Bioresource Technology Reports 18 (2022) 101059

Contents lists available at ScienceDirect

Bioresource Technology Reports

journal homepage: www.sciencedirect.com/journal/bioresource-technology-reports

Tubular photo-MFC reactors as wastewater polishing treatment step with simultaneous electricity production

Silvia Bolognesi [a,b,*], Daniele Cecconet [a,c], Arianna Callegari [a], Sebastià Puig [b], Andrea G. Capodaglio [a]

[a] Department of Civil Engineering and Architecture, University of Pavia, Via Adolfo Ferrata 3, 27100 Pavia, Italy
[b] LEQUiA, Institute of the Environment, Universitat de Girona, Maria Aurèlia Capmany 69, Girona 17003, Spain
[c] Department of Chemistry, University of Pavia, Viale Taramelli 12, 27100 Pavia, Italy

ARTICLE INFO

Keywords:
Bioelectrochemical Systems
Chlorella
Nitrogen removal
Phosphorous removal
Renewable energy
Tubular photo-MFC reactor

ABSTRACT

Wastewater treatment processes energy and emissions issues led researchers to investigate more sustainable alternative technologies, aimed at achieving effective contaminants removal with simultaneous resources recovery (i.e., energy). The combination of microbial fuel cell (MFC) technology with microalgal-based processes in a photo-MFC (PhMFC) could potentially reduce GHGs impact of wastewater treatment, capturing anodically produced CO_2 and photosynthetically convert it into oxygen, with a bioelectrochemical, cathodic polishing step. Two tubular PhMFCs were operated with synthetic wastewater under different conditions. Organic matter and nutrients removals and electricity production were monitored under each tested condition. Energy losses and design issues were also analyzed. The two PhMFCs globally proved to be effective in COD (up to 94%), total nitrogen (55%) and total phosphorus (60%) removal, with simultaneous bioelectricity production (up to $5.5 \cdot 10^{-4}$ kWh m^{-3}). The presence of microalgae also opens the possibility of recovery opportunities connected to the post-processing of the cathodic effluent.

1. Introduction

In the last decades, increasing environmental pressures and fossil fuel resources depletion led researchers to intensify studies and development of alternative technologies for the production of renewable fuels and bioenergy, with the purpose to meet present and future energy demands in a more sustainable, carbon-neutral approach within the frame of circular economy (Callegari et al., 2020). Microbial electrochemical technologies (METs) have aroused the scientific community interest as a possible alternative to face some of the great emerging critical issues of today's society sustainability: constant availability of clean and safe water, energy demand fulfillment and minimization of the carbon footprint of waste streams (Osset-Álvarez et al., 2019). Microbial fuel cells (MFCs) are a sustainable technology for bioelectricity generation from degradable organic matter, suitable for wastewater treatment coupled with low CO_2 emissions and reduced sludge production (Logan et al., 2006; Mologni et al., 2018; Puig et al., 2011). MFCs rely on the catalytic action of electrochemically active bacteria to oxidize organic substrate in an anodic chamber, releasing carbon dioxide, electrons and protons. Electrons travel through an external electric circuit from the anode to the cathode electrode, while protons (or other charge-balancing ions) pass through an ionic selective membrane to reach the cathode. Both electrons and protons are combined with the terminal electron acceptor (TEA), usually oxygen. MFCs can also be equipped with a biocathode, where an electrotrophic biomass acts as the catalyst of the oxygen reduction reaction (ORR), being a possible solution to mitigate costs connected to the use of expensive, metal-based catalysts (He and Angenent, 2006; Nikhil et al., 2017; Xia et al., 2013). One interesting opportunity to minimize costs connected to mechanical aeration is given by the exploitation of photosynthetic metabolism of microalgae in MFCs (Bolognesi et al., 2021; Yahampath Arachchige Don and Babel, 2021a). Microalgae are a well-known third-generation feedstock for biofuels, and they are characterized by fast growth rates, simplicity of management, higher biomass yield than other biofuels-oriented feedstocks, CO_2 capture ability and the wide possibility of integration in high-value product chains (Bolognesi et al., 2022; Callegari et al., 2020; Sevda et al., 2019). Microalgae metabolism and possible products have been extensively studied, and encouraging

* Corresponding author at: LEQUiA, Institute of the Environment, Universitat de Girona, Maria Aurèlia Capmany 69, Girona 17003, Spain.
E-mail address: s.bolognesi@udg.edu (S. Bolognesi).

https://doi.org/10.1016/j.biteb.2022.101059
Received 5 January 2022; Received in revised form 13 April 2022; Accepted 13 April 2022
Available online 27 April 2022

applications in industrial facilities have already been reported. One of the major advantages is that algae can use a wide array of carbon sources: algae-growing facilities could, for example, be operated jointly with carbon-emitting point sources (power plants and industries) to convert the latters' gaseous emissions (insufflated in the cultivation basins) into fuel, without release into the atmosphere. Alternatively, they could be paired to wastewater treatment facilities, where they would uptake dissolved residual nutrients (N and P) reducing their release into surface waters. Heterotrophic (dark) cultivation with synthetic substrate (acetate or glucose) or wastewater as a carbon source was also assessed (Heredia-Arroyo et al., 2010; Wang et al., 2010; Leu and Boussiba, 2014).

In MFC applications, algae may be used as electron donors at the anode, exploiting their ability in removing organic substrates or as substrate themselves, or, more frequently, in photosynthetically aerated biocathodes (Commault et al., 2017; Gude et al., 2013; Kannan and Donnellan, 2021). In the cathode chamber, under sunlight, algae carry out photosynthesis and convert the atmospheric or the anodically produced CO_2 into oxygen and new biomass; on the contrary, in the dark stage, they consume oxygen to produce energy by direct oxidation of organic materials and synthesize new biomass (Ndayisenga et al., 2018; Richmond, 2004; Saba et al., 2017). A wide experience has been gathered in the last decade on microalgal biocathodes. As in conventional microbial fuel cells, electricity is produced from the degradation of organic matter at the anode, while microalgae provide oxygen, the TEA, avoiding the use of chemical mediators and with the advantage of exploiting microalgae pollutant removal properties (Khan et al., 2022). Nitrate reduction in microalgal biocathodes has also been reported (Arun et al., 2022; Nookwam et al., 2022). Many factors can influence the process' overall performance: among all, light/dark cycles and light intensity are key factors influencing O_2 production, biomass growth and algal stress; consequently, they may affect the system efficiency, both in terms of pollutants and nutrients removal, bioelectricity production and target recovery bioproducts. Both pure cultures and naturally occurring mixed cultures have been operated in microalgal biocathodes, with incomparable advantages in using the latter when operating with wastewater due to their increased stability from external contamination (Yahampath Arachchige Don and Babel, 2021a). Furthermore, the perspective of the utilization of the biocathode effluent for the production of added value products such as biomass, lipids, proteins, pigments with several applications, makes the study of new, efficient MFC setups involving microalgae even more appealing (Nookwam et al., 2022).

