

The Contribution of Microalgae in Bio-refinery and Resource Recovery: A Sustainable Approach leading to Circular Bioeconomy

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Population growth supplemented by urbanization and industrial developments has led to elevate the global energy demands, building up risk for the finite and non-renewable petroleum reserves. Besides being at the verge of getting exhausted fossil fuels are major contributors of greenhouse gases to the environment. This led to the expedition for sustainable and renewable energy source and researchers found microalgae an over overwhelmingly rich source of renewable energy, which are termed as tiny biorefineries. Microalgae are the eukaryotic /prokaryotic organisms having the capabilities of fixing carbon (1 kg of algal biomass can fix about 1.5 kg of CO₂) photosynthetically (8.3 % photosynthetic efficiency). The diversified nature of different genera of microalgae allows them to be grown in varying cultivating conditions i.e., high ammonia acidic/basic pH, varied salinity, high/low temperatures. Microalgae are regarded as third generation feedstock in the production of algal biomass which is a source of biofuels and other value-added products. The cost effectiveness is the criterion where microalgae-based biofuels lose the ground to fossil fuels since the cost of cultivation and harvesting is high. But the cost issue can be suppressed if microalgae is cultivated coupled with wastewater resulting in the resource recovery and biomass production at the same time. This can be achieved by blending biorefinery with bioeconomy. Biorefinery paves the way to obtain biofuels and other green chemicals from microalgal biomass and circular bioeconomy directs the best optimum utilization of the obtained microalgal biomass for sustainable and environmentally friendly system. As it promotes the primary objectives of the circular bioeconomy (i.e., reduce and reuse). Valorization of a single product from microalgal biomass is not valued, as it restrains the economic viability, while multiple products from microalgal biomass which are commercially in demand and are environmentally sustainable can compensate the economy. Consolidating bioeconomy in microalgal biorefinery can improve cost-effectiveness and process efficiency, together with resource recovery. This mini review focusses on the primary components of the circular bioeconomy in context of the high pollutants/nutrient composition of different wastewaters. This review gives the overview for the circular bioeconomy concept in biorefinery approach to produce biofuels from microalgae and other useful products, simultaneously treating wastewaters.

1. Introduction

An overwhelming increase in the use of non-renewable resources to match the elevated energy demand has opened the gateway for their depletion. This led to the expedition for sustainable and renewable energy source and researchers found microalgae an over overwhelmingly rich source of renewable energy, which are termed as tiny biorefineries. Microalgae possess following advantages, which makes it a potential alternative for sustainable and renewable source of energy: High growth rate and independency of agricultural land; Works for the sequestration of CO₂ and can be cultivated with wastewater which reduces carbon and water footprint, minimizing the eco-footprint.; Capable of storing carbon in the form of lipids and carbohydrates to produce Biofuels (biodiesel, biomethane, bioethanol and biohydrogen) and other myriad products such as biopeptides, antioxidants, polysaccharides, biopolymers, and pigments (Banu et al., 2020);

and, as the microalgal biomass contains proteins, therefore it can be used to obtain human food and animal feed (Ahmad et al., 2021a).

