IMPACT OF LIGHT WAVELENGTH ON THE PERFORMANCE OF AN ALGAE-ASSISTED MICROBIAL FUEL CELL

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ABSTRACT. In a combined system of the photobioreactor (PBR) and microbial fuel cell support (MFC), studies have been carried out to establish the influence of the light's wavelength on the fuel cell's performance. LED light sources have been used for this purpose at 5 different wavelengths, with maximum - blue (469 nm), green (520 nm), yellow (604 nm), orange (629 nm), and red (659 nm), respectively. The influence of the dissolved oxygen concentration in the cathode zone of MFC has been detected, depending on the wavelength of the aerobic photosynthesis process of microalgae dominated by Scenedesmus sp. The growth curves of the micro-algae are established by the change in optical density and biomass quantity, at different wavelengths, while also tracing the influence on the electrochemical parameters of MFC. The maximum power density values established (26.5 mW/m²) and current density (78.3 mA/m²) in the fuel cell show a clear correlation between dissolved oxygen concentration, cathode potential, and wavelength of the light source.

Keywords: algae, microbial fuel cell, oxygenic photosynthesis, bioenergy.

ВЛИЯНИЕ НА ДЪЛЖИНАТА НА ВЪЛНАТА ВЪРХУ ЕФЕКТИВНОСТТА НА ПОДПОМОГНАТА ОТ МИКРОАЛГИ МИКРОБНА ГОРИВНА КЛЕТКА

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РЕЗЮМЕ. В комбинирана система на фотобиореактор (ФБР) и подпомогната от микроалги микробна горивна клетка (МГК), са проведени изследвания за установяване на влиянието на дължината на вълната на светлината върху ефективността на горивния елемент. За целта са използвани LED източници на светлина при 5 различни дължини на вълната, с максимуми съответно – синя (469 nm), зелена (520 nm), жълта (604 nm), оранжева (629 nm) и червена (659 nm). Установено е влиянието на концентрацията на разтворен кислород в катодната зона на MFC в зависимост от дължината на вълната при процеса на аеробна фотосинтеза на микроалги, доминирани от Scenedesmus sp. Растежните криви на микроалгите са установени чрез промяната на оптичната плътност и количеството на биомасата, при различни дължини на вълната, като едновременно с това е проследено и влиянието върху електрохимичните параметри на МГК. Максималните стойности на плътността на мощността (26.5 mW/m²) и тока (78.3 mA/m²) в горивната клетка, показват ясно изразена корелация, между концентрацията на разтворен кислород, катодния потенциал и дължината на вълната на светлинния източник.

Ключови думи: микроводорасли, микробни горивни клетки, оксигенна фотосинтеза, биоенергия.

Introduction

The use of renewable and net-zero energy sources is one way to reduce the impact of greenhouse gases on the environment. Microalgae are very efficient converters of solar energy into biomass, having some significant advantages over plants, such as requiring less space, having higher growth rates, and accumulating significantly more biomass (Jones and Mayfield, 2012). Microalgae are also attracting considerable interest for the various possible applications related to sustainable environmental management. Such applications are: the use of microalgae for biomass production and valuable value-added substances (Fabris et al., 2020; Liu et al., 2021), wastewater treatment of nitrogen and phosphorus compounds (Nguyen et al., 2022), biofuel production (Hartman, 2008), carbon capture from waste gases (Onyeaka et al., 2021), etc.

Incorporation of microalgae into microbial fuel cells (MFCs) is an innovative concept which provides new opportunities for obtaining additional energy when combining aerobic and/or

anaerobic photosynthesis with other microbial processes occurring in the anode or cathode zone of bioelectrochemical systems (Khandelwal et all., 2023). In MFC, microalgae are used in 2 variants: algae-assisted MFC (AMFC) and photosynthetic MFC (PMFC) (Zhang et al., 2019). The microbial fuel cell technology was developed for energy generation and pollutant removal based on the metabolism of electroactive microorganisms. Microorganisms oxidise a substrate in the anode chamber in the MFC, and electrons generated in the biological process are transferred to the anode and then pass through an external circuit to the cathode. Oxygen as an oxidant receives the electrons on the cathode and is transformed into water (Logan et all., 2006). However, the actual application of MFCs is limited by the low power and high material and maintenance costs of the fuel cell (Kannan and Donnellan, 2021). However, the interest of the global scientific community in MFCs and related other bioelectrochemical systems has grown significantly over the past 10 years (Elshobary et al., 2021). One possible approach to optimise the processes in