The present study aimed to assess the effectiveness of coupling MFC technology with a microalgal-based process in a photo-MFC (PhMFC) reactor, where the biocathode is applied as a polishing wastewater treatment step simultaneously achieving bioelectricity production. A mixed culture of *Chlorella* was responsible for providing oxygen to close the redox reaction and as a secondary step for wastewater anodically pretreated. To accomplish this, the study evaluates the influence of lighting conditions and electron acceptor supply in a PhMFC operated with synthetic wastewater as anodic feed, with an eye to carbon and nutrients (total phosphorous and nitrogen) removals and electric efficiency analysis. Finally, the energy losses and the critical design aspects were also analyzed.

2. Materials and methods

2.1. Experimental setup and operation

Two identical tubular PhMFCs (PhMFC1 and PhMFC2, respectively) were built and operated using a transparent methacrylate tube (d = 11 cm, h = 30 cm) and two PVC cover caps of the same diameter. Each MFC consisted of two concentrical chambers, anodic and cathodic, with a free volume of 430 mL net anodic compartment (NAC) and 1.1 L net cathodic compartment (NCC). The anodic chamber was created by using a tubular cationic exchange membrane (CEM, CMI-7000, Membranes International Inc., USA, d = 3 cm, h = 28 cm). The anode consisted of two intercrossed carbon felt stripes (each 28 × 3 cm, AvCarb G100 PAN, Fuel Cell Inc., USA), with a graphite rod (250 × 4 mm, Sofacel, Spain) as the electron collector. Each cathode was built with two stripes of carbon felt (2 × 28 cm), each modelled into a ring form, with two graphite rods, one as electron collector (250 × 4 mm) and another (100 × 4 mm) as structural support. The design of the reactor was such that the anodic chamber was not completely separated from the cathodic one, since the CEM did not reach the full height of the reactor; thus, the two chambers shared a common headspace, allowing the cathodic chamber to be continuously fed by the overflow from the anodic compartment without the need for external pumping (Fig. 1, insert b). The external electrical circuit was closed by using a 43 Ω resistance as load. This value was close to the static internal resistance of both MFCs, detected by performing polarization curves before the experimentation.

All tests performed during the study were carried out with synthetic wastewater (2 g L^{-1} CH_3COONa, 0.819 g L^{-1} Na_2HPO_4, 0.507 mg L^{-1} NaH_2PO_4, 2.6 10^{-3} g L^{-1} KCl, 0.02 g L^{-1} NH_4Cl). The influent anodic solution was fed to the system using collapsible 10 L jerry cans to limit contact with air. A multichannel peristaltic pump (BT100N, MX6, Shenchen Pump Inc., China) was used to feed the anodic chambers at the selected flow rate.

Anodic chamber was inoculated using the effluent from a parent MFC (Bolognesi et al., 2021) additioned with acetate (1.5 g L^{-1}), and continuously recirculated for one week. During the start-up phase, the two cathodic chambers were initially fed with a phosphate buffer solution (PBS, 10 mM, pH 7) containing macro-elements and an inorganic source of carbon (507 mg L^{-1} NaH_2PO_4, 819 mg L^{-1} Na_2HPO_4, 1000 mg L^{-1} $NaHCO_3$, 130 mg L^{-1} KCl, 310 mg L^{-1} NH_4Cl, modified from Xia et al. (2013)). A mixed culture of microalgae *Chlorella* was inoculated at the biocathode in 20:80 volume ratio with the cathode buffer solution. An internal recirculation loop was activated in each chamber to achieve well-mixed conditions (100 L d^{-1}, BT100N, YZ1515x heads, Shenchen Pump Inc., China).

The system was designed to directly take advantage of the anodic effluent and the CO_2 produced at the biocathode as substrates for the microalgae. Despite direct CO_2 exploitation by microalgae being desired, the presence of the oxygen produced at the biocathode in the common headspace could partially affect the upmost layer at the anode, possibly inducing a "snorkel" effect that might globally decrease the electrical performance of the system. This solution, however, was deemed more practical than the full separation of the two chambers that would have required an extra pump to feed the anodic effluent to the biocathode. Under steady state operation, in fact, the effluent from anodic chamber would overflow directly into the cathodic chamber. The transparent methacrylate structure allowed light to easily penetrate the biocathode chamber and induce photosynthesis. The TEA (oxygen) was photosynthetically produced by microalgae during the daytime. A fish tank aerator was also connected to the biocathode and eventually operated during nighttime.

A level sensor connected to the data acquisition system (NI USB-6008, National Instruments) automatically activated a discharge pump connected to the biocathode recirculation line when the level reached a set limit, preventing reverse communication between anodic and cathodic chambers. The experimental setup is illustrated in Fig. 1.

Both PhMFCs' performances were evaluated under six different conditions, by varying lighting conditions (light/dark ratio 16/8, 12/12), night air supply and flow rate. Each test lasted up to one week, and all were executed in sequence. A summary of the operational conditions operated during the first phase is reported in Table 1.

The operating mode of light and dark was set by illuminating the MFCs using a low energy consumption plant-growth LED lamp of 20 W connected to an electric socket timer, while the supply of air occurred by mechanical aeration, also connected to the timer.

