



Review article

Recent advances in wastewater microalgae-based biofuels production: A state-of-the-art review

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ABSTRACT

Rapidly expanding industrialization and the depletion of non-renewable fossil fuels have necessitated the discovery of feasible renewable alternatives to meet the rising energy demand while reducing carbon dioxide (CO₂) emissions. The present global energy strategy is built on cost-effective and environmentally friendly alternatives; and production of microalgae has the ability to meet these requirements. Microalgae have been found as a promising and sustainable alternative for treating wastewater (WW) concurrently with biofuel production. One potential strategy, which uses microalgae for lowering the level of contamination in WW is called bioremediation. There are substantial gains to be made for both the economy and the environment through the integration of microalgae-based biofuel production with wastewater treatment (WWT). The use of microalgae that have a short life span, a high growth rate, and a high CO₂ usage efficiency is one of the promising approaches for producing biomass from WW nutrients that involves the utilization of renewable resources. Microalgae are one of the most promising biomass resources for use in thermochemical conversion processes for the production of liquid and gaseous biofuels due to their advantages over other biomass feedstocks, such as sustainability, renewability, and productivity. Currently, technology and cost are the primary obstacles limiting industrial applicability, which necessitates an optimum downstream process to minimize production costs. Consequently, the concurrent utilization of microalgae for WWT and biofuel production has made these challenges practical and economically viable. This review provides an overview of microalgae and their bioremediation and bioenergy production applications. It also provides insight for future research to investigate additional possible applications of microalgal biomass. These applications could include not only the bioremediation process, but also the generation of revenues from microalgae through the incorporation of clean and green technology, which would provide long-term sustainability and environmental benefits.

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1. Introduction

Energy has become a critical factor in social and economic development as a result of global population growth, urbanization, and industrialization (Ali and Sun, 2015; Ali et al., 2017; Murillo et al., 2018a; Ali and Sun, 2019). Furthermore, because human society has an insatiable thirst for fuel, the world relies on liquid fuels derived from petroleum (Ali et al., 2020a; Al-Tohamy et al., 2021; Murillo et al., 2019a,b). While energy is necessary for a country's mobility and development, it is also a major source of air pollution (Lu et al., 2022). Carbon monoxide (CO), nitrogen oxides (NO_x), and hydrocarbons are all known carcinogenic greenhouse gas (GHG) emissions (Pereira et al., 2019; Phusuwan et al., 2021). The massive consumption of fossil fuels poses significant risks to society's development, including climate change and fuel demand (Ali et al., 2022, 2021b, 2017b). These factors necessitate the pursuit of renewable transportation energy, with biofuel emerging as the best option. As a result, biofuel is a globally mandated option for combating threats such as scarcity of fossil fuels and fluctuating fuel prices (Ali et al., 2019b, 2021a,h). The microbe-derived biofuel of the third generation has the potential to generate more renewable energy without interference. Therefore, photosynthetic microbes such as microalgae could be used to produce economically and ecologically viable biofuels to replace fossil fuels (Sun et al., 2022). These photosynthetic microbes are advantageous in biofuel production due to their (i) ability to carry out oxygenic photosynthesis, (ii) production of valuable co-products, (iii) lack of food-based competition, (iv) higher growth density and productivity under minimal terrestrial usage, and (v) ability to be grown in a variety of water sources such as wastewater (WW) (Ahmad et al., 2022; Joshi and Mishra, 2022).

