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THANKS TO MICROALGAE FOR GREENER FUTURE: CURRENT STATE AND OUTLOOK FOR POTENTIAL USES OF ALGAE IN MICROBIAL FUEL CELLS FOR IMPROVED POWER PRODUCTION WITH SIMULTANEOUS NUTRIENT REMOVAL AND ALGAE BIOREFINERY

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Abstract: Although there is considerable potential and optimism for the future in energy harvesting from algae's photosynthesis, a complete knowledge of the mechanism of energy conversion is still lacking. It is crucial to develop new design methodologies to comprehend and investigate the bio-electrochemical mechanism of the underlying energy conversion since it involves living biological organisms like algae that are subjected to external stressors. With the method demonstrated, the more environmentally friendly photosynthetic power cell technology that will eventually replace photovoltaic devices will advance.

Keywords - Bioreactor, Microbial Fuel Cell (MFCs), Bioelectricity, Biorefinery, COD & Heavy metal removal

INTRODUCTION

One of the essential components for the advancement of electric vehicles and renewable energy is the production of high-performance electrical energy storage devices. Second batteries and electrochemical capacitors, often known as supercapacitors, are two widely used and efficient methods for storing electrochemical energy, with batteries exhibiting the trait of high energy and supercapacitors providing high power. (Simon and Gogotsi, 2008; Candelaria et al., 2012) If technologies could be created to transform harmful algal blooms into useful, high-value products (Li et al., 2014; Stevens and Dahn, 2000) or what we refer to as "trash to treasure" approaches, it would profoundly and broadly benefit our society and environment. The "treasure" items with high value should ideally be applied to energy storage applications and other uses that advance society's transition to a sustainable energy future. Green microalgae are currently the first sustainable energy source that may be exploited. Green microalgae are produced by increasing nutrients like nitrogen and phosphorus in aquatic ecosystems of rivers, oceans, and lakes. One advantage of employing green microalgae is

that when using it as an anode material for lithium ion batteries, harmful chemicals can be reduced. (Abdel-Raouf et al., 2012; Lam and Lee, 2012).

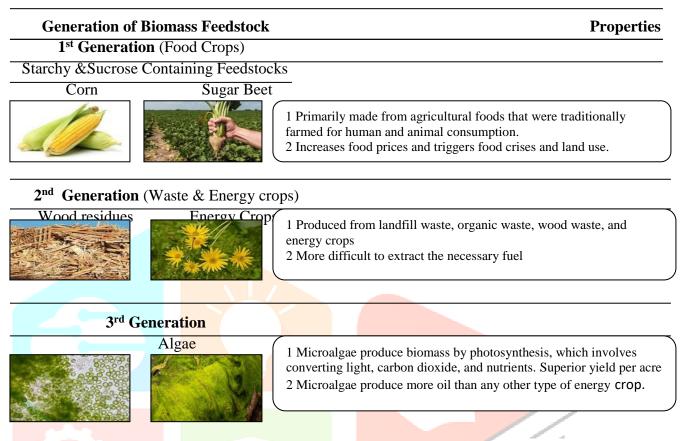


Table 1: Comparison between three generations of biofuel based feedstocks. (Elrayies, 2018)

BIOREACTOR

Microalgae must be grown in large quantities, hence the right culture system is needed. A Photobioreactor (PBR) is the name of the system that microalgae use to perform their biological reactions (Mata et al., 2010). The simplest and most typical method for growing algae in a laboratory setting is fermentation. It has never been established on larger scales because of its small vessel size. The most popular type of farming is done in open ponds (Wolkers et al., 2011). They are shallow swimming holes, just about 15 to 30 centimetres deep. Usually, paddle wheels or gravity are used to move water. Although they are less expensive to build and run, they aren't the most efficient approach. They require enormous tracts of land and are vulnerable to contaminates, the elements, evaporation, and inadequate light penetration. (Mata et al., 2010; Abdel-Raouf et al., 2012)

Genin asserted that the current designs of algal film PBRs are not currently practical for incorporation into structures, notwithstanding the biofilm PBR prototype (algae cloth) created by Bogias(Bogias,2014) Yoo et al. claim that biofilm PBRs might be flat, horizontal, or vertical tubular in shape. (Yoo et al., 2013)

CLOSED PBRs

To address issues with open ponds, many methods have been used to build closed bioreactor systems. Although many various methods have been tested, only a few number of techniques can be used on an industrial basis (Wencker, 2011). The distinctive traits of various microalgae species have an impact on closed PBR design as well. Because of this, numerous closed PBRs have been developed to accommodate various microalgal strains.