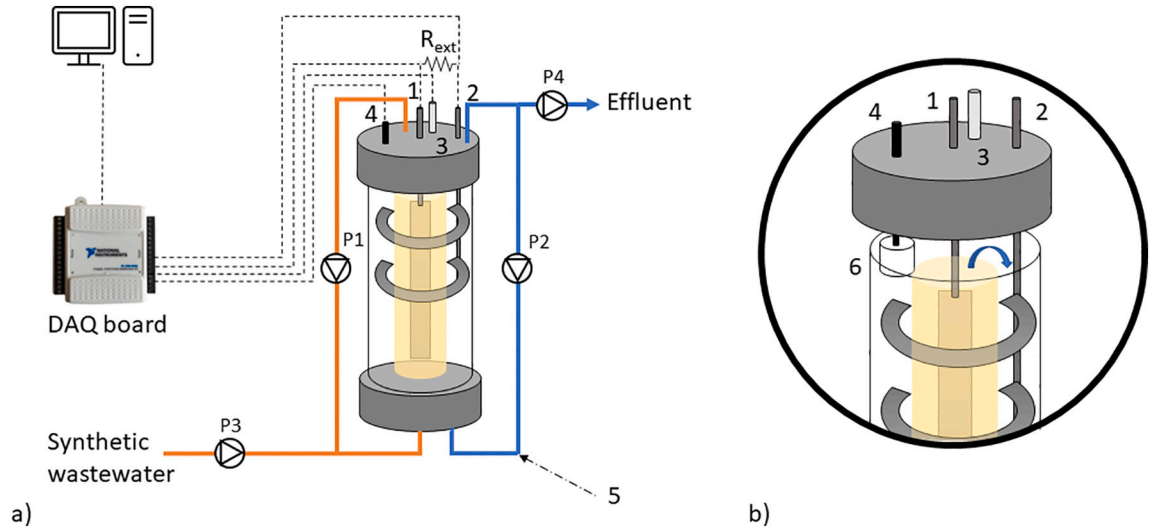

Fig. 1. Experimental setup configuration. a) orange line: anodic recirculation line; Blue line: cathodic recirculation line; dashed line: electrical connections. P1: anodic recirculation pump; P2: cathodic recirculation pump; P3: (anodic) feeding pump; P4: discharge pump. 1: anode; 2: cathode; 3: reference electrode; 4: level sensor connection; 5: air supply. b) detail of the hydraulic setup of the cell: anodic overflow to the cathode and cathodic discharge activated by the level sensor (6). DAQ board: I/O data acquisition system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Operational conditions throughout the first phase of the experimentation.

Test	Operation time [d]	Light/dark ratio	Q [L d^{-1}]	Night aeration
1	14	16/8	0.25	No
2	7	16/8	0.25	Yes
3	10	12/12	0.25	No
4	11	12/12	0.25	Yes
5	4	16/8	0.1	No
6	6	16/8	0.5	No

2.2. Data analysis and evaluation

The PhMFC electric potentials were monitored by an automatic data acquisition system (NI USB-6008, National Instruments Italy, Milan) connected to a PC, recording voltage (V), current (I) and power (P) at 1-min intervals. An Ag/AgCl reference electrode (+197 mV vs Standard Hydrogen Electrode, Xi'an Yima Opto-electrical Technology Co., China) was used to monitor anodic potentials. Power (P) was determined from continuous current (I) and voltage measurement (V). Chemical oxygen demand (COD), total nitrogen (TN) and total phosphorous (TP) were determined for both the influent solution and effluent samples by spectrophotometer (HI83224 Wastewater Treatment Photometer, Hanna Instruments, Italy). Conductivity and pH were monitored three times per test for influent, anodic and cathodic effluents (IntelliCAL™ probes + HQd™ Digital Meter, Hach Lange, Italy). Anodic coulombic efficiency (CE) and organic matter removal efficiency (ηCOD - %) were determined as described in Cecconet et al. (2018). Energy losses were calculated using the energy balance equation according to the equation reported by Molognoni et al. (2014):

$$E_{cell} = E_{emf} - E_{\Delta pH} - \eta_{an} - \eta_{cat} - E_{ionic} - E_T \quad (1)$$

where the parameters are described as follows: E_{cell} (cell voltage), E_{emf} (cell electromotive force), $E_{\Delta pH}$ (pH gradient loss), η_{an} (anode overpotential), η_{cat} (cathode overpotential), E_{ionic} (ionic loss), and E_T (transport loss).

Polarization curves were also performed to evaluate the variation in the total internal resistance of the system using a potentiostat (Nanoelectra, NEV4). The electric circuit was disconnected 30 min before the polarization curve was performed, starting from the open circuit value (OCV) measured between anode and cathode electrode with a multimeter, and the polarization curve was performed at a scan rate of 1 mV s^{-1}.

3. Results and discussion

The data collection and monitoring phase lasted 52 days. The operational phase described in the following paragraphs was preceded by a period of inoculation/stabilization of the PhMFCs. During this phase, no overflow occurred from the anode to the cathode. Both PhMFCs were maintained under ideal conditions for the growth of biomass for a month. During the inoculation phase (one week), the system was operated in recirculated batch mode, and then switched to continuous operation for the remaining three weeks (stabilization phase).

3.1. Electrical production

Fig. 2 shows the electrical performances for each PhMFCs under each tested condition in replicates (Table 1). PhMFC2's performance generally overcame PhMFC1's in terms of electricity production. Voltage in night-aeration tests 2 and 4 (Fig. 2b, d) was generally higher than corresponding non-aerated test values (Fig. 2a, c). An average current density of 5.06 and 17.58 mA m^{-2} was achieved in Test 1 for PhMFC1 and PhMFC2, respectively, while 24.72 and 31.95 mA m^{-2} were obtained from Test 2 under the same light conditions (16/8) with night aeration applied.

In Tests 3–4, a different lighting condition was applied (12/12), and also, in this case, a better result in terms of current density as shown in the nightly-aerated test. 7.94 and 14.41 mA m^{-2} were produced by PhMFC1 and PhMFC2 in the test without aeration, against 20.20 and 25.29 mA m^{-2} in the test with aeration applied.

Considering the performance of PhMFC2, more stable throughout the study, two different flow rates (0.1 and 0.5 L d^{-1}) were studied under non-aerated 16/8 lighting conditions in Test 5 and 6. In this case, PhMFC1 in Test 5 presented an average current density of 17.91 mA m^{-2}, against 20.21 mA m^{-2} of Test 6. In this last test, PhMFC1 reached performances similar to those of aerated tests, thus maintaining the periodicity of the profile of a non-aerated test. This indicated that increased availability of substrate leads to better performance. As PhMFC1, also PhMFC2 achieved a current density of 13.81 mA m^{-2} in Test 5, against 29.23 mA m^{-2} obtained in Test 6, confirming PhMFC1's results. Maximum current production from PhMFC1 (69.02 mA m^{-2})