Biofuels derived from biomass have transformed the scientific community's interest into a valuable source of sustainable energy resources (Bani et al., 2021). In this context, agricultural, forest, and algal biomass were investigated for the production of biofuels including bio-oil, biodiesel, biogas, bioethanol, and biohydrogen (Mahmud et al., 2022; Haosagul et al., 2021; Park et al., 2022). Because they have many advantages and can grow in WW, algae are an easy-to-find and good bio-resource for producing biofuels (Krishania et al., 2020). They can grow in any type of water, absorb nutrients from the water and carbon dioxide (CO₂) from the air for photosynthesis and growth, use less water than land plants, and can grow all year around (Ananthi et al., 2021). Algae accumulate more lipids in their biomass and have a shorter life cycle when exposed to harsh conditions (Pugazhendhi et al.,

2020). Furthermore, cultivating and harvesting WW microalgae revealed a dramatic difference in biomass recovery technologies when compared to other techniques (Arun et al., 2021). The photosynthetic efficiency of microalgae is 50 times greater than that of terrestrial plants (Blaas and Kroeze, 2014). Numerous studies have been conducted to better understand the role of microalgae in wastewater treatment (WWT) and simultaneous biomass production (Arun et al., 2020a). Thus, it is reasonable and prudent to cultivate microalgae in wastewater for biofuels production.

Microalgae are photosynthetic organisms that comprise approximately 3000 aquatic species (Chong et al., 2021). The vast majority are autotrophic organisms. Microalgae can grow in a variety of water sources and convert sunlight and CO₂ from the atmosphere into biomass. Microalgal biomass has recently been recognized as a carbon-neutral fuel due to its diverse phytochemical biomass characteristics. For these reasons, the development of microalgal biorefineries has the potential to successfully reduce fossil fuel consumption and GHG emissions, thereby mitigating the related concerns of global warming and climate change. Furthermore, because it can be grown all year around with higher yields, microalgal biomass is an important feedstock for biofuel production (Avila et al., 2021). By 2030, the algal-based biofuel industry will account for approximately 75% of the biofuel market (Gambelli et al., 2017). Since microalgae can extract nutrients from water resources for biomass production, their biofuel production costs are lower (Maghjian et al., 2022). Compared to cultivation media, WW is the most accessible and inexpensive medium for algal growth. The cultivation of microalgal biomass on WW will reduce CO₂ emissions and the cost of microalgae-based biofuel production, making it more achievable and practical (Liu et al., 2020). Lipids are the key components of microalgae for biofuel production, and under optimal conditions, different microalgal strains can accumulate between 50 and 70% lipids per dry weight (Chisti, 2007). Biodiesel and methane gas produced from algal biomass grown in WW had an energy density of 37.7 and 50 MJ/kg, with a fuel density of 0.38 and 1.3 km/MJ for internal combustion vehicles (biodiesel) and battery electric vehicles (methane), respectively (Campbell et al., 2011). Furthermore, bio-oil derived from algal biomass had a calorific value of 42.07 MJ/kg (Arun et al., 2019).

For the production of biofuel from biomass, researchers commonly investigate gasification, fermentation, pyrolysis, transesterification, liquefaction, and anaerobic digestion (Mohanrasu et al., 2020). Microalgal biomass is converted into biofuel after oil extraction and transesterification (Inayat et al., 2019). In addition to biomass waste products, such as used cooking oils and animal