Temperature and sunlight also significantly affect PBR design (Sierra et al., 2018). Despite the fact that microalgae can be produced all year round and that they can grow at a variety of temperatures (Kunjapur and Eldridge, 2010; Öncel et al., 2016), the best growth depends on the kind of algae.

TUBULAR PBRs

In tubular systems, tubes are placed either vertically in numerous arrayed layers or horizontally in a single layer. One-layer tubes increase exposure to sunlight and, as a result, high light intensities that slow the growth of microalgae. In a closed system, the diameter of the tube is constrained (often 0.1 m) (Suali and Sarbatly, 2012; Xu et al., 2009) since an increase in diameter causes the surface-to-volume ratio to decrease. Through the use of airlift technology (Öncel et al., 2016; Xu et al., 2009), a centrifugal pump (Matthes et al., 2015), or quantum fracturing, the algae should be mixed and circulated through the tubes. In order to accommodate a thin layer of culture suspension, optimal light exposure, low pumping energy consumption, and contaminant purity, many tubular PBR designs have been created (Wencker, 2011).

FLAT PANEL PBRs

A flat, transparent tank made of glass, plexiglass, polycarbonate, or polyethylene film serves as the vessel for the flat-panel PBR system.(Qiu,2014; Singh and Sharma, 2012; Cheng et al.,2019) To ensure light penetration (Marsullo et al., 2015) in the medium, flat-panel PBRs shouldn't be thicker than 5-6 cm, according to Marsullo et al. Flat-panel PBRs have a higher surface-to-volume ratio (Suali and Sarbatly, 2012; Xu et al., 2009) than tubular bioreactors. Panels could be stacked in parallel or adjacent plates for outdoor cultivation. Therefore, optical fibres or LED lights could be employed for additional internal illumination (Suali and Sarbatly, 2012; Xu et al., 2009) to achieve an efficient use of light in the culture and to increase light penetration. Fresnel lenses may also be used to follow the sun's path and guide sunlight into shadowed locations (Machado et al., 2013). Because pressure rises with volume, flat panel PBRs can't withstand pressures that are quite high. (Cheng et al., 2019)

MECHANISM AND OPERATION OF ALGAE-BASED PHOTOSYNTHETIC OXYGENATION IN MICROBIAL FUEL CELL CATHODES

According to Eq. (1), autotrophic algae species use CO_2 as a carbon source and light to produce carbohydrates and oxygen. Some species of microalgae can use organic matter as a carbon source instead of CO_2 as mentioned in Eq. (2) since they are heterotrophs. Different algae species may combine autotrophic and heterotrophic modes of metabolism to produce cathodic and anodic reactions in microbial fuel cells for producing energy from sewage (Pandit et al., 2012; Zhou et al., 2012). In this, the power generation cycle is completed by a terminal electron acceptor (TEA), which accepts the electrons at the cathode (Noori et al., 2016; Zhang et al., 2011). Through intermediaries, an algal cell can directly take in electrons from the cathode. The mediator is reduced from a higher to a lower oxidation state using the electrons moving from anode to cathode, and the reduced mediator is subsequently incorporated into the algal cell wall. The bioconversion of CO_2 to glucose and oxygen consumes the mediated electrons in the metabolic pathway of the algal cell (Powell et al., 2009).