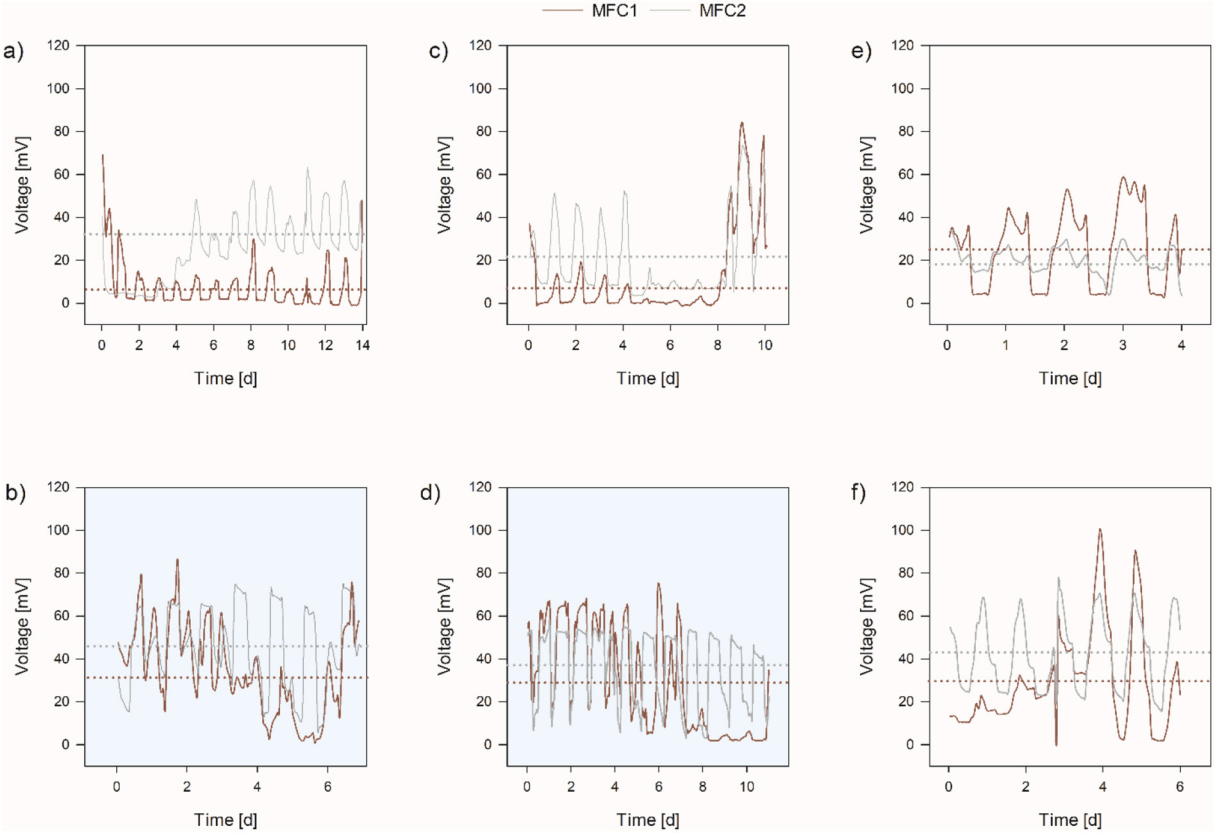

Fig. 2. Electrical production in PhMFC1 and PhMFC2. a) 16/8 without night aeration; b) 16/8 with night aeration; c) 12/12 without aeration; d) 12/12 with night aeration; e) 16/8, Q = 0.1 L d^{-1}; f) 16/8, Q = 0.5 L d^{-1}. Dotted lines: average voltage.

and PhMFC2 (51.72 mA m^{-2}) were both achieved during Test 2, corresponding to $5.5 \cdot 10^{-4}$ kWh m^{-3} and $3.1 \cdot 10^{-4}$ kWh m^{-3}, respectively, in terms of electricity production. It is important to point out that electricity production peaks occurred during nighttime in aerated tests, during daytime in tests without aeration.

3.2. Organic matter removal efficiency and coulombic efficiency

Organic matter removal efficiency (ηCOD) and coulombic efficiency (CE) were evaluated for each tested condition. During the first four tests, the influent solution's organic load rate (OLR) was nearly constant (0.491 ± 0.014 kg COD m^{-3} d^{-1}), however, the two PhMFCs present different performances in terms of ηCOD, with generally better performance by PhMFC1. This achieved between 52 and 77% COD removal, against 44 and 71% of PhMFC2 (Fig. 3). Such values are lower than those reported in other studies; this can be imputed to preferential internal hydrodynamics pathways in the anodic compartment due to electrode construction. In the last two tests, in which different flow rates were applied, the situation appeared drastically changed. In Test 5, ηCOD increased up to 90.2% for both reactors, while in Test 6, ηCOD reached 84.9% for PhMFC1 and 79.8% for PhMFC2, respectively. Results from Test 6 are particularly surprising since the flowrate increase led to augmented removal performance, likely connected to different hydrodynamics linked to an improved substrate distribution and

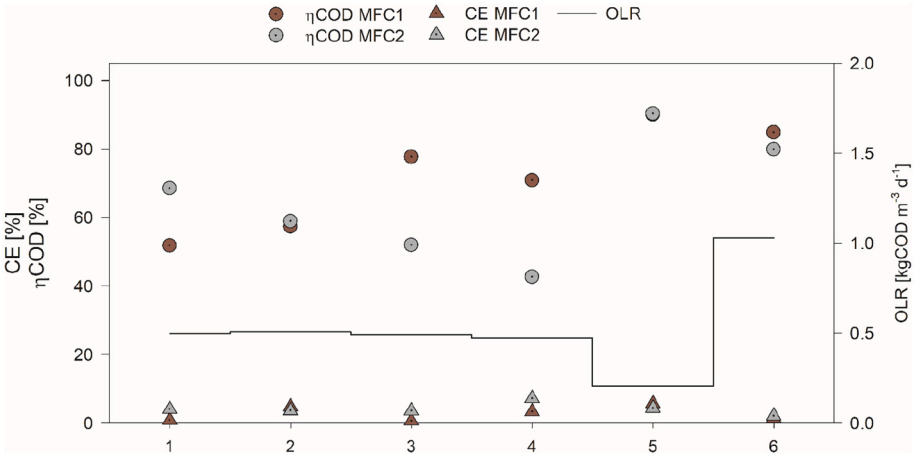

Fig. 3. OLR, COD removal and CE for PhMFC1 and PhMFC2 throughout the study.

biomass composition (Vilà-Rovira et al., 2015). CE varied throughout the study between 1 and 7%, depending on flowrate operated, organic loading rate, light conditions, and presence of night aeration, with overall better results for PhMFC2. The best results in PhMFC2 operation were achieved in tests without night aeration (7.16%). The lowest CE in both PhMFCs was obtained during Test 6 (1%). Such values are lower than previous studies from the group and reported in the literature, confirming the presence of competitive bacteria such as methanogens may be responsible for the augmented organic matter degradation (Bolognesi et al., 2021).

