

1 **Bioelectrochemical systems using microalgae – A concise research update**

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32

33 **Abstract**

34

35 Excess consumption of energy by humans is compounded by environmental pollution, the
36 greenhouse effect and climate change impacts. Current developments in the use of algae for
37 bioenergy production offer several advantages. Algal biomass is hence considered a new
38 bio-material which holds the promise to fulfil the rising demand for energy. Microalgae are
39 used in effluents treatment, bioenergy production, high value added products synthesis and
40 CO₂ capture. This review summarizes the potential applications of algae in
41 bioelectrochemically mediated oxidation reactions in fully biotic microbial fuel cells for
42 power generation and removal of unwanted nutrients. In addition, this review highlights the
43 recent developments directed towards developing different types of microalgae MFCs. The
44 different process factors affecting the performance of microalgae MFC system and some
45 technological bottlenecks are also addressed.

46

47 **Keywords:** Microbial fuel cell, microalgae and cyanobacteria, double chamber algae MFCs,
48 Integrated photo-bioelectrochemical system, Bioelectricity

Contents

49	
50	
51	1. Introduction.....XX
52	2. Microalgae MFCs systemsXX
53	2.1. Single-chamber algae–MFCs.....XX
54	2.2. Double-chamber algae–MFC.....XX
55	2.3. Photosynthetic sediment MFCs (PSMFC)XX
56	2.4. Algae-based microbial carbon capture cells (MCC)XX
57	2.5. Anode-catalyzed microalgae MFCsXX
58	2.6. Algae as substrate supplier in dark MFCs anodic end.....XX
59	2.7. Integrated photo–bioelectrochemical systems.....XX
60	3. Effects of process parameters.....XX
61	4. Direct electron transfer in microalgae and cyanobacteria assisted MFCs.....XX
62	5. Concluding remarks.....XX
63	6. Acknowledgements.....XX
64	7. References.....XX
65	

66 **1. Introduction**

67

68 The global population is rising fast and it is estimated to be beyond 9 billion by 2050
69 (Hosseini et al., 2013). In addition, due to rising economic growth, there is also increased
70 demand for energy and thus a more pronounced use of fossil fuels which then leads to more
71 serious problems such as energy crisis and more consequential environment pollution.
72 Combustion processes for energy production also produce toxic greenhouse gases such as
73 CO₂, which in turn leads to global warming (GW) (Saratale et al., 2015). In the year 2010, the
74 global energy-related CO₂ emissions into the atmosphere were estimated about 110 billion
75 metric tonnes (bmt). It is now predicted that this amount will exceed 140 bmt in the year
76 2035 (Petroleum, 2014). To maintain energy and climate security, it is therefore very crucial
77 to reduce and stop the emission of greenhouse gases into the environment to prevent the
78 harmful impacts of GW (Singh and Ahluwalia, 2013; John et al., 2011).

79 Biofuels are being viewed earnestly as energy sources responding to the forthcoming
80 demands (Brennan and Owende, 2010). First generation biofuels are usually obtained from
81 food and oil crops but they are facing challenges due to crops for food usage. Also, at this
82 moment, low conversion rate is one of the major limiting steps regarding second generation
83 biofuels and which make the relevant process economically unfeasible (Saratale et al., 2013;
84 Adenle et al., 2013). Fuels derived from algae are third generation biofuels. Algae are
85 considered an alternative to land-based plants and biomass forms. From the primary
86 investigations of biofuel production from algae at bench scale, algae appears to be one of the
87 best possible alternative feedstocks which can aim to displace a fraction of fossil fuel (Najafi
88 et al., 2011; Chisti, 2007; Khayoon et al., 2012). Based on their size variations and different
89 morphologies, algae are either microalgae (phytoplankton) or macroalgae (macrophytes).
90 Microalgae are microscopic, unicellular photosynthetic plants which are able to convert solar
91 energy with an intake of CO₂ and H₂O by using nutrients to finally generate more biomass
92 (Demirbas, 2010; Slade and Bauen, 2013; Alam et al., 2012). Macroalgae are comprised of
93 multiple cells and are found near the seabed (Chen et al., 2009). Algae can transform solar
94 power into biochemical energy via photosynthesis, have better growth rates compared to
95 forest-derived biomass, agricultural residues and aquatic species (Brennan and Owende,
96 2010; Ndimba et al., 2013). Moreover, rapid growth rates and the ability to survive stringent
97 environmental conditions make algae, as a whole new source of biomass, a potential
98 alternative source of renewable fuel. Yet, the selection of the most appropriate and adapted
99 species and providing the optimum environmental conditions are very essential aspects to be

100 fully addressed before being able to achieve the accelerated rates of algal growth.
101 Additionally, algae are capable of living in diverse environmental conditions with a relatively
102 minimal nutrients requirement. Hence, algae cultivation is much feasible in areas where they
103 are not habitually supported by mainstream agricultures (Ndimba et al., 2013; Slade and
104 Bauen, 2013). Typically, algae are cultivated in photo-bioreactors (PBR) or in large open
105 ponds producing biomass and are successively harvested to be processed for producing
106 biofuels. Different aqueous systems like open ponds, closed ponds, hybrid PBR or PBR are
107 widely used for the growing of microalgae. Microalgae also have a wide application in
108 wastewater treatment and in thesequestration of CO₂ into potential biomass which can be
109 considered as a potential feedstock for the production of renewable energy fuels such as
110 biodiesel, biomethane, biohydrogen and bioethanol (Popp et al., 2014; Brennan and Owende,
111 2010; Chen et al., 2009; John et al., 2011).