For instance, it was discovered that C. vulgaris, which was cultivated in cathode half-cells, was operating as TEA through facilitated electron transfer (Powell et al., 2009). Yeast fermentation unit with an anode half-cell and C. vulgaris cultivated in a cathode half-cell chamber were combined to create a complete MFC to generate energy.

$6CO_2 + 12H^+ + 12e^- \rightarrow C_6H_{12}O_6 \text{ (biomass)} + 3O_2$	(1)
$C_6H_{12}O_6 + 6H_2O \longrightarrow 6CO_2 + 24H^+ + 24e^-$	(2)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	(3)

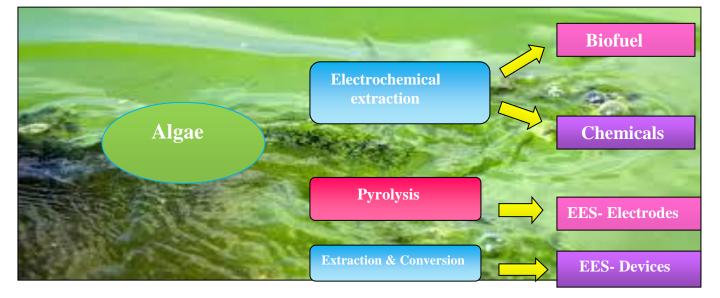


Figure 1 : Algae and electrochemistry: Using algae, you can make chemicals and biofuel.
Ees electrodes (anode and cathode) made from algae via electrochemical extraction; algae should be pyrolyzed and the remaining components of the ees device (binder, electrolyte, and membrane) from algae by removing/converting algae. (Parsimehr & Ehsani, 2020).

As an alternative, O₂ generated at the cathode during algae photosynthesis might potentially be employed as the only TEA (Pei et al., 2018). Mechanical aerators are used in traditional MFCs to provide oxygen to the cathode through passive or active aeration (Jadhav and Ghangrekar, 2009; Santoro et al., 2012). Under natural or artificial light, algae can be grown in glass bottles separate from MFCs (referred to as photo-bioreactors) (Wu et al., 2013), and the oxygen produced can be delivered to the cathode of MFCs with an air-breathing cathode (Gajda et al., 2015). To produce and use O₂ in-situ, algae can also be cultivated inside the cathode chamber itself (Angioni et al., 2018; Colombo et al., 2017). A glass bottle-based external PBR coupled to an air-cathode MFC was employed by Kakarla et al. (2015). A-MFCs have undergone several unique designs and configurations over time to maximise power production and reduce reactor fabrication costs.

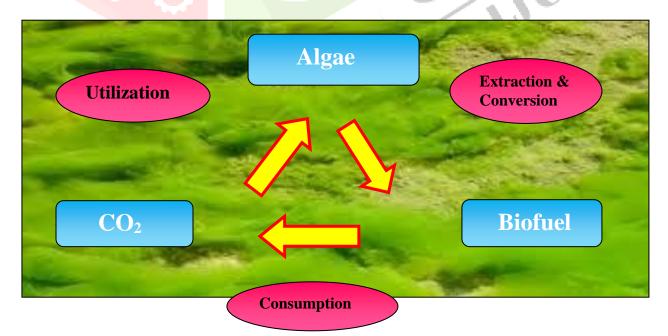


Figure 2: The carbon cycle of algae. (Parsimehr & Ehsani, 2020).

OPERATIONAL FACTORS IMPACTING THE PRODUCTION OF BIOELECTRICITY IN MICROBIAL FUEL CELLS

DO, Temperature, Ph, Light Intensity, and CO2

Algal development is significantly influenced by the light intensity around the cathode chamber, which in turn impacts oxygen generation and hence the overall performance of A-MFCs (Wu et al., 2014). The high dependence of lighting circumstances on the power output of A-MFCs was validated by a recent study on A-MFC done at several light/dark regimes, namely 18/6h, 12/12h, and 6/18h (Kakarla and Min, 2019). In a tubular PBR-MFC, Wu et al. (2013) found better power density under continuous illumination compared to intermittent illumination.