MFCs is the use of oxygen microalgae in the cathode zone of the MFC. Microalgae introduced into the cathode chamber of the MFC convert light energy and CO² through photosynthesis into chemical energy and produce oxygen. Higher oxygen concentration in the cathode chamber can save the cost of additional aeration in the catalyst and is a prerequisite for obtaining higher cathode potential and power of the MFC (Kannan and Donnellan, 2021).

The effect of light intensity and wavelength on the accumulation of microalgal biomass depends on the particular species and environmental factors. Microalgae use light wavelengths from 400 to 700 nm for the process of photosynthesis, and depending on the species, microalgae absorb different wavelengths. Growth is accelerated by increasing light intensity to a point that varies depending on the microalgae species (Metsoviti at., 2019). Photoinhibition can be caused by high light intensity beyond the saturation point (Difusa et all., 1016). On the other hand, there is also a clear correlation between the intensity of microalgal development and dissolved oxygen levels in the medium. Oxygenic microalgae introduced into the cathode zone of the fuel cell can provide significant concentrations of dissolved oxygen, which is the preferred electron acceptor in electron transfer (Khandelwal et al., 2023)

To this moment, to optimise the cathode potential of oxygenated microalgae-assisted microbial fuel cells, the influence of wavelength on the oxygen concentration in the catholyte has been insufficiently investigated. An example of typical oxygenic microalgae is Scenedesmus sp., which are among the most common types of microalgae found in both natural and wastewater (Ortiz-Betancur et al., 2022). At the same time, they are also among the frequently applied species in the cathode zones of MFCs (Elshobary et al., 2021).

A major objective of the study was to determine the influence of the wavelength of the light source on the oxygen capacity of the studied microalgae in the cathode zone of the MFC. One of the most important tasks is tracking the technological parameters of an algae-assisted microbial fuel cell, to establish the optimal conditions for energy extraction and biomass production.

Materials and methods

A mixed culture of microflora dominated by Scenedesmus sp. was used for laboratory tests, isolated from natural water sources. The cultivation was performed in a flat-type photobioreactor with a volume of 0.8 dm³ with continuous recirculation of the liquid phase through a buffer vessel with a volume of 0.4 dm³ (Fig.1). For the cultivation of microalgae, the modified nutrient medium BG11 was used, with the following composition for 1 L - 1.5 g NaNO₃, 0.5 g Na₂CO₃, 0.04g K₂HPO₄, 0,075g MgSO4.7H2O, 0.036g CaCl2.2H2O, 0.045g Citric acid, 0.0015g, Ferric ammonium Citrate, 0.045g EDTA (disodium salt), and 1ml trace elements solution consisted of 2.86 g/l H3BO3; 1.81 g/l MnCl2.4H2O; 0.222 g/l ZnSO4.7H2O; 0.39 g/l NaMoO4.2H2O; 0.079 g/l CuSO4.5H2O; 0.0494 g/l Co(NO3)2.6H2O. Algae were inoculated at 10% (Vinoculation/Vmedia) in a volume of 1.2 dm³ of PRB together with the buffer vessel. Cultivation of the microalgae was carried out at room temperature in the range of 24-290C. The photobioreactor (PBR) was aerated using an air pump with a flow rate of 1.5 L/h, without further addition of $CO₂$ to the air.