112

113 **2. Microalgae MFC systems**

114

115 MFCs represent a novel and promising technology where microbial catalytic reactions at the
116 anode end result in electric power generation from waste and renewable biomass (Inglesby et
117 al., 2012; Rosenbaum et al., 2010). MFCs also assist in the bioremediation of specific
118 pollutants and nutrients in wastewaters (Mathuriya and Yakhmi, 2014). Recovery of heavy
119 metals, decolourisation of dyes, production of bioenergy such as biomethane, biohydrogen
120 and even biomass are yet other applications of MFCs (Mathuriya and Yakhmi, 2014; Mohan
121 et al., 2014a). Thus, MFCs have the dual benefits of power generation and wastewater
122 treatment by which the process becomes as a whole more eco-friendly and economically
123 feasible (Logan et al., 2006). The abiotic cathode reactions can catalyse the reduction of
124 oxygen to form water. However, in such processes, the use of expensive elements namely
125 platinum makes the process less economically unfeasible (Rosenbaum et al., 2010).
126 Substantial research is being conducted to explore the potential of microalgae in different
127 MFC systems for electricity generation. Bajracharya et al. (2016), Buti et al. (2016), Singh et
128 al. (2012), Freguia et al. (2012) and Kelly and He (2014) have made excellent reviews on the
129 different MFC types and discussed the main distinctive characteristics of each system. Algae
130 in MFC systems become favorable because they may be used as efficient electron acceptors
131 during the photosynthetic reactions at the cathodic end or as electron donors at the anodic end
132 of the cell, and therefore are also capable in removing organic substrates (Wu et al., 2013;

133 Gude et al., 2013; Commault et al., 2014). Algae-based MFCs make up a syntrophic
134 interaction between bacterial populations and algal biomass and this system functions with a
135 minimal net energy input. The mechanism of algal MFC involves the oxidation of the
136 biodegradable substrates and generating electrons at anode and the evolution of CO₂ at the
137 cathode (He et al., 2009; Powell et al., 2011). It was observed by some workers that oxygen
138 production at cathode mainly depends on the oxygenic photosynthesis for the transfer of
139 electrons from water to NADP⁺ using the PSI, PSII and cytochrome b₆f complex and by
140 small plastoquinone and plastocyanin mobile molecules (Juang et al., 2012; Wu et al.,
141 2013; Commault et al., 2014). In the cathode chamber and in the presence of sunlight, algae
142 carry out photosynthesis and convert CO₂ to generate different types of organic matter,
143 oxygen and biomass; whilst in the dark stage, they use up oxygen and produce energy by direct
144 oxidation of the previously produced organic materials (Commault et al., 2014; Wu et al.,
145 2013). In some cases, as reported by Mohan et al. (2014b) and Rosenbaum et al. (2010), it
146 has been observed that certain photosynthetic cyanobacteria could act as a bioanode catalyst
147 for yielding higher electrogenic activity without producing O₂ (Parlevliet and Moheimani,
148 2014).

149 Ma et al. (2017) designed a photosynthetic microbial fuel cell (MFC) for the production of
150 *Chlorella* biomass by utilizing wastewater and reported that the system was sustainable for
151 both biomass and energy production. Zhu et al. (2016) studied the potential of MFCs for
152 nitrification/denitrification and found that nitrogen removal efficiencies were much improved
153 using MFCs. Salar-Garcia et al. (2016) reported that the use of catholyte from ceramic MFCs
154 enhanced lysis of microalgae under light/dark cycle conditions and increased electricity
155 generation. Saba et al. (2017a) reviewed MFCs for energy generation as well as wastewater
156 treatment and biomass production and also discussed the effects of several parameters on
157 energy production from MFCs. Likewise, Xu et al. (2016) reviewed different emerging
158 technologies integrated with MFCs as well as their development while also proposing a
159 direction for further research. Later, Baicha et al. (2016) reviewed the utilisation of
160 microalgae for bioenergy production from MFCs while also highlighting the use of CO₂ for
161 biomass cultivation in the cathode chamber of the MFC. Besides MFC, other studies have
162 investigated the use of algae in microbial desalination cells (MDCs) and bioelectrochemical
163 systems (BES). Saba et al. (2017b) compared the use of *Nannochloropsis salina* and
164 KFe(CN)₆ as catholyte for power generation from MDCs and reported highest desalination
165 efficiency with *Nannochloropsis salina* as catholyte and highest power generation with
166 KFe(CN)₆ as catholyte. Using a similar system, Zamanpour et al. (2017) evaluated the effects

167 of salt concentrations on power density, salt removal rate and algal growth and reported that
168 higher salt concentrations resulted in maximum power density with higher salt removal rates
169 and algal growth. Khalfbadam et al. (2016) reported the use of a BES for removal of soluble
170 chemical oxygen demand with and without current generation and obtained highest removal
171 of soluble chemical oxygen demand with the system without current generation. Luo et al.
172 (2016) reviewed the application of integrated photobioelectrochemical system for wastewater
173 treatment and bioenergy production by highlighting the challenges with this system and
174 proposing collaboration between the different experts for further progress in this field. Wu et
175 al. (2016) studied the effects of light sources viz. incandescent and fluorescent on the growth
176 rate, productivity and chlorophyll α content of *Desmodesmus* sp. A8 prior to electricity
177 generation from a BES inoculated with the microalgae and found that incandescent light was
178 more suitable for biomass production as well as energy production. Given the rising interest
179 and constructive research efforts in this field of bioenergy generation, this review will revisit
180 selected research findings and provide a concise update on algal MFCs and their key features
181 of operation and performance.