According to a related study, an A-MFC produced increased power density during higher light times, such as 24/0, as opposed to 16/8h and 12/12h (Bazdar et al., 2018). The algal photosynthesis actually took place in the cathode chamber, and the longer light time allowed for a higher power density in the A-MFC. A possible explanation is that during the day, algae could produce more oxygen through photosynthesis to support the oxidation-reduction reaction (ORR), whereas, at night, oxygen is used for respiration, causing DO depletion at the cathode chamber and lowering the overall performance of MFCs.

Numerous studies have indicated a proportional rise in DO concentration with an increase in light intensity (Gouveia et al., 2014). This is because the photosynthetic synthesis of oxygen at the cathode chamber is directly related to light intensity. A constraint in the kinetic and mass transfer of oxygen reduction on the cathode may be the reason why the ORR of the cathode did not rise proportionally with an increase in DO by increasing light intensity (Noori et al., 2019).

It was discovered that by choosing the proper light intensity range, the minimum level of DO can be preserved. However, it was shown that the ideal light intensity varied depending on the species of algae, for example, 5000 lx for C. vulgaris and 7000 lx for mixed culture algal strains (Kakarla and Min, 2019). Although changes in temperature can impact the activation or inactivation of important enzymes throughout the photosynthesis process, they do not significantly affect light-dependent activities like photosynthesis. Blue-green algae were shown to thrive best at temperatures between 20 and 30 °C (Konopka and Brock, 1978).

As a result, the region and geographic position of the experimental sites should be taken into consideration while choosing an algae species for a microbial fuel cells. Additionally, temperature is a crucial parameter for MFCs and plays a significant effect in the kinetics of reactions, the rate of mass transfer, and microbial activity. For improved biochemical conversion in MFCs, an ideal temperature of between 30 and 35 °C has been chosen in the majority of cases (Song et al., 2017; Wei et al., 2013; Zhang et al., 2014). Most algal strains grow exceptionally well in environments with pH values between 6.2 and 6.8 (Reed and Klugh, 1924).

There were a few pH-tolerant algal strains that could, however, only grow slowly at a pH of about 9.5 (Pendersen and Hensen, 2003). CO_2 can be fed to A-MFCs using both ex situ and in situ methods (Neethu et al., 2018). The performance of AMFCs is significantly impacted by the ideal load of CO_2 addition.

According to Gonzalez Del Campo et al. (2013), algae growth required only 0.5 hours of CO₂ bubbling in the A-MFC's cathode chamber.

In a microbial carbon capture cell (MCC), Pandit et al. (2012) evaluated the effects of various CO_2 concentrations in CO_2 -air mixtures (1-7% v/v), and discovered that 5% CO_2 -air mixture was the ideal concentration for maximal power generation.

WASTEWATER TREATMENT BY ALGAE GROWTH IN THE CATHODE OF MFCs

The use of algae for wastewater cleanup and the potential for bioenergy production from the biomass were both discussed by Oswald and Golueke in 1966. By combining waste/ wastewater resources with algal systems for a more comprehensive application, the nutritional and chemical needs of algae can present chances for enhanced wastewater treatment (Hwang et al., 2016). Algae that can perform photosynthetic functions can be used in MFCs to remediate wastewater in addition to producing bioelectricity (Berk and Canfield, 1964). When compared to traditional wastewater treatment methods, A-MFCs have a number of benefits, including the removal of both organic carbon and nutrients from wastewater, the sequestration and use of CO_2 , the generation of O_2 for suspended aerobic bacteria, the removal of heavy metals, and the generation of biomass for the production of bioenergy and biofuels (Nagendranatha Reddy et al., 2019; Bansal et al., 2018)

