1
Introduction

Energy demands are on a continuous rise. Currently, non-renewable fossil fuels meet 90% of the world's energy requirements, and these are depleting fast. Also, the indiscriminate use of fossil fuels has led to an increase in air pollution. Scientists & Industries are exploring alternative energy options that are sustainable and renewable [Slate et al., 2019]. Biofuels hold particular promise as these can completely replace conventional fuels. Algae, in particular, are envisioned as a sustainable source of third-generation biofuels. Algae also produce several low volume high-value products, which enhances its prospects of use in a biorefinery [Li, S. et al., 2019]. Algae cultivation is the first step towards biofuel production. Algae growth requires light, water, inorganic carbon, and nutrients such as nitrates and phosphates. The oxygen produced during photosynthesis also become inhibitory and needs to be quenched during cultivation [Kazbar et al., 2019]. The cathodic cultivation of algae in a Microbial Fuel Cell (MFC) can help overcome some of the challenges mentioned above. For example, oxygen is quenched by oxygen reduction reaction at the cathode; inorganic carbon emanates from the anode. The separator may allow diffusion of nutrients and organic matter to support mixotrophic algae growth.

An MFC produces energy due to the exoelectrogenic activity of anaerobic microbes [Gao et al., 2020]. These microbes oxidize electron donor substrate and reduce anode giving electrical power [Chen et al., 2019]. The terminal electron acceptor captures the electrons at the cathode [Trapero et al., 2017]. The anode and cathode chambers have differences in redox potential, which is often maintained with the ion-exchange membrane's help. In Photosynthetic Microbial Fuel Cell (PMFC) or algae-based MFC, the cathode is assisted by algae, which carries out photosynthesis and liberates oxygen as a by-product, which in turn serves as terminal electron acceptor [Shukla and Kumar, 2018; Reddy et al., 2019]. MFC and algae cultivation complement each other in several ways. However, most of the promising MFC studies are limited to the lab scale. Several factors affect the scale-up and outdoor operation of algae assisted MFCs [Gajda et al., 2018].

The main factors which affect the scaled-up process include the high capital cost associated with the MFC reactor's fabrication & operation, high-priced cathode catalysts & proton exchange membrane, the requirement of continuous supply of electron donor substrate in anodic chamber, low power output & energy recovery in scaled-up reactors, etc. In this context, algae-assisted MFCs are not extensively researched as bioenergy technologies ad scale-up is not attempted in the literature. Therefore, the present study was designed to address all the above mentioned issues with the following points of novelty:-

1. The innovation of the work is the successful use of lipid extracted algae biomass (*Chlorella vulgaris*) as an electron donor substrate in algae-assisted MFC, first at the lab scale and then 10 L scale operated under outdoor conditions.
2. The study describes a closed loop process wherein algae biomass generation at the cathode chamber complements the lipid extracted algae biomass degradation at the anode.
3. The process can be described as a zero carbon and zero waste producing energy in the form of algal lipids and electricity.
4. The scaled-up (10 L) study reports for the first time an operation of an outdoor algae assisted MFC with an estimated system cost of $11.225 only.

5. A low-cost cathode catalyst suitable for algae-based microbial fuel cell (MFC) application was developed.

In order to accomplish these outcomes the present work was initiated with the following objectives:-

1. To develop a closed-loop self-sustainable MFCs wherein algae biomass generation at the cathode is complemented by algae biomass degradation at the anode.

2. To scale up the MFCs using low-cost materials and operation in outdoor conditions.

3. Identification of key exo-electrogenic bacteria which are growing on lipid extracted algal (LEA) biomass in the anodic chamber.

4. To develop a suitable electrode catalyst for algae-based cathodes.

1.2 BRIEF RESULTS, SCOPE AND FUTURE PROSPECTS OF THE WORK

The thesis is presented in six chapters. The second chapter provides a review of literature in area summarizing the significance of 3rd generation biofuels, integration of 3rd generation biofuels with MFCs, MFCs principle & applications, scaled-up MFC operation, and algae assisted MFCs related studies. The subsequent three chapters talk about the detailed experimental results which are outlined as follows:

Microbial fuel cell powered by lipid extracted algae: A promising system for algal lipids and power generation (Chapter 3: published as Khandelwal et al., 2020; Bioresource Technology, 247; 520-527)