182

183 **2.1. Single-chamber algae–MFCs**

184

185 Single chamber (membrane-less) MFCs have been studied very well so far. The
186 photosynthetic biocatalysts have shown the ability to transport electrons to the electrode
187 surface without having to resort to “electron shuttle mediators” (Lin et al., 2013). *Spirulina*
188 *platensis*, a type of blue–green microalgae, has been studied without using membranes. This
189 MFC system produced electric power in the presence of light with a power density output of
190 0.132 mW m^{-2} and with an output of 1.64 mW m^{-2} in dark conditions (Fu et al., 2009). The
191 electric power thus generated under the dark conditions more than that of generated under
192 light condition. Due to these properties of being functional with better yields of power under
193 extreme conditions of light, single-chambered MFC can operate for longer periods of time.
194 This type of MFC design is also useful for the better attachment of microalgae on the surface
195 of the electrodes and could be hence utilized as a photosynthetic biocatalyst for bioelectricity
196 generation (**Figure 1**). Typically, single-chamber MFC configurations have both electrodes
197 (the anode and the cathode) connected through an electric circuit. Moreover, some workers
198 have designed single-chamber algal MFCs wherein bacteria and algae were added and their
199 synergistic actions increase the efficiency of the process. In this type of system and in the
200 presence of light, microalgae produce organic acids which are used as substrates by the

201 bacteria to produce electricity (**Figure 2**). Nishio et al. (2013) have used “*single chamber*
202 *MFC bioreactors*” consisting of algae utilizing *Lactobacillus* and *Geobacter* for producing
203 electricity from *Chlamydomonas reinhardtii* grown photosynthetically, and observed that
204 their system could give a power density in the tune of 0.078 W m^{-2} . Yuan et al. (2011) have
205 studied a blue-green algae powered single chamber MFC and this system showed significant
206 chemical oxygen demand (about 78.9%), and total nitrogen (about 96.8%) removal
207 efficiencies with an ultimate power density yield of 114 mW m^{-2} of maximum power density.
208 This system also was found effective for the removal of algal toxins such as microcystins
209 released from blue-green algae. The results from Yuan et al. (2011) hence suggested that
210 single-chambered algal MFC have the capability for the remediation of contaminated
211 environments with a simultaneous production of electricity. Caprariis et al. (2014) have
212 developed bio-photovoltaic cells for the production of clean energy using the photosynthetic
213 activity of green microalgae *Chlorella vulgaris*. In the system of Caprariis et al. (2014), the
214 anode was dipped in the broth and the cathode left exposed to the surrounding air, and thus
215 no organic substrate and mediators were required. Alongside, Caprariis et al. (2014)
216 observed that there was no net CO_2 production. Due to exo-electrogenic activities of
217 *Chlorella vulgaris* in this system, the production of electricity at a power density of $14 \mu\text{W}$
218 m^{-2} was possible and it meant as a whole that there was a major scope for research in
219 developing this type of system for power production.

220

221 **2.2. Double-chamber algae-MFCs**

222

223 In this type of system, two compartments are separated by a “*proton exchange membrane*”
224 (**Figure 3**). Recently, Gajda et al. (2015) demonstrated that an MFC consisting of anaerobic
225 biofilms at the anode could generate current, whilst the phototrophic biofilm at the cathodic
226 end had produced oxygen through the oxido-reduction reaction and algal biomass
227 production. This system had achieved both wastewater remediation and power generation
228 along with biomass production. Few microalgae strains such as *Chlorella vulgaris* (Zhang et
229 al., 2011; Zhou et al., 2012; Wang et al., 2010), *Spirulina platensis* (Fu et al., 2009)
230 and *Pseudokirchneriella subcapitata* (Xiao et al., 2012) have been used in a double-chamber
231 MFC. Some investigators have demonstrated that mixed algal cultures could also be used in
232 the development of MFC cathodes (Jiang et al., 2012; Chandra et al., 2012; Strik et al., 2010;
233 He et al., 2009). Strik et al. (2008) have utilized mediator-less photosynthetic algal
234 microbial fuel cell in an open system for 100 days to generate electricity, and reported a

235 maximum power production performance of the MFC at 110 mW m^{-2} of photobioreactor
236 surface area. Mitra et al. (2012) have developed a MFC system based on *Chlorella vulgaris*
237 at the cathodic end and *Saccharomyces cerevisiae* and which was operated under continuous
238 flow regimes. Mitra et al. (2012) reported a peak power density of 0.6 mW m^{-2} . Similarly,
239 Zhang et al. (2011) have used green algae in the cathodic chamber and demonstrated both
240 good nutrient removal and electricity production at $68 \pm 5 \text{ mW m}^{-2}$ with a 1000Ω resistor. In
241 some cases, MFC systems show a poor performance with relatively small power generation
242 and especially so when the oxygen supplied by algal growth becomes a form of
243 inhibition/limitation to further use the system for long term operation (McCormick et al.,
244 2011; Zhang et al., 2011). Some investigators have developed micro MFC (μMFC) to
245 undertake the screening of *Rhodospseudomonas palustris* using acetate and *Arthrospira*
246 *maxima* feedstock. The μMFC system showed power developed by Inglesby et al. (2012) had
247 a power density output of 10.4 mW m^{-3} and it was also found that the power generation was
248 independent of *R. palustris* concentrations and growth patterns. Nevertheless, micro MFC
249 devices could be revamped and thereafter used for high-throughput screening and as well as
250 in carrying out sensitivity analysis of the different process parameters involved in the
251 complex bio-electrochemical reactions. This could be an avenue of research whose
252 outcomes will probably prioritize the process parameters and allow research efforts to focus
253 on optimization studies and simulations.