3.3. COD and nutrient removals

In the latter phase of the experimentation, COD, nitrogen and phosphorous removals were evaluated. COD, TN and TP analysis were repeated two times in duplicates during Test 6 (Table 2).

PhMFCs' cathodes as polishing step for anodic treatment of wastewater, with better overall performance for PhMFC2 in terms of nutrient removal (up to 62% TP removal and 55% TN removal, considering the performance of both chambers), while PhMFC1 achieved better performance in terms of COD removal (up to 94% in the anodic plus cathodic compartment performance). From these results, it appears that the microbial community developed differently in the two cell replicates, both in the anodic and the cathodic compartments, with a stronger microalgae community in PhMFC2. The alternate of light and dark phases switched the metabolism from autotrophic to mixotrophic, actively contributing to acetate removal.

4. Assessing PhMFC setup in terms of energy losses and internal resistance

The performance of the systems was assessed in terms of polarization curves and energy losses. Energy losses represent the difference between theoretical maximum voltage (i.e., electromotive force) and measured voltage at the electrodes of an MFC. Several factors affect the electric performance of MFCs: anode and cathode overpotentials, membrane overpotentials, pH and conductivity (ionic) gradients. Fig. 4 represents the distribution of energy losses for PhMFC1 and PhMFC2.

In the two PhMFCs, cathode overpotentials accounted on average for 78% of PhMFC1's losses, 84% of PhMFC2's, while anode overpotentials for 18% in PhMFC1, and 8% in PhMFC2, representing the second major source of energy losses, confirming cathode efficiency as the limiting step in MFC technology (Puig et al., 2012). Anodic overpotential may be caused by increased competitive microbial community activity, such as methanogenic bacteria (Molognoni et al., 2014). The high concentration of COD and high OLR operated in this study may have affected the anodic performance. Karamzadeh et al. (2020) reported that an increased concentration of organic feed reduces the efficiency in electrons production and transfer, likely to the development of competitive biomass, while Kaur et al. (2014) suggested anodic starvation as a technique to inhibit methanogens. Membrane overpotentials only moderately affected the overall balance (3 and 4% of overall losses), while pH and electrolyte overpotentials were considered negligible, as expected from the recirculation of the same medium in both chambers with a low gradient in terms of pH (8.47 ± 0.21) and conductivity (2.65 ± 0.53 mS cm^{-1}).

Cathode overpotentials in both units were extremely high, thus reactor design and development of a strong catalyst should be improved. To reduce cathode overpotentials different strategies can be applied, for example, the use of more biocompatible electrode materials (Kalathil et al., 2018) and increasing the electrode surface (Karamzadeh et al., 2020). In this study, the cathode electrode surface was minimized to allow light passage inside the reactor to enhance the microalgae photosynthetic reaction; it has also to be taken into account that using algal biocathodes may reduce electron transfer efficiency due to fouling phenomena, as already detected in previous studies (Bolognesi et al., 2021).

The electrochemical characterization was complemented with the polarization curves. They were performed to evaluate variations in the internal resistance of the two PhMFCs. Fig. 5 shows the polarization curves and the relative internal resistance values obtained in each test. The performance of the two reactors was different, with better results for PhMFC1. The electrochemical performance of the two PhMFC was not very similar, despite the same conditions were applied to both reactors. One of the two reactors (PhMFC2) presented some hydraulic issues at the beginning of the experimentation, and this affected its performance under all aspects, including the electrochemical one. Table 3 resumes the electrochemical parameters detected during the experimentation. It is possible to notice that the open circuit value OCV of PhMFC2 was generally higher than PhMFC1's. All electrochemical parameters (I_{sc}, short circuit current; P_{mpp}, maximum power point; I_{mpp} and V_{mpp}, current and voltage at maximum power point, respectively) are lower for PhMFC2 in almost all conditions tested, with the exception of the last test, where the values were alike for both PhMFCs. Internal resistance values (R_{int}) calculated, consequently, were also always higher for PhMFC2. Considering the slope of the first part of the polarization curves achieved in this experimental, activation losses were predominant in all conditions tested, thus, better design of electrodes to improve the electron transfer is necessary to overcome the limitations emerged in this study. It is possible to notice an increasing trend in internal resistance for both units over time, except PhMFC2 in Test 5, where the maximum value (247 Ω) was detected. This gradual increase may be imputed to the growth of microalgae over time, causing progressive fouling phenomena on the electrode surface and membrane. The external resistance originally applied (43 Ω), calculated from polarization curves performed after the startup of the two PhMFCs, was three times lower than the one detected at the end of the experimentation.

5. Implications of microalgae integration in PhMFCs

Using microalgae as biocathode catalysts and TEA providers in a PhMFC system can improve its economic/energy balance by decreasing (or eliminating) the cost of aeration, and reducing GHG emissions by direct consumption of the anodically-produced CO_2. The presence of microalgae can also improve the overall economic balance and Circular Economy value of wastewater treatment, by exploiting different materials and biofuels precursors potentially recoverable from the conversion of algal biomass, especially regarding liquid biofuels (Dasan et al., 2019; Liang et al., 2015).

Currently, costs for biodiesel production from microalgae are very high, with artificial light and carbon source supply having greater impacts. By increasing the lipid content of biomass, the cost of biodiesel

Table 2
Nutrient removals in Test 6.