The main disadvantages of producing biofuels and other products from microalgae is the high energy demand and cost of production. The processes of microalgal cultivation followed by the harvesting and drying are neither energy efficient nor economically viable. Cutting edge photobioreactor technology followed by the economic downstream processing are essential requisites to achieve economically viable and environmentally sustainable metabolites from microalgal biomass. Biogenic microalgae can become an alternative solution to petroleum biorefinery. The algal biorefinery concept will provide biofuel production, resource recovery and reduction in the overall cost of upstream (strain selection, light, nutrients, and aeration) and downstream processes. Recently circular bioeconomy is gaining popularity and interest of researchers to make algal based biorefinery as a state of art green technology. Bioeconomy can be defined as scientific utilization and production of natural biological resources and innovation oriented biological procedures and principles to sustainably provide essential utilities and benefits to all the economic cross sections. Circular bioeconomy can be defined as a sustainability concept to restrain or limit the parent resource utilization by increasing and boosting the resource, recycle and recovery. Circular bioeconomy can deliver as panacea to improve the condition of resource depletion and environmental pollution in an economically viable manner (Giampietro, 2019). Microalgal Bioeconomy concept involves the utilization of microalgal biomass as an essential component to produce bioenergy, biochemicals and other bioproducts through the biorefinery as shown in Figure 1. The compositional richness of various microalgal species can be understood by Table 1. To get efficient results microalgal wastewater treatment can be coupled with the production of biomass, biofuels, and other bioproducts as shown in Figure 2. To exemplify, the production of biodiesel from the microalgal lipids can reduce the CO₂ emissions by about 80 %. The biomass left after the lipid extraction can be used to produce biomethane, which can further be exploited to generate electricity. The electricity generated can be utilized to run the overall setup of biodiesel production and sometimes if it is in surplus amount, that can be traded to cover up the cost of producing biodiesel. Showing that by efficiently intruding the concept of circular bioeconomy, the biofuel production can be made economically sustainable (Dasan et al., 2019). The continuous evolution in the research based on microalgal technology have unlocked various sustainable applications in terms of wastewater bioremediation, resource/nutrients recovery, biofuel production and production of myriad products. Circular bioeconomy directs the best optimum utilization of the obtained microalgal biomass for sustainable and environmentally friendly system. As it promotes the primary objectives of the circular bioeconomy (i.e., reduce and reuse). This mini review focusses on the primary components of the circular bioeconomy in context of the high pollutants/nutrient composition of different wastewaters. This review gives the overview for the circular bioeconomy concept in biorefinery approach to produce biofuels from microalgae and other useful products, simultaneously treating wastewaters. This will contribute to both environmental and economic sustainability. The previous review papers summarized the aspects of bioremediation of wastewater and biorefinery approaches separately, this mini review will provide overview of both the aspects together as they are interrelated and of much practical significance.

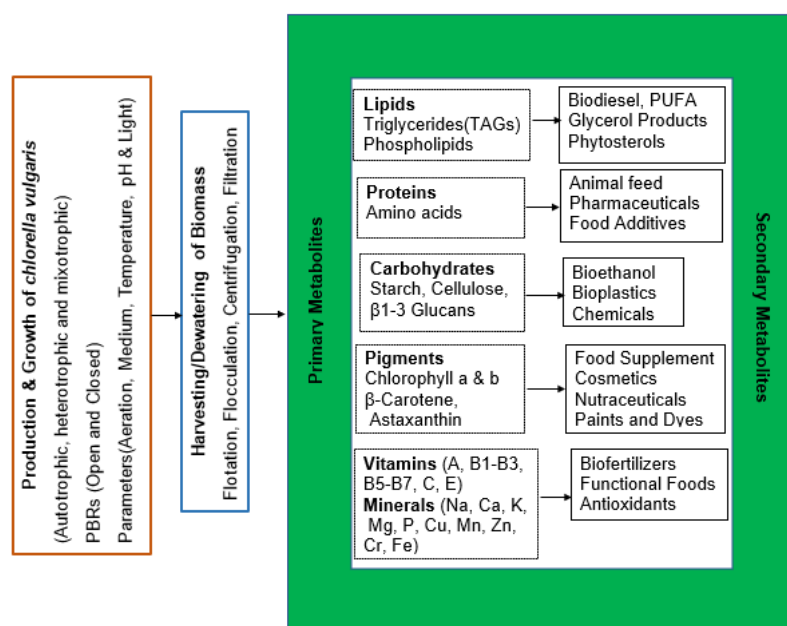


Figure 1: Cultivation to valorisation in Microalgal Biorefinery

Table 1: Compositional richness in Microalgal Biomass (Ubando et al., 2020)