254

255 **2.3. Photosynthetic sediment MFCs (PSMFC)**

256

257 Photosynthetic-sediment MFC is made up of an anode arranged in the sediment and a
258 cathode compartment filled with microalgae and which is present on the top of sediment. The
259 anodic bacterial activity produces CO_2 which then gets consumed at the cathode
260 compartment by the algal cells therein. Oxygen is then produced and power generated. He
261 et al. (2009) have constructed a “*sediment-type self-sustained phototrophic MFC*” which
262 produced a maximum current of $0.054 \pm 0.002 \text{ mA}$ at a resistance of $1 \text{ k}\Omega$ in a system which
263 had been operated for over 145 days. Commault et al. (2014) recently developed a
264 membrane-less sediment-type MFC consisting of a photosynthetic biocathode containing a
265 complex microbial community along with microalgae and cyanobacteria which were able to
266 produce a maximum power density 11 mW m^{-2} over 180 days with no feeding.

267

268

269 **2.4. Algae-based microbial carbon capture cells (MCC)**

270

271 Recently, some investigators demonstrated the performance of algae-based microbial carbon
272 capture cell (MCC) under illumination. Liu et al. (2015) utilized such a system in both light
273 and dark condition where they observed a peak power density of 187 mW m^{-2} under light
274 illumination, and this output was relatively higher than that of 21 mW m^{-2} obtained under
275 dark conditions. The results from Liu et al. (2015) supported that algal photosynthesis is
276 crucial in such systems. Recently, Pandit et al. (2012) evaluated the MCC performance with
277 *Anabaena* biocathode sparged with a CO_2 -air mixture, and they reported a peak power
278 output which was higher in comparison to the biocathode that had been sparged with air only.
279 Wang et al. (2010) had earlier developed an MCC using *C. vulgaris* to reduce CO_2
280 emissions and reported significant CO_2 reduction and a peak power density of 5.6 W m^{-3}
281 (Wang et al., 2010). Some investigators proved that the application of immobilized cells as
282 compared to suspended cells could increase the columbic efficiency up to 88% (Zhou et al.,
283 2012).

284

285 **2.5. Anode-catalyzed microalgae MFCs**

286

287 There are few reports where microalgae or photosynthetic bacteria have been utilized for
288 electron production in the anode compartment and have ability to transfer to the anode
289 without electro mediators. —

290 Chang et al. (2015) utilized live *Chlorella pyrenoidosa* in the anode of a MFC where
291 this species had acted as an electron donor. Under optimized conditions of oxygen levels, the
292 density of algal cell populations and the intensity of incident light, a peak power density of
293 6030 mW m^{-2} was obtained. In addition, it has also been seen that some bacteria such as
294 *Rhodospseudomonas* and other purple non-sulphur bacteria can also effectively utilize
295 biomass found in the anode compartment of an MFC (Xing et al., 2008). Highlights of other
296 studies which probed the performance of anode-catalyzed microalgae are summarized in
297 Table 1.

298

299 **2.6. Algae as substrate supplier in dark MFCs anodic end**

300

301 The literature shows that algal biomass consists of adequately high carbohydrates, proteins
302 and lipids contents for electricity generation in MFCs, including live algae and dry algae

303 biomass at the anode compartment (Li and Zhen, 2014). Utilization of microalgae biomass
304 showed dual benefits including pollution control and cost effective feedstock in MFC
305 processing. Some microalgae have very high cellulose and hemicellulose content and
306 pretreatment of the algal biomass is often obligatory to increase the efficiency of the
307 process—Additionally, dry algae biomass has been assessed as a substrate in MFC for the
308 growth of oxidizing bacteria at the anodic end (Gouveia et al. 2014, Velasquez–Orta et al.
309 2009; Rashid et al. 2013; Cui et al. 2014).

310 Velasquez–Orta et al. (2009) – have tested *Chlorella vulgaris* and *Ulva*
311 *lactuca* feedstocks in dry powder at the anodic end of the MFC system they designed, and
312 subsequently recorded a peak power density of 0.98 W m^{-2} from the *Chlorella vulgaris* and
313 760 mW m^{-2} for the scenario of *Ulva lactuca* –. Rashid et al. (2013) have used activated
314 sludge and *Scenedesmus* algal biomass as a nutrient source at the anode, and then observed
315 that sonication and thermal pre–treatment of algal biomass had enhanced the microbial
316 digestibility of the algae and also increased the overall performance of the MFC test unit. In
317 other studies, e.g. Nishio et al. (2013), formate produced by green algae e.g. *Chlamydomonas*
318 *reinhardtii* and *Geobacter sulfurreducens* have also been assessed for its influence on
319 electricity generation in MFC environment. Lakaniemi et al. (2012) have used *Chlorella*
320 *vulgaris* and *Dunaliella tertiolecta* in MFCs and recorded a peak power density of
321 $15 \text{ mW} \cdot \text{m}^{-2}$ at the cathode with *Chlorella vulgaris* in comparison with *Dunaliella*
322 *tertiolecta* which yielded almost thrice a lower power density of 5.3 mW m^{-2} . Wang et al.
323 (2012) have studied raw algal sludge and alkaline pre–treated algae sludge in MFC and
324 reported a peak power density was 2.8 and 4.0 W m^{-3} , respectively. In this same work, the
325 removal efficiency for the full quantities of oxygen demands was 33% and 57%, respectively
326 (Wang et al., 2012). These specific results inferred that pretreatment of biomass may be
327 envisaged as a useful step to enhance the bioelectrokinetics in the MFC for higher power
328 generation.