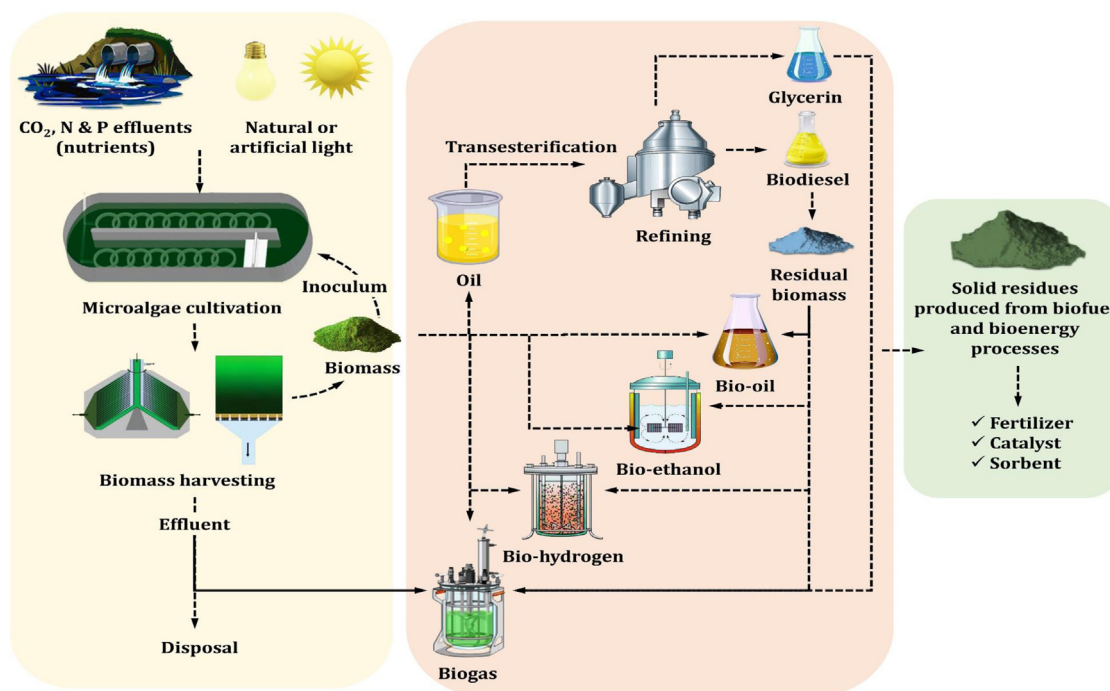


Fig. 1. Schematic diagram depicting the major aspects of using wastewater microalgae for biofuels production.

fats, biodiesel production is being investigated as a promising and alternative step toward biofuel production from hazardous materials (Fawaz and Salam, 2018). An extremely valuable bio-oil was produced by liquefying biomass using a hydrothermal process under supercritical conditions. If the biomass has a high percentage of moisture, the hydrothermal liquefaction (HTL) process was chosen rather than the pyrolysis method.

Significant efforts have recently been made toward the development of an ecologically friendly microalgae-specific technology. At current, the key constraints that limit industrial applicability are technology and cost; hence, it is necessary to have an optimal downstream process in order to decrease production costs. Research improvements in the technology of microalgae have opened the way to a wide variety of applications, including the production of biofuel, the treatment of WW, and bioremediation. The simultaneous use of microalgae for the WWT and biofuel production has made it possible to overcome these challenges on a practical and economic level. The full potential of microalgae to be used as a green technology process needs to be explored. The purpose of this review is to provide a comprehensive analysis of the biofuel production potential of wastewater microalgal biomass. It aims to explore the advancement of green technology concerning the simultaneous use of microalgae for WWT and biofuel production. In comparison to fossil fuels, the significance of biofuel from an energy and zero-emissions perspective is highlighted. This review will provide a platform for the cultivation of microalgal biomass from WW and the applicability of algae-based technologies for WWT and biofuels production. Fig. 1 depicts the outline of this review article and its focus routes.

2. Methodology of this review

In this review, a methodology was followed to investigate recent developments in the production of WW microalgae-based biofuels. This methodology is an example of a potential method for applying qualitative analysis to text data. The literature scanning allowed the authors to define the analytical structures used for data analysis. Elsevier, Taylor & Francis, Google Scholar, and