	C_{IN} [mg L^{-1}]	$C_{OUT,A1}$ [mg L^{-1}]	$C_{OUT,C1}$ [mg L^{-1}]	$C_{OUT,A2}$ [mg L^{-1}]	$C_{OUT,C2}$ [mg L^{-1}]	ηA1 [%]	ηC1 [%]	ηA2 [%]	ηC2 [%]	η_{tot} PhMFC1 [%]	η_{tot} PhMFC2 [%]
COD	800	193 ± 15	51 ± 12	363 ± 39	117 ± 14	76	74	55	68	94	85
TP	666	375 ± 54	325 ± 23	340 ± 42	255 ± 16	44	13	49	25	51	62
TN	20	10 ± 2	9 ± 1	16 ± 2	9 ± 0	50	10	20	44	55	55

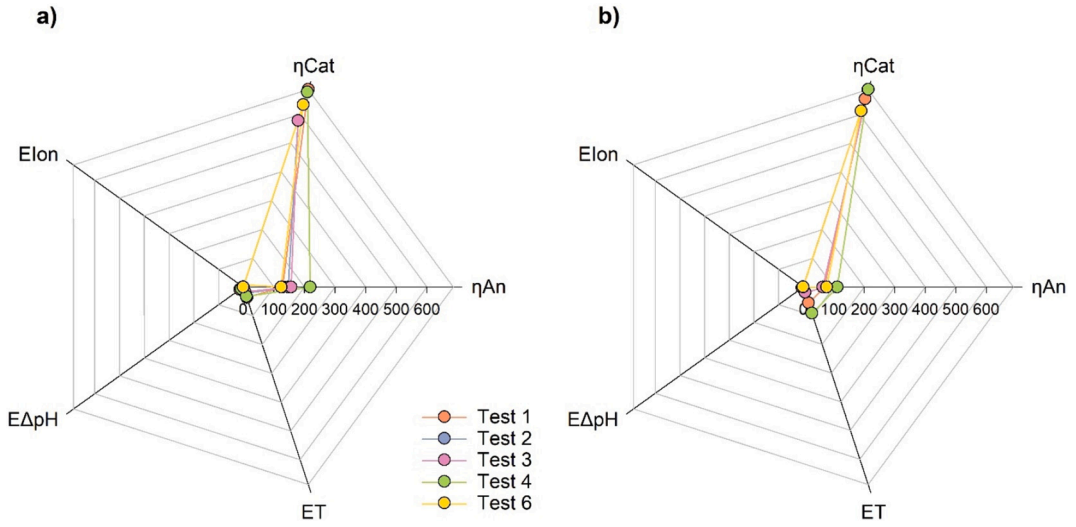

Fig. 4. Energy losses (mV) throughout the experimentation.

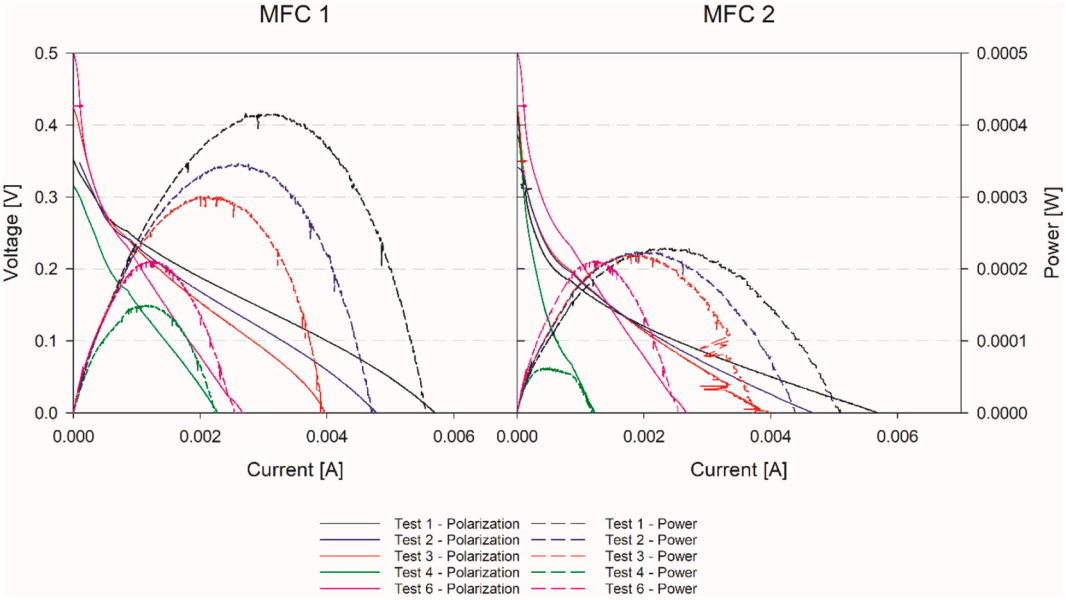

Fig. 5. Polarization and power curves for MFC1 and MFC2 and relative internal resistance variation throughout the experimentation.

Table 3
Electrochemical performance of PhMFC1 and PhMFC2.

	PhMFC1						PhMFC2					
Test	OCV [mV]	R_{int} [Ω]	P_{mpp} [mW]	I_{mpp} [mA]	V_{mpp} [mV]	I_{sc} [mA]	OCV [mV]	R_{int} [Ω]	P_{mpp} [mW]	I_{mpp} [mA]	V_{mpp} [mV]	I_{sc} [mA]
1	260	51	0.34	2.64	134	4.71	340	57	0.22	2.02	112	4.65
3	390	59	0.30	2.29	134	3.93	370	71	0.22	1.79	126	3.93
5	190	102	0.15	1.23	125	2.28	240	243	0.06	0.54	126	1.23
6	380	135	0.21	1.28	172	2.68	450	137	0.22	1.28	173	2.54

production from algae could decrease from 5.1 $ L^{-1} to 2.3 $ L^{-1} (Fei et al., 2015). It should be noted that, apart from oils, algal biomass also contains significant amounts of proteins, carbohydrates and other nutrients (Morales-Sánchez et al., 2015). Alternative product outcomes, such as chemicals and recovery of different materials, can also be considered, enhancing the overall economics of microalgae biorefineries (Yu et al., 2017).

Another possible application is as slow-release fertilizers, which are recoverable in form of dried biomass or biochar from pyrolysis, depending on process operational parameters during thermal treatment (Bolognesi et al., 2019). Biofertilizers and biostimulants appear to be one of the most economically appealing fields in algal technology, with market prices in the range of 9–23 € kg^{-1} for biostimulants, and 0.2–0.5 € kg^{-1} for biofertilizers (Daneshgar et al., 2018; Voort et al., 2015).

Thus, perspectives for the combined use of MFCs and microalgae, exploiting liquid waste streams' embedded resources and reducing

wastewater treatment energy requirements, could be both sustainable and economically interesting when considering the worth of the products potentially obtained from algal biorefinery, and not only the (still limited) bioelectricity production.