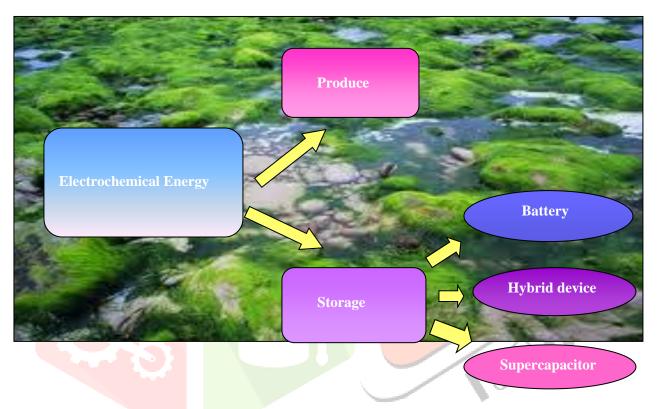


Figure 3: Produce and storage electrochemical energy from algae. (Parsimehr & Ehsani, 2020).

COD REMOVAL BY ALGAE GROWTH IN THE CATHODE OF MFCs

The most crucial element for the growth of algae is typically the availability of carbon sources. Algae are typically categorised as photoautotrophic, heterotrophic, or mixotrophic depending on the amount of carbon source that is available to them (Perez-Garcia and Bashan, 2015; Delrue et al., 2016). Since heterotrophic growth of algae is often faster than autotrophic growth, heterotrophic mode could greatly increase power output, handling simplicity, and biofuels productivity (Cui et al., 2014; Perez-Garcia and Bashan, 2015). When anodic effluent is delivered to the cathode chamber of the MFC, algae not only improve overall performance but also eliminate excess COD and nutrients. Over the past ten years, A-MFC efficiency for carbon removal and power generation has significantly increased (Ma et al., 2017).

The fact that organics and nutrients from the anode chamber can electromigrate to the cathode chamber during MFC operation suggests that the cathode chamber only removes a small amount of COD.

In conclusion, the heterotrophic or mixotrophic modes of operation used by algae in the cathode chamber allow them to efficiently utilise the carbon contaminant found in wastewater.

NUTRIENT AND OTHER POLLUTANTS REMOVAL BY A-MFC

For a wide range of chemicals collected from the home, industrial, and developing pollutant wastewater sectors, algae are known to be potential pollution scavengers. According to Luo et al. (2017), they have a reputation for surviving in wastewater that is harmful to other microbes. The mineralized forms of this pollutants viz., ammonium(NH4+), nitrate (NO3–),phosphate (PO43–), etc. will act as nutrient source for the growth of algae and the same has been depicted in many studies (Kakarla and Min, 2019; Uggetti and Puigagut, 2016; Nagendranatha Reddy et al., 2019; Nagendranatha Reddy and Venkata Mohan, 2016; Venkata Mohan et al., 2016; Delrue et al., 2016).

The quicker consumption of ammonium by algae or its oxidation via nitrification can be blamed for the increased elimination of ammonium. This is demonstrated by the operation's considerable rise in nitrate concentration, which can serve as a productive electron acceptor at the cathode (Fang et al., 2010). Phosphate removal at higher pH levels can take the form of phosphate precipitation. The removal efficiencies of nitrogen and phosphorus in a sediment-type photomicrobial fuel cell (PFC) were up to 87.6 and 69.8%, respectively, with an algal biomass yield of 0.56 kg/m3 (Zhang et al., 2011). Additionally, increased reductions of nitrogen (98%) and phosphate (82%) were attained after optimising the reactor architecture and enhancing the buffering capacity (Xiao et al., 2012).

The treatment of wastewater in dual chamber MFCs separated by porous membranes also significantly depends on the migration of ions from one chamber to another (Colombo et al., 2017). Colombo et al. (2017) documented the electromigration of nutrients from the anodic chamber to the cathodic chamber.

HEAVY METALS REMOVAL

Large concentrations of heavy metals are present in the wastewater produced by various sectors, such as metal cleaning, electroplating, etc., making their treatment challenging. According to studies by Li et al. (2013) and Hwang et al. (2016), algae have a great potential to bioremediate industrial wastewater and leachate containing heavy metals. Algal cell walls have a high binding affinity, which contributes to their efficient biosorption capacity (Hwang et al., 2016). Class III metallothioneins (MtIII) in algae mediate the mechanism of heavy metal accumulating and detoxification (Suresh Kumar et al., 2015). To decrease and precipitate in electrochemical cells, heavy metal-containing groups with high redox potentials can be used as electron acceptors (Mathuriya and Yakhmi, 2014). As a result, wastewater containing heavy metal ions can be removed and recovered using MFCs.