A Bürker counter camera for a light microscope (BoecoR, BM-800) was used to determine the number of microalgae, as well as the parallel determination of the optical density of the cell suspension during the cultivation of the microalgae at a wavelength of 650 nm and a red filter. In the continuous mode of operation of the photobioreactor (PBR), 6 variants of operation of the MFC microbial fuel cell integrated into it were investigated (Fig. 1). These modes of operation differed only in the type of light source used to illuminate the photobioreactor. For this purpose, LED light sources were used with six different wavelengths with characteristics shown in Table 1. White light with a mixed spectrum-type LED-4300K was used as a control. In each of the 6 buffer vessels, air was supplied with a flow rate of 1.5 l/h, through air pumps. For all variants, samples were taken at certain time intervals to determine the optical density of the liquid phase. A 30 W LED illuminator was placed in each Flat-PBR, installed 3 cm from the surface of the photobioreactor in the lighting mode - 12h light: 12h dark.

MFC electrical parameters were measured with a Keithley 2000 digital multimeter, using a precision potentiometer with a maximum value of – 11 kΩ for load resistance. The maximum power value, Pmax, was established by constructing polarisation curves. Current density and power were calculated based on the geometric area of the electrodes in the anode/cathode chambers and the voltage across the load resistors (R1/R2). The dissolved oxygen concentration was measured using an oxygen optical sensor - VernierR DO-BTA, and using the LabQuest^R interface. In addition, the illuminance of each of the options was measured, as well as the Photosynthetic Active Radiation (PAR) value, using sensors of the Vernier-PAR and Vernier-LS types.

The microbial fuel cell (MFC) used is of a classical H-shaped design, with equal volumes of the anode and cathode chambers of 0.5 dm³. Graphite rods with a diameter of 8 mm and a length of 100 mm were used for the electrodes. A cation exchange membrane (CEM), CMI-7000S (Membrane International Inc.) with a diameter of 30 mm was used as the separator. To study the influence of microalgae on the cathode potential of the MFC, after reaching the exponential (log) phase, the catholyte was moved from the buffer volume to the cathode zone of the fuel cell and after reaching constant values of the open circuit voltage (OCV- open circuit voltage), the power curves and polarisation curves were measured. An abiotic anode was used in the microbial fuel cell, with an anolyte composition typical of sulfide fuel cells (Beshkov et al., 2018).

Table 1. *Spectral characteristics of LED-based light sources used in the research*

The average wavelength, nm	469 nm	520 nm	604 nm	629 nm	659 nm	420-750 nm
Illumination (Lx)	5960	9210	9105	8340	5750	6070
PAR, $(mmol/m-2. s-2)$	1531	1272	503	1331	946	706

Fig.1. Laboratory installation to research the influence of wavelength on the growth and development of microalgae used in the cathode zone of the MFC.

For this purpose, under abiotic conditions, an HSconcentration of approximately 300 mg/l was provided in the aqueous solution of the anolyte by adding Na2S.9H2O and adjusting the pH to 8.0 using a 1N NaOH solution. In this way, a constant value of the anodic potential in the MFC was ensured, and the variation of the cathodic potential during the experiments was reported against a comparative calomel electrode.

Results and discussion

Investigation of the influence of the wavelength of the light source on the growth and development of microalgae in a flat-type photobioreactor.

In this research, microalgae were cultivated in a laboratory installation consisting of 6 flat-type photobioreactors, buffer vessels, recirculation pumps and air pumps (Fig. 1). All laboratory photobioreactors were constructed with equal volumes of 800 ml connected to buffer vessels with liquid phase volume of 400 ml. During cultivation, the entire liquid phase was recirculated with a peristaltic pump at a flow rate of 6 l/h. In each of the 6 buffer vessels, air was supplied with a flow rate of 1.5 l/h, through air pumps. For all variants, samples were taken at certain time intervals to determine the optical density of the liquid phase. In each Flat-PBR, a 30 W LED illuminator was installed, placed 3 cm from the surface of the photobioreactor in the lighting mode - 12h light: 12h dark. Based on that data, the dynamics of the optical density for the 6 investigated variants was determined (Fig. 2a).