Springer were that served as the research sources for this review. In Web of Science database, the mode “Advanced search” was used in order to narrow the search to the specific criteria. Microalgae, wastewater treatment, Energy crisis and sustainability, and biofuels were at the top of the list of the most popular search terms simultaneously. While the use of this level of publisher database resulted in a confirmation of the aggregate searches conducted to collect all applicable material from the literature, this level of publisher database was still utilized. In order to ensure that the academic fields were represented by the most credible materials and publications with exceptional managerial impact, the analysis was limited to including only peer-reviewed journal articles, books, and conference proceedings written in English. Due to these significant achievements in the fields of efficacy, global sustainability, microalgae, biofuels production, wastewater microalgae, and biofuels derived from microalgae, the target date for this investigation was set between the years 2000 and 2022. Each stage of the evaluation phase is structured around the subsections processes, findings, and discussion, which enables the reader to acquire a more in-depth understanding of how the data are evaluated and to follow the implications of both the process and the data that are produced as a result of the evaluation. Among 357 papers only 192 of the available full-text post-review papers were used following the identification and screening processes. This was because duplicates and abstract reviews were disregarded. In order to make a final determination regarding microalgae, wastewater microalgae, biofuels production, and sustainability, eligibility was determined based on abstracts, and the complete content of outstanding papers was reviewed within the context of the research questions. Screening was performed on all the 192 papers to ensure that they adhered to the protocol for the systematic literature review that was being conducted for this study.

3. Global energy crisis and sustainability

Over the course of the last half-century, the expansion of the world's population has resulted in an ever-increasing demand for essential natural resources such as fuel and water.

Fossil fuels account for approximately 80% of the world's total demand for primary energy (Ahmad and Zhang, 2020; Isaac et al., 2022). Over the course of the last few decades, advances in technology have made it possible for industries that produce renewable energy sources to do so in a safe manner. The solar, hydroelectric, and wind energy industries are all now present on a global scale, and they are able to produce vast quantities of environmentally friendly electricity that is fit for consumption by humans (Menegazzo and Fonseca, 2019; Rahman and Wahid, 2021). However, because these forms of energy cannot be stored, they are unable to fulfill all of our energy requirements. This is especially true regarding the requirement for a portable energy source. This highlights the requirement for the production of a liquid fuel that can be transported and is compatible with the infrastructure that is already in place. As a result of the availability of biofuels as an alternative to fuels derived from fossil fuels, the renewable energy industry will be better able to contribute to the well-being of the economy and the environment (Saba and Ngepah, 2022; Li et al., 2022b).

The establishment of a fuel industry that is open to competition will result in increased fuel security for the government and the economy. The newfound prominence of Brazil as a leading global economy can be seen as a case study illustrating the benefits of being largely energy-independent from fossil fuels, an effort that was prompted by the worldwide energy crisis that occurred in the 1970s (Chia et al., 2018). In addition to their positive effects on the economy, biofuels have a positive impact on the environment because they break the carbon loop, do not contribute to carbon emissions, and present an opportunity to further decarbonize our society by putting the Paris agreement into practice on a global scale (Santos, 2020). The Paris Agreement's goals for clean energy included lowering annual emissions of greenhouse gases in order to "keep the average global temperature well below 2 °C above pre-industrial levels" (Sovacool et al., 2021). In order to accomplish these goals, government mandates are currently being put into place; for instance, India planned to implement a regulation requiring a mixture of 20% biofuel by the year 2020 (Mahmud et al., 2022).

The global consumer demand for readily available biofuels would rise as a result of increased stability, which would also make it possible for biofuels to be traded as commodities. Because of this, the viability of any process for the production of biofuel is severely undermined by the social and environmental consequences (Edwards et al., 2021). On the other hand, increased regulatory compliance can be attributed to worries about declining fossil fuel supplies. The trend toward designing environmentally friendly and sustainable processes as a direct result of manufacturers is placing a higher priority on creating products with a smaller environmental footprint. Market leaders have started to come to the realization that a shift toward sustainable planning is not only necessary for their companies' long-term growth and profitability, but it can also reduce the negative impact that industrial production has on the surrounding environment (Dwivedi et al., 2022). The idea of sustainable development has many facets; it covers the entirety of human endeavor, addressing and, as a result, being profoundly interdisciplinary in nature, as well as issues that are cultural, social, political, and economic (Xu and Chen, 2020). When it comes to the development of new chemical processes, one of the most significant challenges faced by the chemical industry is integrating environmental and sustainability goals with conventional design priorities. The chemical industry faces a one-of-a-kind challenge in the form of the urgent need to speed up the production of biofuels, which offer the possibility of being more stable and safer than traditional fuels. It is necessary to take into consideration simultaneously environmental and green externalities that go beyond the standard process architecture (Cai et al., 2019).