Microalgae Species	Lipids* (%)	Carbohydrates* (%)	Proteins* (%)	Applications
<i>Chlorella vulgaris</i>	12.18	11.88	51.45	Food Supplement, Feed
<i>Scenedesmus obliquus</i>	30.85	35.05	19.52	Health foods, Pharmaceuticals
<i>Chlorella sorokiniana</i>	31.85	35.43	28.81	Nutraceutical compounds
<i>Ankistrodesmus falcatus</i>	35.9	33.88	30.59	Biofuels
<i>Dunaliella salina</i>	6	32	57	Health food, feeds
<i>Haematococcus pluvialis</i>	15	27	48	Pharmaceuticals
<i>Nannochloropsis oculata</i>	11	15	63	Food for juvenile marine fish & larval
<i>Spirulina plantesis</i>	9	14	63	Cosmetics

*%Dry weight of biomass

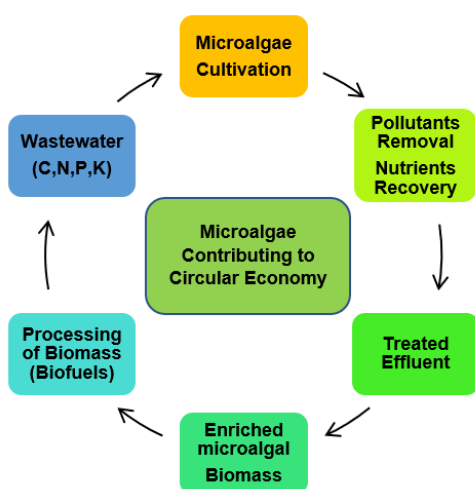


Figure 2: Coupling of wastewater treatment with microalgal cultivation-A circular Bioeconomy perspective

2. Microalgae: Biorefinery for high value products

Microalgae biorefineries are there to convert biomass into green chemicals, cosmetics, food, feed, fuel, and other value-added products. Microalgae have shown immense potential in the generation of energy from sustainable resources without making any compromise with the agricultural land, food security and water footprint. The commercial production of microalgae started in 1960s by Japan, exploiting *chlorella* for its various applications (Sathasivam et al., 2019). Some of the value-added products obtained from different types of microalgae are astaxanthin, carotenoids, docosahexaenoic acid (DHA), natural pigments and dyes, eicosapentaenoic acid (EPA), cancer prevention agent and polysaccharides. In the last two decades phycologists have worked a lot on some exclusive and remarkable microalgal species enlisted in Table 1 to achieve myriad products. The yearly global production of microalgae is about 7.5 Mt, while the global market for small scale algal growth is estimated to be about USD 6.5 billion. It encompasses aquaculture, DHA production and health segment (Bhattacharya and Goswami, 2020).

2.1 Lipids

Microalgae garners about 3-20 % of their dried biomass if cultivated under optimal conditions. Lipids obtained from microalgae can be classified into two categories: (i) Fatty acids which have 14-19 carbon atoms chain length and would be transformed to biodiesel; and (ii) Polyunsaturated fatty acids (PUFAs) having in excess 19 carbon atoms chain length and generally identified as microalgal PUFAs like DHA and EPA.

These ω -3 lipids because of their nutritional importance are of much interest for their application as health supplement (Lai, 2015). Making them economically viable, sustainable, and vegetarian alternative to the lipids extracted from fish oil.

2.2 Carbohydrates

Carbohydrates constitutes more than half of the dry weight of biomass. Mostly they contain starch and cellulose which later becomes the feedstock to produce bioethanol. Starch obtained from microalgae can be used as renewable source of raw material for fermentation instead of molasses, contributing in terms of sustainable agriculture and environment (Sathasivam et al., 2019). Starch consists of amylopectin & amylose and together with sugars they provide cell's energy storage. Cellulose is high resistance structural polysaccharide, which provides a protective fibrous barrier at the cell wall (Lordan et al., 2011). These highly bioactive sulphated polysaccharides are having the potential to produce pharmaceutical and nutritional products as well as beauty care items.