In this study, a promising MFC system has been developed, wherein algae is cultivated in the cathode chamber, algae biomass is harvested and lipids are extracted. The lipid extracted algal (LEA) biomass was then used as an electron donor substrate. The performance of MFCs fed with LEA biomass was compared with that of fruit waste fed MFCs (FP-MFCs), wherein LEA-fed MFC was superior in all aspects. The power density of 2.7 W/m^3 was obtained by LEA-fed MFCs, which is 145% and 260% higher than FP MFC and control MFC, respectively. The volumetric algae productivity of 0.028 $kg/m^3/d$ in the cathode chamber was achieved. The system was able to generate 0.0136 kWh/kg COD/d of electric energy and 0.0782 $kWh/m^3/d$ of algal oil energy. The proposed system is a net energy producer that does not rely heavily on the external supply of electron donor substrates.

Performance evaluation of algae assisted microbial fuel cell under outdoor conditions (Chapter 4: published as Khandelwal et al., 2020; *Bioresource technology*, 310; 123418)

This study reports for the first time an operation of an outdoor algae assisted MFC. The MFC (10 L) comprised of low-cost materials like rock phosphate blended clayware & low-density polyethylene bags as anodic & cathodic chamber, respectively. Algae biomass after lipid extraction at 2 g/l served as electron donor at the anode. *Chlorella vulgaris* at cathode provided oxygen as an electron acceptor and served as a lipid source. The MFCs performed well in all aspects, namely energy recovery, algae productivity, and cost of operation. The 5% RP-MFCs gave 0.307 $kg/m^3/d$ algal productivity, 0.09 $kg/m^3/d$ lipid productivity, and 11.5318 kWh/m^3 of net energy recovery (NER). Rock phosphate served as a slow and constant source of phosphorus supporting algae growth. Proteobacteria (45.14%) were the dominant phyla, while *Alicyliphilus* (5.46%) and *Dechloromonas* (4.74%) were the dominant genera at the anode. The estimated cost of the system was $11.225 only.

Superiority of activated graphite/CuO composite electrode over Platinum based electrodes as cathode in algae assisted microbial fuel cell (To be submitted)

This study was done to develop a low-cost cathode catalyst suitable for algae-based MFC application. The nanoparticles (NPs) of CuO, MnO_2, and Fe_3O_4 were mixed with activated graphite and shaped into an electrode. The composite electrodes were compared with Pt coated C-cloth (an active oxygen reduction catalyst). The graphite/CuO composite outperformed other composite electrodes and Pt/C electrode in terms of power & current density, algal growth, and electrocatalytic activity. The graphite/CuO exhibited 6 W/m^3 of power density, 25 A/m^3 of current density, and 0.256 d^{-1} as a specific algal growth rate. The composite graphite/CuO electrode showed better catalytic activity towards oxygen reduction reaction (ORR) on the cathode.

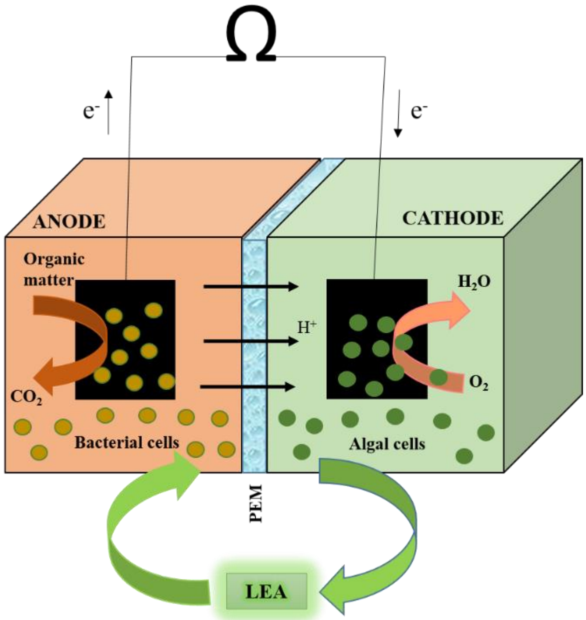

Figure 1.1: A schematic representation of the theme employed in this thesis work.

In short, this thesis work attempts to develop a low-cost algae-assisted MFC for algae cultivation and power generation. The closed-loop process was developed, scaled up, and studied for sustainability parameters. The promise associated with the process was demonstrated.

…