329

330 **2.7. Integrated photo–bioelectrochemical systems**

331

332 Some investigators have developed integrated photobio–electrochemical systems by
333 incorporating an MFC within an algae–based bioreactor. Such a system has been found to be
334 useful in the generation of electricity and algal biomass. Xiao et al. (2012) reported
335 significant removal of COD of up to 92%, ammonium nitrogen removal of 98% and
336 phosphate removal of 82% with a concomitant peak power density yield of 2.2 W m^{-3} . Strik

337 et al. (2008) developed an integrated system by annexing a glass photobioreactor to an MFC
338 for electricity generation and for algal biomass production. Similarly, Jiang et al. (2013)
339 demonstrated that an up flow MFC- photobioreactor coupled system could bring about
340 the generation of electricity and remediation of the effluents. De Schamphelaire and
341 Verstraete (2009) have constructed a closed-loop system to transform sunlight into biogas.
342 In this work of De Schamphelaire and Verstraete (2009), the algal biomass generated was
343 employed as feedstock in an anaerobic tank, and under the specific experimental conditions,
344 an algal biomass production of 24–30 tonnes VS ha⁻¹ year⁻¹ and a biogas production of
345 0.5 N m³ kg⁻¹algae were reported. Hence, there is evidence to support the suitability of
346 integrated systems for the simultaneous production of different types of biofuels at a
347 relatively low cost and with low environmental impact.

348

349 **3. Effects of process parameters**

350

351 Different process parameters such as illumination, light intensity, electrode material, air
352 sparging and concentration of CO₂ may affect the overall performance of microalgae–MFCs.
353 However, a detailed investigation of these parameters is limited in the literature. Light
354 illumination and the intensity of the light has been so far found to significantly influence the
355 algal biocathode reactions and the performance of MFCs. Lan et al. (2013) have investigated
356 the effects of different types of light and light intensities in photo MFCs
357 containing *Chlamydomonas reinhardtii* transformation F5 and reported that higher light
358 intensities gave better performance whereas red light illumination showed significant power
359 density production (12.95 mW m⁻²_{cathode}) as opposed to blue light illumination. Similarly,
360 Wu et al. (2014) investigated the influence of different light intensities on *Desmodesmus* sp.
361 A8 assisted biocathode in which the anode and cathode resistances were strongly affected by
362 changes in light intensity. Moreover, several other workers have studied the effects of
363 illuminated and non-illuminated cycles on algae biocathode-assisted MFC systems where
364 under dark conditions no power was produced (Xiao et al., 2012; Wang et al., 2010, ; Chandra
365 et al., 2012; Strik et al., 2010; Zhang et al., 2011). When assessing the mode of operation of
366 the MFC, Gonzalez del Campo et al. (2013) achieved a higher power output with continuous
367 mode operation as compared to sequencing–batch mode operation. On another note of
368 parameter influence, Kakarla and Min (2014) have demonstrated the influence of cathode
369 materials on MFC performance in devices that included algae–assisted cathodes. In this study
370 of Kakarla and Min (2014), carbon fiber brush and plain carbon paper were used as materials

371 for the *Scenedesmus obliquus* assisted biocathode reaction. In addition, also in this study, it
372 was observed that oxygen supply was beneficial for algal biocathode reactions as compared
373 to mechanical aeration.

374

375 **4. Direct electron transfer in microalgae and cyanobacteria assisted MFCs**

376

377 Extracellular electron transfer is an important mechanism which helps to understand and then
378 develop new functions in bioelectrochemical systems. In MFC, the electron transfer
379 mechanism for exo-electrogens namely *Geobacter sulfurreducens* has been studied very well
380 (Malvankar et al., 2012). According to Gorby et al. (2006), the electron transfer mechanisms
381 can be carried out by “*indirect transfer via flavin*”, by direct transfer in proteins and in some
382 rare instances, the cytochromes of terminal reductases have participated in the pathways. In
383 algal MFC, the majority of research has been devoted for improving current outputs using
384 potential algal strains and by employing engineering approaches to some extent. In cathodic
385 microalgal MFC, mediators are required and this is a major limitation for scalability to higher
386 scale of production with regards to sustainability, cost and toxicity considerations. Moreover,
387 these mediators may influence intracellular components and electrobiochemical mechanistic
388 pathways of algal system (Wu et al., 2013). However, the electron transport or electron flow
389 pathway between the microalgae and electrode system has not been studied well, and hence
390 there is a very limited information of the functions and characteristics of the
391 electrode–microalgae interactions (Rosenbaum et al., 2010). Very few reports describe the
392 electrode–microalgae interactions. Wu et al. (2013) have isolated nine green microalgae from
393 wastewater and studied their electron transport capacity between the cells and electrodes. Wu
394 et al. (2013) reported that the *Desmodesmus* sp. demonstrated its capability of direct electron
395 transport via the “*membrane-associated proteins*” and “*indirect electron transfer via*
396 *secreted oxygen*” (Wu et al., 2013). The study of Wu et al. (2013) was a first in its kind to
397 have given an elementary model which could be further made comprehensive to study the
398 mechanistic pathways bringing about electron transports. In a study by Cereda et al. (2014),
399 mediatorless biophotovoltaic devices consisting of cyanobacterium *Synechocystis* sp.
400 PCC6803 were shown to have the ability for direct electron transfer through conductive
401 nano-wires at the anode chamber under excess light and CO₂ limiting condition (Cereda et
402 al., 2014).

403 Upon scaling-up MFCs from a 170 mL single chamber open air cathode treating
404 spent wash to a 100 L chamber, Dimou et al. (2014) observed that COD removal efficiency

405 had risen to 90% and electricity production had been optimized from 0.4 V to 0.65 V. Dimou
406 et al. (2014) also reported that the robust microbial community had effectively treated large
407 volumes of anaerobically generated digestate, thus showing a high potential for MFCs to be
408 scaled-up to industrial application. Mohan et al. (2014c) have also indicated that in-depth
409 analysis of any biocatalyst performance, electron transfers and redox mechanisms and
410 technology scale-up aspects are crucial to further promote the integration of MFC as viable
411 energy and environmental solution. Indeed, according to a number of studies and lastly from
412 Li and Sheng (2012), Liu and Cheng (2014), Butti et al. (2016) and Bajracharya et al. (2016),
413 the potential for scalability of MFCs is a key challenge which needs to be comprehensively
414 addressed with more adapted research and development efforts. In particular, the scalability
415 issues which demand more work are related to (i) the synthesis and use of more efficient,
416 effective and less costly materials, (ii) the design of more energy efficient reactor
417 configurations, (iii) developing mechanistic strategies which will augment the recovery of
418 power and enhance power density yields, (iv) reducing the impacts of low selectivity, (v) and
419 finally limiting the risks from unwanted microbial contaminations which in turn hamper the
420 overall mass-transfer coefficients. In addition, the reproducibility of effective laboratory scale
421 investigations to pilot scale systems need to be also looked into for making the algal MFCs
422 technology economically viable and environmentally workable.