4. Microalgae cultivation systems

Microalgae are the plant-like organisms that grow at the quickest rate on the planet (Yap et al., 2021). Microalgae are able to survive in a wide range of pH levels and temperatures because they have adapted to live in a variety of different ecological habitats, the most common of which are brackish water, seawater, and fresh water (Mastropetros et al., 2022). Due to these factors, microalgae make up the greatest proportion of all living things on the planet (John et al., 2011). Fig. 2 depicts the main constituents and components of microalgae (Bature et al., 2022; Mulgund, 2022). There is virtually no cellulose present in microalgae, but they can contain up to half their weight in protein (Chandrasekhar et al., 2021). Polar and neutral lipids make up the vast majority of the lipids. *Nannochloropsis*, for example, was found to contain 25% polar lipids and 15% neutral lipids, while another species of *Chlorella*, *Chlorella vulgaris*, was found to contain 0.7% polar lipids and 57.2% neutral lipids (Yao et al., 2015). Conventional methods of cultivating microalgae include growing the organisms in either open raceway ponds or closed photobioreactors. This section provides an overview of the production designs for microalgae as well as the cultivation processes involved.

4.1. Raceway ponds

When it comes to the cultivation of microalgae, open raceway pond systems are superior to closed photobioreactors in terms of capital efficiency due to the lower initial investment costs associated with the former (Kannan and Magar, 2022). Open raceway pond systems are also superior in terms of their ability to remove nutrients from municipal WW (Pawar, 2016). The most common type of artificial ponds are those that contain raceway systems. In open raceway ponds, the paddle wheels that are used to maintain the circulation of algae broth and nutrients are typically constructed into the ponds (Fig. 3A). It is recommended that open raceway ponds have a maximum depth of no more than 30 centimeters, as this will allow adequate sunlight to penetrate the water (Abreu et al., 2012). One of the open raceway pond system's drawbacks is that it is easily contaminated. Table 1 represents the various strategies that can be utilized to keep predatory contamination under control in microalgae cultivation systems (Kim et al., 2017a; Rego et al., 2015; Park et al., 2016; Zhang et al., 2021; Huang et al., 2014; Zhang et al., 2020). When compared to a closed photobioreactor, an open raceway system is susceptible to excessive water loss due to evaporation, which lowers the efficiency with which microalgae utilize CO₂. The amount of biomass produced by microalgae can be negatively impacted when open raceway ponds are contaminated with other organisms. Certain configurations of raceway ponds incorporate greenhouses as a means of mitigating the effects of water loss, pollution, and rainfall (Chisti, 2007).

According to a concern, if future efforts are made to produce biofuels that are cost-competitive with conventional fossil fuels, this may result in pasturelands being converted into land for the cultivation of algae and other terrestrial feedstocks that are dedicated to the production of biofuels. This concern can be attributed in large part to the requirement of a large land area for the cultivation of microalgae on an industrial scale in a raceway pond in order to produce biofuel. Forty percent of pasturelands have the potential to be converted into feedstock supply systems that utilize either algae (1.0×10^6 ha) or terrestrial organisms (1.7×10^6 ha) (Langholtz et al., 2016). However, it was found that there is no cause for concern regarding the level of competition that exists between algal and terrestrial biomass. Instead, from the point of view of policy, it presents an opportunity for synergy regarding the production of bioenergy. It is possible that the synergy will simultaneously develop both industries in order to increase domestic production of renewable energy.