2.3 Proteins

Proteins are of prime importance in the chemical composition of microalgae. Their role contributes to the growth and repair of the cell while working as chemical carriers, cellular activity regulators, and defenders against the risk of foreign invasion. The nutritional quality aspect of proteins is evaluated, based on its amino acid profile. Most of the microalgal species have their amino acid profile matching with the WHO and FAO recommended and standardized profile of human nutrition (Safi et al., 2014). It is also expected that Microalgal proteins can become a future source of proteins for humans reducing the excessive reliance on meat and contributing towards sustainability (Lum et al., 2013).

2.4 Pigments

The elemental and common pigments contained in microalgae are chlorophyll, carotenoids, and phycobiliproteins. Chlorophylls are pigments which are necessary for the photosynthesis of microalgae. Astaxanthin: a prominent carotenoid possesses antioxidant properties, that can be utilized for immunity enhancing, anti-inflammatory, and anti-aging applications. These properties make it suitable to produce nutraceutical compounds and health supplements. Phycobiliproteins are significant in providing characteristic colors to pharmaceutical and food items. They display neuro-defensive properties, hostility towards hypersensitivity and cancer preventive properties making it germane for health segment applications (Tiwari et al., 2019).

2.5 Biofuels

Microalgae cells consists of lipids out of which 95 % is constituted by Triglycerides (TAG) and the remaining are mono and diglycerides with little amount of free fatty acids. Composition of fatty acids in microalgal lipids are dominated by oleic acid, stearic acid, and palmitic acid. The production of biodiesel from lipids is achieved via transesterification. Extracted oils and lipids are utilized in transesterification with 6:1 or 3:1 ratios of alcohol to oil in the presence of alkali or acid as catalysts. The final product obtained in transesterification is methyl ester (biodiesel) and the byproduct is glycerol. Microalgal species such as *Chlorella vulgaris* and *Chlorella protothecoides* are considered to have rich oil content in their cells, are rendered favorable for biodiesel production. Microalgal biodiesel has higher quantity of unsaturated fatty acids as compared to saturated fatty acids, fulfilling the initial requirement of fuel (Kumar and Thakur, 2018). The biodiesel obtained from microalgal biomass complies with US and European standards (ASTM 6751 and EN 14214). The biomass which is left after the lipid extraction can further be exploited for electricity production and biomethane production by employing anaerobic digestion (Saad et al., 2019). Therefore, the technology of microalgal biorefinery (cultivation to valorization) make the production of biodiesel economically viable, indeed boosting the circular bioeconomy. Achieving bioethanol from microalgal biomass is being promoted these days because of various advantages like high biomass productivity, considerable proportion of carbohydrate and starch, and efficient photosynthetic rate. Generally, bioethanol production is achieved from microalgal biomass by employing two processes-fermentation and gasification (Robak and Balcerek, 2018). Microalgal biomass can be employed to produce bioethanol by utilizing microbes like yeast, fungi, and bacteria. *Z. mobilis* and *S. cerevisiae* are the prominent microbes used in the production of bioethanol (Khan et al., 2018). Out of brown, red and green algae, brown algae are the most efficient in terms bioethanol production due to the simplicity of culture development and high carbohydrate proportion in the algal cell. Microalgal species which are among the most utilized for bioethanol production are *Chlorella*, *Scenedesmus*, *Dunaliella*, *Arthrospira*, *Spirulina*, and *Gracilaria* (Jung et al., 2013). Some of the companies having significant contribution in the global microalgal market in terms of biorefinery are: BioReal Inc.(Israel), Algenol and Mera Pharmaceuticals Inc.(USA) are producing pigments and biofuels from *Haematococcus pluvialis* and other microalgae species. Cyanotech corporation (USA) is the global leader in producing *Spirulina* as a component of food to about 30 countries. Blue BioTech Int. GmbH (Germany) and Euglena Co. Ltd. (Japan) are the companies involved in the bulk production of *Chlorella*, *Spirulina* and *Euglena gracilis* for protein rich food and feed (Chandra et al., 2019).