423

424 **5. Concluding remarks**

425

426 This short review has addressed the key aspects related to the use of some new types of algal
427 biomass-based microbial fuel cell systems for the generation of electric power. The main
428 types of the microbial fuel cell reactor designs using algae have been surveyed and are
429 namely the single chamber algae–MFC, double chamber algae–MFC, photosynthetic
430 sediment MFC (PSMFC), algae based microbial carbon capture cells, anode catalyzed
431 microalgae MFC, live algae or algal biomass as substrate in dark anode compartment of MFC
432 and integrated photo–bioelectrochemical systems. Most of the MFC systems have their own
433 specific merits and shortcomings, but are all able to bring about the sought energy generation
434 patterns and performance to different extents of complexity and yields of power intensity.
435 However, the exact mechanistic pathways which are essentially a complex mix of biological
436 reactions taking place in an electrochemically controlled medium are not yet fully elucidated.
437 Once these mechanisms may be understood and modeled in simple mathematical forms, the
438 optimization of the different reactor configurations may be undertaken using a

439 comprehensive design of experiments approach. All the more, the many environmental
440 parameters which are inherent to each of the latter MFC systems play a crucial and synergetic
441 role in determining the quality of power production and the effectiveness of the configuration
442 to deliver the actual performance recorded. Once more, there is a need to isolate the more
443 sensitive parameters and optimize them in their influence on the power production regimes.
444 As of the present state, the use of algal biomass constitutes a clean and green bioenergy
445 research niche which is receiving more and more interest. It is envisaged that in the coming
446 decade, following more applied research and process intensification, algal biomass will have
447 become a substantial player in the microbial fuel cell research and development field.
448 Research and development should not only be related to small-scale MFC systems, but there
449 is also a wide need to assess the suitability of the specific MFC system at the different points
450 of use and energy delivery it may best fit in. Such an assessment should be well designed
451 from a complete lifecycle perspective, both technically and from an economic angle. The
452 harmonization of the use of a single type of algae-based MFC or a combination of algal MFC
453 designs for one type of energy production and application will equally demand research and
454 development efforts to be streamlined and concentrated towards more field scale
455 experimentation and validation.

456

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458

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726 **Figure Captions**

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729 **Fig. 1** Schematic diagram of a single chamber co-culture (microalgae and bacteria) catalysed
730 MFC.

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732 **Fig. 2** Schematic diagram of a double chamber MFC (bacteria in anode and microalgae in
733 cathode) integrated with wastewater treatment/hydrogen producing bioreactor

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735 **Fig. 3** Schematic representation of a double chamber MFC with algae/autotrophs acting as
736 biocatalyst in the anode compartment to then provide H⁺ and electrons to the cathode
737 compartment where bacteria/heterotrophs utilise them to produce hydrogen.

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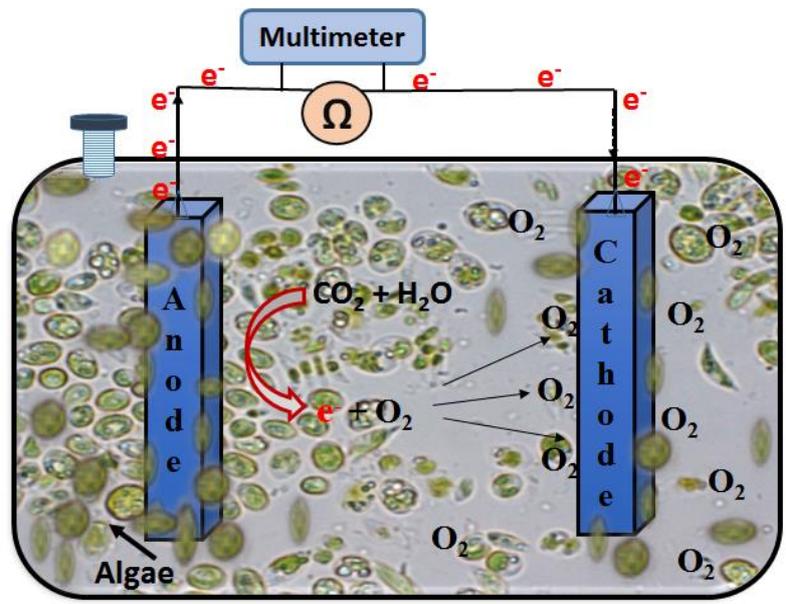
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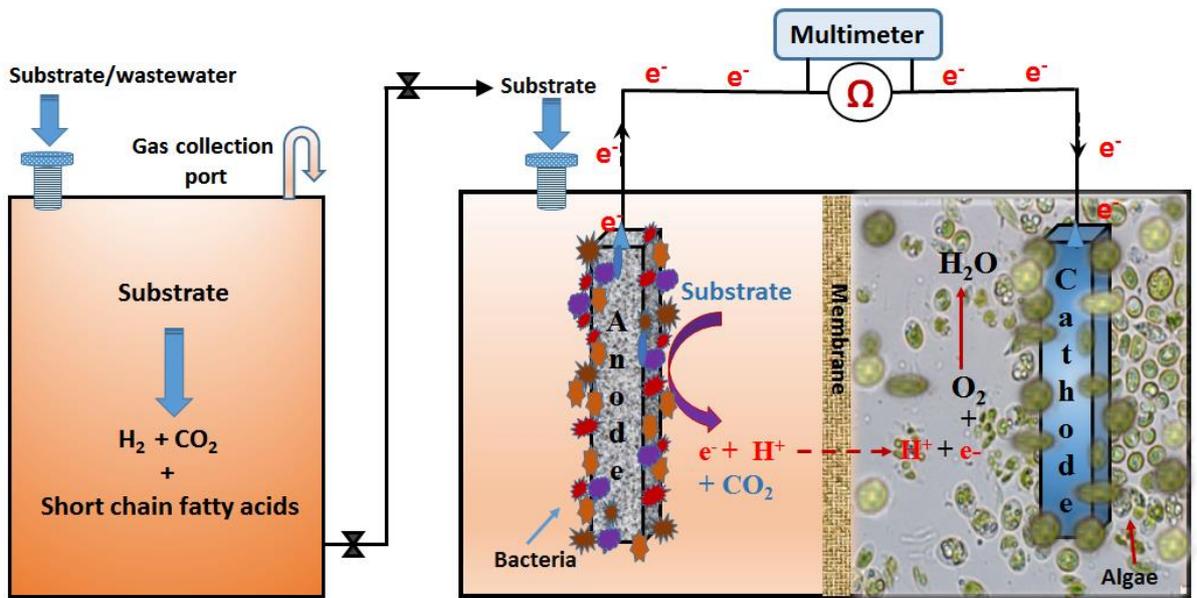