6. Conclusions

This study assessed the performance of two PhMFCs operated continuously for 52 days, varying light/dark conditions, flow rates and oxygen supply method. Both PhMFCs proved effective in COD, TN and TP removal in the combined anode-cathode treatment, reaching ηCOD up to 95%, and ηTP and ηTN between 50 and 60%. Cathode design was probably the cause of high energy losses in the compartment (78 and 84%, respectively). The limitation in the anodically-produced CO_2 photosynthetic conversion into oxygen restrained the electrical energy production. Electricity production and COD removal rate increased at higher applied flow rates due to higher turbulence and OLR.

CRediT authorship contribution statement

S. Bolognesi: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft. **D. Cecconet:** Investigation, Data curation, Visualization. **A. Callegari:** Visualization, Writing – review & editing. **S. Puig:** Conceptualization, Supervision, Resources, Writing – review & editing. **A.G. Capodaglio:** Conceptualization, Supervision, Resources, Writing – review & editing.

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.

Acknowledgements

Silvia Bolognesi holds a Double Doctorate at the University of Pavia and the University of Girona. The study herein described was carried out at the University of Pavia. The authors thank Ludovica Malinverni for her help in collecting the data during the experimentation. S.P is a Serra Húnter Fellow (UdG-AG-575) and acknowledges the funding from the ICREA Academia award. LEQUiA [2017-SGR-1552] has been recognized as a consolidated research group by the Catalan Government.

References

Arun, S., Ramasamy, S., Pakshirajan, K., Pugazhenthi, G., 2022. Bioelectricity production and shortcut nitrogen removal by microalgal-bacterial consortia using membrane photosynthetic microbial fuel cell. J. Environ. Manag. 301, 113871 https://doi.org/10.1016/j.jenvman.2021.113871.

Bolognesi, S., Bernardi, G., Callegari, A., Dondi, D., Capodaglio, A.G., 2019. Biochar production from sewage sludge and microalgae mixtures: properties, sustainability and possible role in circular economy. Biomass Convers. Biorefinery. https://doi.org/10.1007/s13399-019-00572-5.

Bolognesi, S., Cecconet, D., Callegari, A., Capodaglio, A.G., 2021. Combined microalgal photobioreactor/microbial fuel cell system: performance analysis under different process conditions. Environ. Res. 192, 110263 https://doi.org/10.1016/j.envres.2020.110263.

Bolognesi, S., Bañeras, L., Perona-Vico, E., Capodaglio, A.G., Balaguer, M.D., Puig, S., 2022. Carbon dioxide to bio-oil in a bioelectrochemical system-assisted microalgae biorefinery process. Sustain. Energy Fuels 6, 150–161. https://doi.org/10.1039/d1se01701b.

Callegari, A., Bolognesi, S., Cecconet, D., Capodaglio, A.G., 2020. Production technologies, current role, and future prospects of biofuels feedstocks: a state-of-the-art review. Crit. Rev. Environ. Sci. Technol. 50, 384–436. https://doi.org/10.1080/10643389.2019.1629801.

Cecconet, D., Bolognesi, S., Molognoni, D., Callegari, A., Capodaglio, A.G., 2018. Influence of reactor's hydrodynamics on the performance of microbial fuel cells. J. Water Process Eng. 26, 281–288. https://doi.org/10.1016/j.jwpe.2018.10.019.

Commault, A.S., Laczka, O., Siboni, N., Tamburic, B., Crosswell, J.R., Seymour, J.R., Ralph, P.J., 2017. Electricity and biomass production in a bacteria- Chlorella based microbial fuel cell treating wastewater. J. Power Sources 356, 299–309. https://doi.org/10.1016/j.jpowsour.2017.03.097.

Daneshgar, S., Callegari, A., Capodaglio, A.G., Vaccari, D., 2018. The potential phosphorus crisis: resource conservation and possible escape technologies: a review. Resources 7. https://doi.org/10.3390/resources7020037.

Dasan, Y.K., Kee Lam, M., Yusup, S., Wei Lim, J., Teong Lee, K., 2019. Life cycle evaluation of microalgae biofuels production: effect of cultivation system on energy, carbon emission and cost balance analysis. Sci. Total Environ. 688, 112–128. https://doi.org/10.1016/j.scitotenv.2019.06.181.

Fei, Q., Shang, L., Brigham, C.J., Chang, H.N., 2015. Lipid production by microalgae Chlorella protothecoides with volatile fatty acids (VFAs) as carbon sources in heterotrophic cultivation and its economic assessment. Bioprocess Biosyst. Eng. 38, 691–700. https://doi.org/10.1007/s00449-014-1308-0.

Gude, V.G., Kokabian, B., Gadhamshetty, V., 2013. Beneficial bioelectrochemical systems for energy, water, and biomass production. J. Microb. Biochem. Technol. S6, 1–14. https://doi.org/10.4172/1948-5948.S6-005.

He, Z., Angenent, L.T., 2006. Application of bacterial biocathodes in microbial fuel cells. Electroanalysis 18, 2009–2015. https://doi.org/10.1002/elan.200603628.

Heredia-Arroyo, T., Wei, W., Hu, B., 2010. Oil accumulation via heterotrophic/mixotrophic chlorella protothecoides. Appl. Biochem. Biotechnol. 162, 1978–1995. https://doi.org/10.1007/s12010-010-8974-4.

Kalathil, S., Patil, S.A., Pant, D., 2018. In: Wandelt, K.B.T.-E., of I.C. (Eds.), Microbial Fuel Cells: Electrode Materials. Elsevier, Oxford, pp. 309–318.

Kannan, N., Donnellan, P., 2021. Algae-assisted microbial fuel cells: a practical overview. Bioresour. Technol. Rep. 15, 100747 https://doi.org/10.1016/j.biteb.2021.100747.

Karamzadeh, M., Kadivarian, H., Kadivarian, M., Kazemi, A., 2020. Modeling the influence of substrate concentration, anode electrode surface area and external resistance in a start-up on the performance of microbial fuel cell. Bioresour. Technol. Rep. 12, 100559 https://doi.org/10.1016/j.biteb.2020.100559.

Kaur, A., Boghani, H.C., Michie, I., Dinsdale, R.M., Guwy, A.J., Premier, G.C., 2014. Inhibition of methane production in microbial fuel cells: operating strategies which select electrogens over methanogens. Bioresour. Technol. 173, 75–81. https://doi.org/10.1016/j.biortech.2014.09.091.