The obtained results (Fig. 2a) at the end of the exponential phase (8th day) show the highest optical densities at red (559 nm), blue (469), green (520 nm), and white (control- LED-4300) colour of the light source and lower values for yellow (604nm) and orange (629nm).

Fig.2. Variation in optical density under the 6 light source variants investigated (a), and microbial cell number on the 8th day from the start of microalgae cultivation (b).

The obtained curves of the optical density at 650 nm, after comparison with the number of cells (measured by a counting camera), can be used as comparative growth curves for the specific case of microalgae of the Scenedesmus sp. (Fig. 2b). These results could be employed in the selection of the light source to be used in the photobioreactor to obtain an optimal amount of biomass of the cultivated microalgae.

Results similar to those obtained were reported by Keerthi et al., 2022 when cultivating a mixed culture of Chlorella sp. and Scenedesmus sp. and studying growth curves at 4 different light source wavelengths.

Investigation of the oxygen productivity of microalgae and its influence on the electrochemical parameters of the microbial fuel cell (MFC).

To establish the influence of the wavelength on the amount of oxygen produced in the cathode zone of the MFC, at the end of the exponential phase, the day-and-night dynamics of the dissolved oxygen concentration was tracked for each of the 6 investigated variants.

The obtained values for oxygen were compared with the change in the cathode potential of the MFC. According to the presented data from the growth curves, the 8th day from the beginning of the experiment was accepted as the moment of the cultivation of the microalgae, when the exponential (log) phase is reached.

Fig.3. Change in the concentration of dissolved oxygen and the cathodic potential, with a 24-hour lighting cycle - 12 (light): 12 hours (dark) for 469 nm wavelength.

The obtained results prove the role of microalgae as producers of oxygen in the cathode zone of the MFC. For example, at 469 nm, the oxygen concentration varies from 8.3 mg/l during the dark phase to 10.2 mg/l during the light phase (Fig.3). At the same time, the cathode potential of the microbial fuel cell changes in a similar way – in the range from 104 mV (dark phase) to 366 mV (light phase). The results are similar for the rest of the tested options shown in Table 2, where the maximum measured values of dissolved oxygen and cathode potential are indicated. The highest dissolved oxygen and cell potential values were achieved with blue (469 nm) and red (659 nm) light at 366 and 355 mV, respectively. The results are shown in the Table. 2. They also correspond with the obtained data from the growth curve (Fig. 2), when the oxygen productivity of the algae is highest with the greatest accumulation of biomass in the cathode zone.

Examining the polarisation curves and power curves of the MFC, for each of the 6 variants, confirms the influence of higher oxygen concentrations on the obtained higher values of the

power density 26.5 mW/m² and the density of current 78.3 mA/m² in the system (Fig. 4).

Table 2. *Average values of dissolved oxygen (DO) and cathodic potential in MFC, during the photosynthetic light cycle at 6 different light source wavelength variants*

The established maximum power density values are in the range of 469 nm (blue) and 659 nm (red), and the difference with the values at 604 nm (yellow) and 629 (orange) reaches 39.9 %. This proves that the influence of wavelength on the electrochemical parameters of MFCs is significant.

Fig.4. Power curves (a) and polarization curves (b) of the MFC measured for the 6 variants studied.

The results of these studies could serve for further optimisation of MFCs based on oxygenic microalgae in the biocathode area. Because the real practical application of microalgae is realised both in open and in closed cultivation systems, to achieve more favourable MFC power values, it is appropriate to use MFCs integrated with photobioreactors in

which appropriate combinations of light filters tailored to the specific type of microalgae are placed.

Conclusions

In the present research, the influence of the wavelength of the light source in 6 different variants on the growth curves of microalgae, dominated by Scenedesmus sp., was determined. The influence on the electrochemical parameters of the MFC was also established and tracked, reaching maximum values of power density - 26.5 mW/m² and current - 78.3 mA/m² at 659 nm wavelength. The results clearly show the influence of the spectral characteristics of the used light source on the oxygen productivity of the microalgae, and from there on the electrochemical parameters of the MFC.

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