Algae consortium type and quantity, heavy metal type and concentration, temperature, pH, etc. are a few variables that affect the metal removal by algae in the cathode of MFC (Suresh Kumar et al., 2015; Hwang et al., 2016).

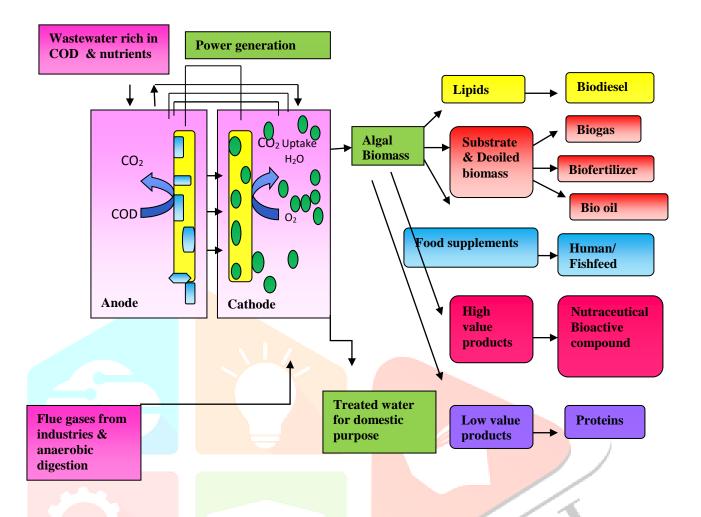


Figure 4: Proposed closed-loop algae MFC operation in continuous mode for power production with cuttingedge wastewater treatment and algae biorefinery. (Reddy et al., 2019)

USING A BIOREFINERY TECHNIQUE, ALGAL BIOMASS COLLECTED FROM MFC CATHODES IS CONVERTED INTO BIOFUEL AND BIOPRODUCTS.

Algae will absorb the nutrients required for its metabolism in the cathode chamber of MFC processes, which helps to improve the water quality (Li et al., 2013). By altering the algae cellular factories, genetic engineering and algal-based biofilms will improve the production of biomass and desirable chemicals, respectively. By doing so, it may be possible to generate more value-added goods and enhance biofuel technology (Bansal et al., 2018). The high calorific value of algal biomass makes it a viable alternative to coal and other substrates in biological processes (Hwang et al., 2016). Other research (Bazdar et al., 2018; Commault et al., 2017; Cui et al., 2014) have also documented the production of algal biomass in the cathode chambers of MFCs when operated with various wastewaters and operational conditions. According to Baicha et al. (2016), the cellular structure of algae has the capacity to synthesise macromolecules like lipids, biodiesel, and other active metabolites that can be employed as colourants, medications, cosmetics, and preservatives.

In order to grow C. vulgaris in the cathode chamber, which collects the CO_2 produced in the anode, Powell and Hill (2009) linked a yeast fermenter with a microalgae bioreactor. The cathode chamber's produced algal biomass might potentially be used as a substrate in the anode chamber to produce bioelectricity. According to Gouveia et al. (2014), C. vulgaris in the cathode chamber of a photosynthetic algal MFC (PAMFC) demonstrated the effects of nitrogen stress and light intensity on the production of the pigments lutein,

canthaxanthin, beta-carotene, and chlorophyll. Algal biomass can be utilised in a variety of ways to produce biofuels (biodiesel, substrate for the production of biohydrogen, biomethane, bioethanol, biomethanol, bio-oil, etc.), as well as value-added products like pigments, carotenoids, nutraceuticals, bioactive compounds, feed for aquaculture, and biofertilizers, among other things. It can also be used as fish and human food, a biofertilizer, a substrate for the production of biogas, and other items with commercial value. The finished treated effluent can be put back to use in home settings. As a result, the proposed biorefinery concept will function as a workable answer to the production of green energy and wastewater treatment.