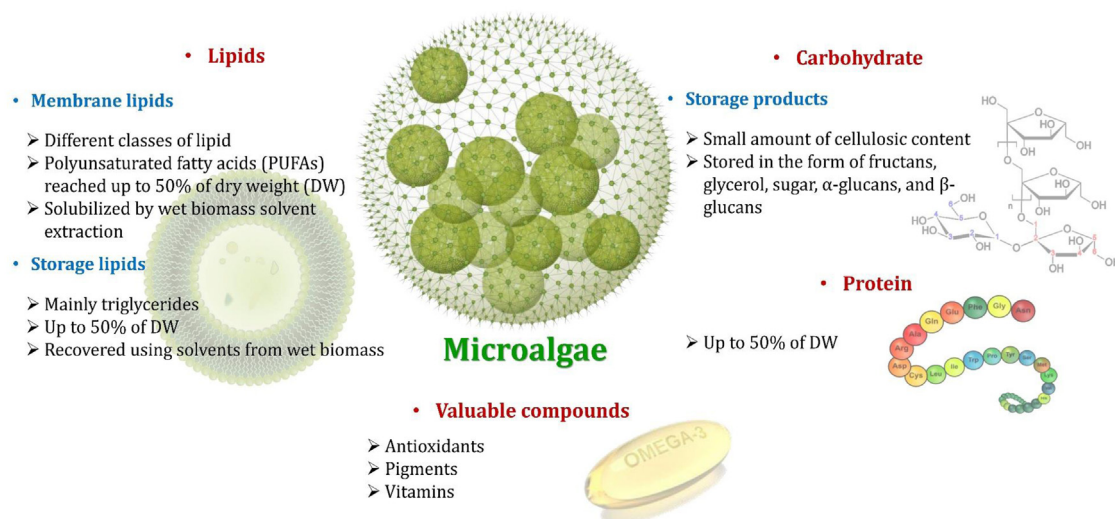


Fig. 2. Main constituents and components of microalgae.

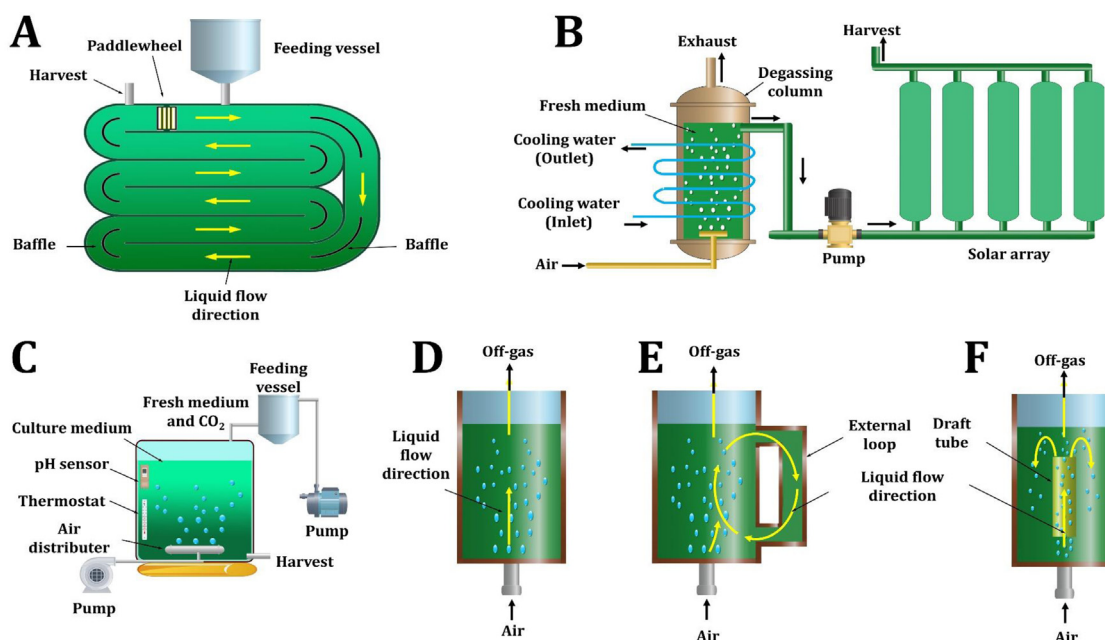


Fig. 3. Microalgae cultivation systems. Raceway pond (A), bubble column (B), flat plate (C), tubular (D), and airlift photobioreactor with external (E) and internal (F) draft tube.