3. Microalgal wastewater treatment and resource recovery

Microalgae are having the capability of carbon sequestration photosynthetically, having high photosynthetic efficiency of 8.3 % as compared to 2.4 % of C3 plants. The metabolic diversity and flexibility of different species of microalgae enable them to be cultivated on varying conditions of temperature, pH, CO₂, and salinity. This feature makes them a potential bioremediation agent of wastewaters (Ahmad et al., 2021b). Details of some of the treatments coupled with biomass production are shown in Table 2.

- Microalgal wastewater treatment (MA-WWT) can be effectively coupled with the existing treatment facilities to achieve biofuel production, promoting circular bioeconomy approach.
- The energy required by MA-WWT is comparatively lower than the conventionally employed activated sludge process. Study in Spain revealed the treatment carried using conventional treatment methods led to the energy requirement of about 0.5 kwh/m³ of wastewater but it can be brought down to 0.2 kwh/m³ of wastewater by using MA-WWT (Acién Fernández et al., 2018). During MA-WWT, microalgae utilize light (sunlight/artificial) to assimilate nutrients in wastewater and photosynthetically converting carbon into biomass. Reducing the GHG emissions and contributing to environmental sustainability.
- Conventional wastewater treatment methods use dissimilatory mechanisms for removing the nutrients which dissipating C, N, P to the atmosphere. At the same time MA-WWT use assimilatory mechanisms for nutrients removal, and the nutrients are recovered in the microalgal biomass. Resource sustainability and nutrients recovery are an imperative component of microalgal circular bioeconomy (Nagarajan et al., 2020).

Table 2: Microalgal wastewater treatment coupled with biomass production

Microalgal Species	Type of Wastewater	Treatment Details	Biomass Production	Pollutants and Nutrient removal	Reference
<i>Chlorella vulgaris</i>	Anaerobically digested municipal wastewater	Glass photobioreactor, (1 L), 25 °C, 3000 lux, 12/12 h light/dark cycle, CO ₂ (15 L/h)	99.21 mg/l/d	TP: 99.2 % TN: 96.5 % COD: 83 % NH ³ -N: 97.8 %	(Xu et al., 2019)
<i>Chlamydomonas sp.</i>	Palm oil mill effluent (POME)	Erlenmeyer flasks 2 L, 25 °C, 20,000 lux, 16/8 h, aeration 2 % CO ₂	0.917 g/L	COD: 29.13 % TN: 72.97 % NH ³ -N: 100 % TP: 63.53 %	(Ding et al., 2016)
<i>Scenedesmus sp.</i>	Tannery wastewater	1 L flask, 25 °C, 182.5 μmol/m ² /s, 12/12 h, air supply at 1 L/min,	0.9 mg/L	COD: 80.33 % NH ⁴ -N: 85.63 % TP: 96.78 %	(da Fontoura et al., 2017)
<i>Chlorella pyrenoidosa</i>	Textile industry wastewater	1 L flask PBR, illumination at 440 W, 16/8 h, 25 °C	3.97 g/L	BOD: 24.05 % NO ³ -N: 74.43 % PO ⁴ -P: 28.01 % Cl: 61 %	(Brar et al., 2019)

4. Conclusion

The paper will provide an insight about the contribution of microalgal biorefinery in the circular bioeconomy leading to environmental sustainability. It also summarizes the advantages and contribution of microalgae-based wastewater treatment in pollutants removal and resource recovery, making it a potential tool in bioremediation of various wastewaters and simultaneous production of nutrient rich biomass, tremendously contributing to circular bioeconomy and sustainability. Continuous research is going on to achieve economically viable and sustainable primary and secondary metabolites using different microalgal species as discussed in the review.

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