LIMITATION

Despite the fact that A-MFCs have a lot of benefits, there are still a few obstacles that must be addressed before this innovative technology can be commercialised and used in field-scale applications. Techno-economic assessment is regarded as one of the fundamental instruments that may analyse the entire cost accounting and attain commercial viability during the commercialization or scaling up of A-MFC.

The waste management systems should make significant efforts to adopt low carbon technologies (De Bhownick et al., 2019). Commercial A-MFC installation must take into account capital, operating, and maintenance expenses (Bhola et al., 2014; Powell and Hill, 2009). The ideal setup and operational parameters should be assessed in order to maximise the overall economic and environmental effectiveness of A-MFC. The entire level of energy independence is increased through the incorporation of green energy generation, nutrient recovery, and biochemical production. Few nations provide low interest government loans for "green" initiatives to promote the development of sustainable technology (Powell and Hill, 2009). By connecting several processes into a biorefinery model, it is possible to minimise overall costs while also directing future research (Mondal et al., 2017).

If the cost-effectiveness and applicability of the distinctive CO_2 scrubbing plant with the humidity swing technology are established, they will, nevertheless, outweigh this problem. It is important to draw attention to other innovative CO_2 harvesting technologies, such as Carbon Engineering's Air Contactor (Holmes and Keith, 2012)

FUTURE PROSPECTS

- ✤ A-MFC offers numerous noteworthy benefits in the production of power and the treatment of wastewater, in addition to additional high-value bioproducts derived from the extraction of algae.
- In order for A-MFC to be competitive with other bioenergy technologies utilising organic wastes, power generation must be improved. In order to increase ORR, optimise operational conditions (HRT, substrate concentration, C/N ratio, photosynthesis conditions, etc.), and optimise reactor design (reactor configuration, membrane, optimal interspace of electrodes, etc.), modified cathode electrodes with electrochemical catalysts can be used in A-MFCs.
- Significant research is required to resolve this issue because the choice of algae strains (pure culture vs. mixed culture) for inoculation in the cathode is still unclear in terms of power production, wastewater treatment, and biomass (bioenergy) recovery. Microalgae species that have undergone genetic modification can be chosen for traits like high oxygen generation, improved nutrient removal, high biofuel outputs, etc.
- By closing the loop and adhering to the zero liquid discharge approach, innovative A-MFC configuration or integrative processes (proposed biorefinery concept of algal biomass generated in the cathode chamber of A-MFC) could be investigated for multipurpose use, including bioelectricity generation, wastewater remediation, and bioproducts production.

- Bioreactors can be used into architecture in other ways besides just the façades of buildings. For example, they can be used to create urban canopies and street art projects. These urban installations have a wide range of uses. They generate biofuel, let in light, give off shade, and make people aware of alternate energy.
- Essentially, the use of microalgal PBRs in architecture and the built environment can improve iconic values while addressing issues of national energy security, economic security, and climate change.
- ✤ As the only renewable energy source that can both trap CO₂ from the atmosphere and produce O₂, microalgae biomass, which is used to make bio-façades, promises to rid the air in our densely populated cities of hazardous carbon emissions. Microalgae are therefore thought of as a climate-neutral energy source.

CONCLUSION

An innovative dual-purpose device, the algae-microbial fuel cell treats wastewater and demonstrates the possibility of producing renewable energy in a sustainable manner.

The infrastructure of wastewater treatment systems currently offers a chance to assess large-scale algal-based biofilm technology operations that include waste remediation and biomass production. The improvement in nutrient recovery and the collection of the energy contained in the organic pollutants of wastewater could be used as a sustainable option to increase the energy recovery balance.

Therefore, enclosed biofilm MFCs and photo-bioreactors present an alternative to traditional tertiary treatment techniques for nutrient removal that may be more cost-effective

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