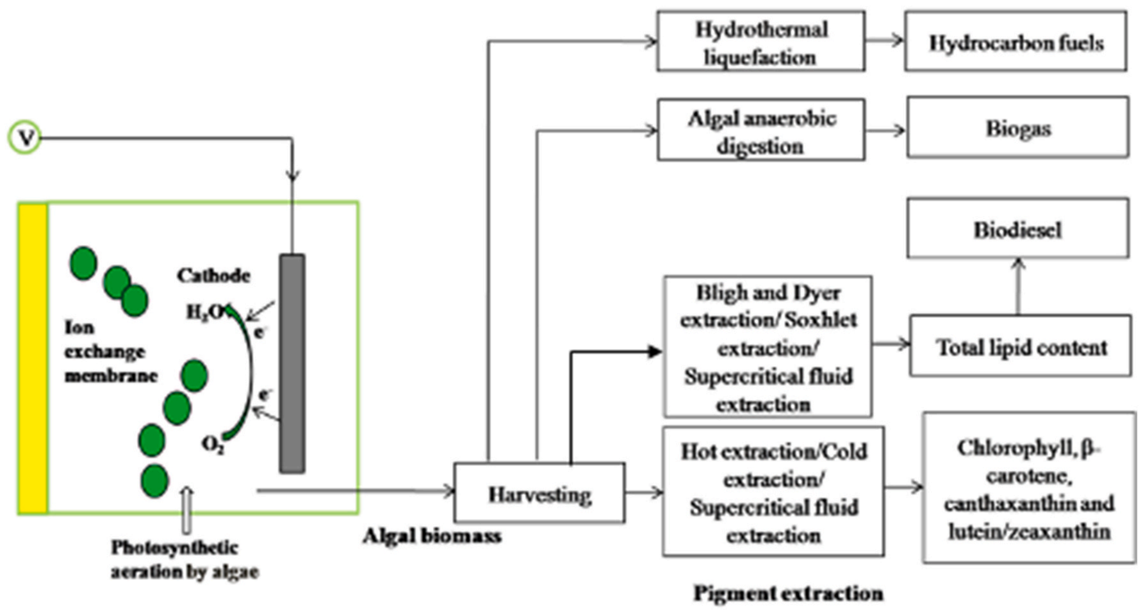

Fig. 5. Stages and extraction methods required in the construction of PAMFCs in dual role systems that generate electricity, biodiesel, biogas and value added chemicals.

The biofilm formation was also influenced by pH, CO_2 concentration, light intensity and mass transfer conditions.

A recent study revealed effective biofilm formation of *Scenedesmus obliquus* on a platinized cathode using the produced oxygen as the electron acceptor [14]. This study observed a high exchange current density for oxygen reduction on the electrode due to its direct oxygen transfer by algal biofilms. The algal biomass was recovered from the biofilm system by scraping. Algal biofilm production is attractive for harvesting the biomass, even though there is no information about its use in MFCs for producing electricity and harvesting microalgae for production of other value added chemicals. There is, however, a need for detailed studies on algal biofilm formation for improved O_2 transfer, better MFC performance, high algal biomass production and its effective harvesting from the cathode compartment [11].

6.4.2. Biorefinery approach combining the dual role of microalgae based MFC systems for power generation and value-added chemical production

A MFC system using microalgae for production of value added products requires various steps. The first step is to harvest the algal biomass from the cathode compartment (e.g. biofilm formation). Separation of algal biomass from the cathode compartment can be achieved using low-cost harvesting techniques, including bio-flocculation, cell immobilization, biofilm formation or membrane separation. Recovery of value added chemicals from microalgae in the MFCs is the next step, which may require pre-treatment of the algal biomass. Generally, microalgae in MFCs will be present as mixed consortia and the composition may vary depending on the inoculum used.

Fig. 5 shows a bio-refinery approach with the dual role of generating electricity and value added chemicals in MFCs using microalgae, which produces five different types of pigments: chlorophyll, β-carotene, canthaxanthin, lutein and zeaxanthin. The produced biomass can be used as a source of biogas (CH_4) production, and the byproduct CO_2 can be used as an inorganic carbon source for algae. Alternatively, whole biomass or the biomass residue after lipid extraction can serve as animal feed [5].

7. Conclusions

Algae based MFCs are effective for the production of power. However, there are so far limited large scale applications. Suitable applications will be found when CO_2 and nutrient (N and P) removal are preferred, or when the biomass obtained can be used for the recovery of value-added products or biofuels. In these conditions, the additional costs for harvesting the algal biomass, MFCs construction and CO_2 supply will be compensated by energy savings and advantages in resource recovery. Before algae based MFCs methods can be commonly applied for wastewater treatment, further research is warranted aimed at (1) selection of algal strains suitable to be used in both the anode (substrate) and cathode compartment, (2) understanding and control of the mechanisms of the cathodic reaction (electron transfer) and CO_2 uptake to improve power generation, biomass control and recovery of biomass, (3) scale-up and modeling of algae based MFCs and (4) development of new sustainable treatment techniques like wastewater treatment based MFCs or integrated MFCs-photobioreactor methods to improve biomass recovery and produce value added products from the algal biomass.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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