Khan, M.J., Singh, N., Mishra, S., Ahirwar, A., Bast, F., Varjani, S., Schoefs, B., Marchand, J., Rajendran, K., Banu, J.R., Saratale, G.D., Saratale, R.G., Vinayak, V., 2022. Impact of light on microalgal photosynthetic microbial fuel cells and removal of pollutants by nanoadsorbent biopolymers: updates, challenges and innovations. Chemosphere 288, 132589. https://doi.org/10.1016/j.chemosphere.2021.132589.

Leu, S., Boussiba, S., 2014. Advances in the production of high-value products by microalgae. Ind. Biotechnol. 10, 169–183. https://doi.org/10.1089/ind.2013.0039.

Liang, Y., Kashdan, T., Sterner, C., Dombrowski, L., Petrick, I., Kröger, M., Höfer, R., 2015. Algal biorefineries, industrial biorefineries and white. Biotechnology. https://doi.org/10.1016/B978-0-444-63453-5.00002-1.

Logan, B.E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K., 2006. Microbial fuel cells: methodology and technology. Environ. Sci. Technol. 40, 5181–5192. https://doi.org/10.1021/es0605016.

Molognoni, D., Puig, S., Balaguer, M.D., Liberale, A., Capodaglio, A.G., Callegari, A., Colprim, J., 2014. Reducing start-up time and minimizing energy losses of microbial fuel cells using maximum power point tracking strategy. J. Power Sources 269, 403–411. https://doi.org/10.1016/j.jpowsour.2014.07.033.

Molognoni, D., Chiarolla, S., Cecconet, D., Callegari, A., Capodaglio, A.G., 2018. Industrial wastewater treatment with a bioelectrochemical process: assessment of depuration efficiency and energy production. Water Sci. Technol. 77, 134–144. https://doi.org/10.2166/wst.2017.532.

Morales-Sánchez, D., Martinez-Rodriguez, O.A., Kyndt, J., Martinez, A., 2015. Heterotrophic growth of microalgae: metabolic aspects. World J. Microbiol. Biotechnol. 31, 1–9. https://doi.org/10.1007/s11274-014-1773-2.

Ndayisenga, F., Yu, Z., Yu, Y., Lay, C.H., Zhou, D., 2018. Bioelectricity generation using microalgal biomass as electron donor in a bio-anode microbial fuel cell. Bioresour. Technol. 270, 286–293. https://doi.org/10.1016/j.biortech.2018.09.052.

Nikhil, G.N., Suman, P., Venkata Mohan, S., Swamy, Y.V., 2017. Energy-positive nitrogen removal of pharmaceutical wastewater by coupling heterotrophic nitrification and electrotrophic denitrification. Chem. Eng. J. 326, 715–720. https://doi.org/10.1016/j.cej.2017.05.165.

Nookwam, K., Cheirsilp, B., Maneechote, W., Boonsawang, P., Sukkasem, C., 2022. Microbial fuel cells with photosynthetic-cathodic chamber in vertical cascade for integrated bioelectricity, biodiesel feedstock production and wastewater treatment. Bioresour. Technol. 346, 126559 https://doi.org/10.1016/j.biortech.2021.126559.

Osset-Álvarez, M., Rovira-Alsina, L., Pous, N., Blasco-Gómez, R., Colprim, J., Balaguer, M.D., Puig, S., 2019. Niches for bioelectrochemical systems on the recovery of water, carbon and nitrogen in wastewater treatment plants. Biomass Bioenergy 130, 105380. https://doi.org/10.1016/j.biombioe.2019.105380.

Puig, S., Serra, M., Coma, M., Balaguer, M.D., Colprim, J., 2011. Simultaneous domestic wastewater treatment and renewable energy production using microbial fuel cells (MFCs). Water Sci. Technol. 64, 904–909. https://doi.org/10.2166/wst.2011.401.

Puig, S., Coma, M., Desloover, J., Boon, N., Colprim, J., Balaguer, M.D., 2012. Autotrophic denitrification in microbial fuel cells treating low ionic strength waters. Environ. Sci. Technol. 46, 2309–2315. https://doi.org/10.1021/es2030609.

Richmond, A., 2004. Handbook of Microalgal Culture: Biotechnology and Applied Phycology. Blackwell Science Ltd.

Saba, B., Christy, A.D., Yu, Z., Co, A.C., 2017. Sustainable power generation from bacterio-algal microbial fuel cells (MFCs): an overview. Renew. Sust. Energ. Rev. 73, 75–84. https://doi.org/10.1016/j.rser.2017.01.115.

Sevda, S., Garlapati, V.K., Sharma, S., Bhattacharya, S., Mishra, S., Sreekrishnan, T.R., Pant, D., 2019. Microalgae at niches of bioelectrochemical systems: a new platform for sustainable energy production coupled industrial effluent treatment. Bioresour. Technol. Rep. 7, 100290 https://doi.org/10.1016/j.biteb.2019.100290.

Vilà-Rovira, A., Puig, S., Balaguer, M.D., Colprim, J., 2015. Anode hydrodynamics in bioelectrochemical systems. RSC Adv. 5, 78994–79000. https://doi.org/10.1039/C5RA11995B.

Voort, M.P.J.Van Der, Vulsteke, E., Visser, C.L.M.de, 2015. Macro-economics of Algae Products. Swansea.

Wang, L., Min, M., Li, Y., Chen, P., Chen, Y., Liu, Y., Wang, Y., Ruan, R., 2010. Cultivation of green algae Chlorella sp. in different wastewaters from municipal wastewater treatment plant. Appl. Biochem. Biotechnol. 162, 1174–1186. https://doi.org/10.1007/s12010-009-8866-7.

Xia, X., Tokash, J.C., Zhang, F., Liang, P., Huang, X., Logan, B.E., 2013. Oxygen-reducing biocathodes operating with passive oxygen transfer in microbial fuel cells. Environ. Sci. Technol. 47, 2085–2091. https://doi.org/10.1021/es3027659.

Yahampath Arachchige Don, C.D.Y., Babel, S., 2021. Comparing the performance of microbial fuel cell with mechanical aeration and photosynthetic aeration in the cathode chamber. Int. J. Hydrogen Energy 46, 16751–16761. https://doi.org/10.1016/j.ijhydene.2020.09.068.

Yu, K.L., Show, P.L., Ong, H.C., Ling, T.C., Chi-Wei Lan, J., Chen, W.H., Chang, J.S., 2017. Microalgae from wastewater treatment to biochar – feedstock preparation and conversion technologies. Energy Convers. Manag. 150, 1–13. https://doi.org/10.1016/j.enconman.2017.07.060.