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Single chamber Algae-MFC

Fig. 1

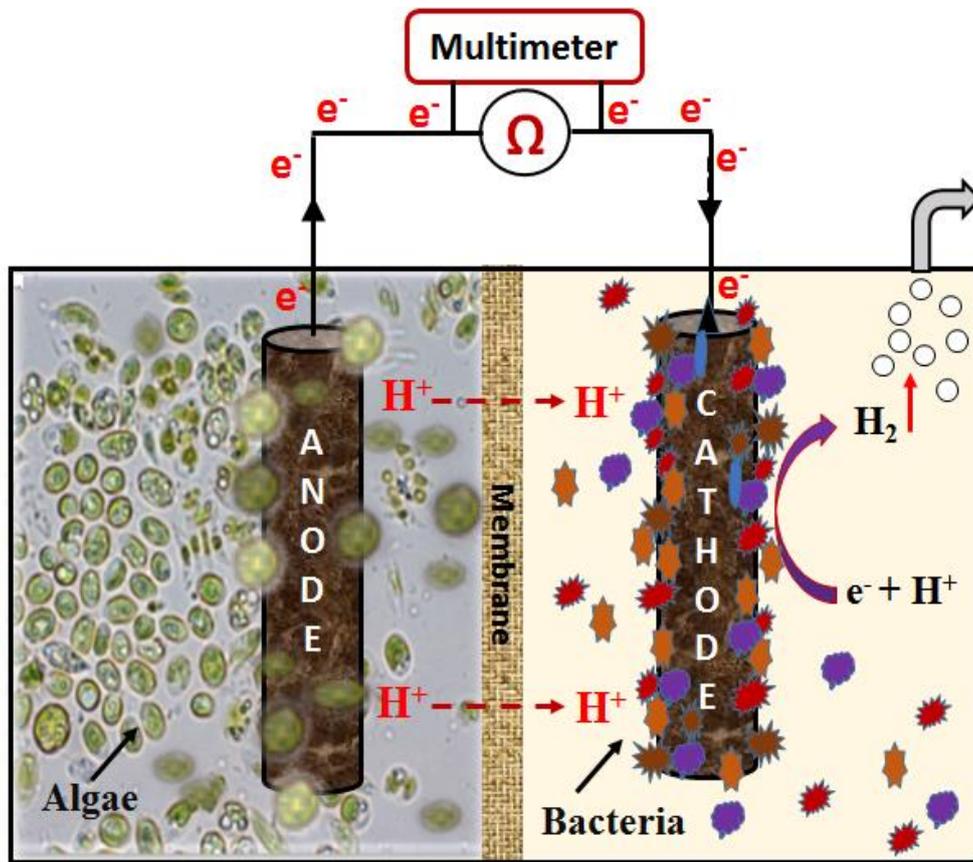
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Fig. 2

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Fig. 3

Table 1: Microalgae MFC systems and their corresponding process highlights

Algal and cyanobacteria used	Type of MFC	Electrode	Maximum power density	Process highlights	Reference
<i>Chlorella vulgaris</i>	Single chamber	Anode: Carbon paper Cathode: Carbon paper containing Pt	0.068 W m ⁻²	Produce electricity and algal biomass. Sequester carbon, nitrogen and phosphorus	Zhang et al. (2011)
<i>Chlorella vulgaris</i> , <i>Dunaliella tertiolecta</i>	Double chamber	Anode: Graphite plate electrodes Cathode: Graphite plate electrodes	0.015 W m ⁻²	Peak power density higher with <i>C. vulgaris</i> than <i>D. tertiolecta</i>	Lakaniemi et al. (2012)
<i>Scenedesmus obliquus</i>	Double chamber	Anode: Plain carbon paper Cathode: platinum coated carbon paper	153 mW m ⁻²	Microalgae sustained MFC processes and development of an algal biofilm enhanced direct oxygen transfer	Kakarla and Min (2014)
<i>Chlorella pyrenoidosa</i>	Double chamber	Anode: Graphite rod Cathode: Graphite rod	30.15 mW m ⁻²	Higher current generated and denser algal biomass produced	Xu et al. (2015)
<i>Scenedesmus obliquus</i>	Double chamber	Anode: Toray carbon paper Cathode: Toray carbon paper	102 mW m ⁻²	74% COD removal; lactate and acetate produced from algal biomass during power production	Kondaveeti et al. (2014)
<i>Arthrospira axima</i> (<i>Spirulina</i>)	Double chamber	Anode: Graphite Cathode: Graphite	20.5 mW m ⁻²	63% TCOD removal with 10.4% energy capture	Inglesby and Fisher (2013)

<i>maxima</i>)					
<i>Chlorella vulgaris</i>	Single chamber	Anode: glassy graphite rods Cathode: glassy graphite rods	2.7 mW m ⁻²	Successful removal of CO ₂	Powell et al. (2009)
<i>Chlorella vulgaris</i>	Double chamber	Anode: Toray carbon cloths with 10% Teflon Cathode: Toray carbon cloths with 10% Teflon	13.5 mW m ⁻²	Polarization resistance more significant at cathode	Gonzalez del Campo et al. (2013)
<i>Cyanobacteria (Synechococcus) and Green alga (Chlorella vulgaris)</i>	Single chamber	Anode: Indium tin oxide-coated polyethylene terephthalate	10.3 mW m ⁻²	Exoelectrogenic activities took place in photosynthetic microbes and gave pronounced electricity production	McCormick et al. (2011)
Mixed microalgal culture	Double chamber	Anode: Graphite plate electrodes Cathode: Graphite plate electrodes	57 mW m ⁻²	MFC reactions in spring season yielded higher bioelectrogenic activity (57.0 mW m ⁻²) over summer (1.1 mW m ⁻²)	Mohan et al. (2014b)
<i>Spirulina platensis</i>	Single chamber	Anode: Platinum electrodes Cathode: Platinum electrodes	6.5 mW m ⁻²	Higher power density from PMC under non illuminated conditions	Fu et al. (2010)

<i>Chlorella vulgaris</i>	Double chamber	Anode: Carbon felt Cathode: Carbon fiber cloth	8.79 mW m ⁻²	There was a very high COD removal reaching 84.8% and the corresponding peak power density recorded was 2485.35 mW m ⁻³ at 7.9 A m ⁻³ . The Coulombic efficiency equaled 9.40%	Zhou et al. (2012)
<i>Chlorella vulgaris</i>	Single chamber+sediment	Anode: Graphite felt Cathode: Multi-walled carbon nanotubes	21 mW m ⁻²	Power density from sediment microbial fuel cells with an algae-assisted cathode system reached 21 mW m ⁻² . This power density performance was enhanced to 80.95% when coating material in the form of carbon nanotube was applied to the cathode	Wang et al. (2014)
<i>Chlorella vulgaris</i>	Double chamber	Anode: Carbon fiber brush Cathode: Carbon cloth	19.45 mW m ⁻²	The peak power densities varied from 4.1 to 5.6 W m ⁻³ . The interesting feature of this work was that the complete amounts of CO ₂ produced from the anodic region was fully consumed by the catholyte, and the soluble fraction of the inorganic carbon was transformed to algal biomass	Wang et al. (2010)
<i>Chlorella vulgaris</i>	Double chamber	Anode: Carbon fiber brush Cathode: Carbon cloth	1926 mW m ⁻²	In this work, the maximum power density reached 8.77 Wm ⁻³ and the corresponding Coulombic efficiency topped at 6.5% for a COD of 2500 mg COD L ⁻¹ of microalgal biomass. The microalgal biomass equally sequestered CO ₂	Cui et al. (2014)

<i>Chlorella vulgaris</i>	Double chamber	Anode: Plain Graphite Cathode: Plain Graphite	62.7 mW m ⁻²	In this work, it was shown that higher light intensity varied from 26 to 96 μE m ⁻² s ⁻¹) had enhanced the extent of power density up to nearly 600%	Gouveia et al. (2014)
<i>Desmodesmus sp. A8</i>	Double chamber	Anode: Plain graphite felt Cathode: Plain graphite felt	99.09 mW m ⁻²	Microalgae–microbial fuel cells are specifically designed configurations which allow the effective and efficient conversion of solar energy to electrical power using certain complex biological mechanisms	Lee et al. (2015)
<i>Escherichia coli</i>	Single chamber	Anode: Mn ⁴⁺ graphite Cathode: Fe ³⁺ graphite	91 mW m ⁻²	Electron mediators may be integrated into graphite electrodes to significantly enhance electricity production	Park and Zeikus (2003)
<i>H. praevalens and Marinobacter hydrocarbonoclasticus.</i>	Single chamber	Anode: Activated carbon electrodes Cathode: Activated carbon electrodes	47 mW m ⁻²	Coupling of MFCs with capacitive deionization will sustain desalination and reuse of hypersaline effluents.	Monzon et al. (2017)
<i>Geobacter spp.</i>	Double chamber	Anode: Graphite Cathode: Graphite	0.16–1.14 A m ⁻²	<i>G. sulfurreducens</i> enhanced the performance of MFCs	Bond and Lovley (2003)
<i>Klebsiella pneumoniae L17</i>	Double chamber	Anode: Carbon felt Cathode: Carbon felt	1.2 (A m ⁻²)	<i>K. pneumoniae</i> biofilms induced the direct electron transfers from fuels to electrodes	Zhang et al. (2008)

Sludge wastewater	Double chamber	Anode: Graphite carbon electrode Cathode: Graphite carbon electrode	125 mW cm ⁻²	Enhanced power density of florescent light limits electricity output of MFCs	Juang et al. (2012)
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