Table 1
Techniques for preventing predatory contamination in microalgae cultivation systems.

Technique	Microalgae	Predatory contaminant	Cultivation system	Reference
Physical (hydrodynamic cavitation)	<i>Nannochloropsis salina</i>	<i>Brachionus rotundiformis</i>	Flat panel photobioreactor (10 L) for 7 days	Kim et al. (2017a)
Physical (pulsed electric fields)	<i>Chorella</i> sp.	Fungi, rotifers, and bacteria	Tubular photobioreactor	Rego et al. (2015)
Chemical (sodium hypochlorite bleach)	<i>Chlorella kessleri</i>	<i>Brachionus calyciflorus</i>	Conical flasks (1 L)	Park et al. (2016)
Chemical (dodecylbenzene sulfonate)	<i>Chlorella pyrenoidosa</i>	<i>Brachionus calyciflorus</i>	Raceway pond (1000 L)	Zhang et al. (2021)
Biological (toosendanin and celangulin)	<i>Isochrysis</i> , <i>Nannochloropsis</i>	<i>Brachionus plicatilis</i>	Conical flasks with aeration tubes (100 mL)	Huang et al. (2014)
Biological (toosendanin and celangulin)	<i>Nannochloropsis oculata</i>	<i>Brachionus plicatilis</i>	Continuous culture in laboratory flasks	Zhang et al. (2020)

4.2. Photobioreactors

Photobioreactors are superior to open raceway ponds in terms of the amount of biomass they produce because they are not

dependent on the weather and are less likely to be contaminated by other organisms that are predatory (Singh and Sharma, 2012). Table 1 presents the various strategies that can be utilized to prevent predatory contamination in photobioreactors. Enclosed photobioreactors, in contrast to open raceway ponds,

allow for a greater degree of control over the various aspects of the culture, and consequently, they are capable of producing more biomass (Chisti, 2007). In addition, photobioreactors require a smaller amount of land and emit a lower amount of CO₂ and water into the atmosphere (Kumar et al., 2011; Rosli et al., 2020). As is the case with the cultivation of microalgae on a commercial scale for the treatment of WW, photobioreactors do not perform well when used on a large scale (Sirohi et al., 2022). To be more specific, it is no longer possible to let light into the photobioreactor in an efficient and even manner when the volume of the operational unit is between 50 and 100 L or higher (Chen, 1996). The fact that photobioreactors are more expensive than raceway ponds is one of the most significant factors preventing widespread adoption of this technology (Rosli et al., 2020). The most common configurations for photobioreactors are the bubble column (Fig. 3B), flat plate (Fig. 3C), and tubular (Fig. 3D).

5. Advancement in microalgae cultivation systems

The cultivation of algae requires a specific kind of bioreactor, which is an essential component. The species being cultured and the reason for doing so both have an impact on the layout of the bioreactors. Numerous technologies, such as open pond systems (Paul et al., 2021) and photobioreactors, also known as closed systems (Sirohi et al., 2022), are utilized in the production of microalgae biomass, which is then put to use in the treatment of WW and the industrial production of biofuel. The open culture system is a relatively simple method for the cultivation of microalgae because it calls for minimal operation, low energy costs, and minimal maintenance (Paul et al., 2021). The inability to control water temperature and lighting, as well as inefficient CO₂ utilization, which leads to low productivity and biomass concentration, are the challenges that are associated with open pond systems (Vadiveloo et al., 2022). Open ponds are also susceptible to the effects of weather conditions (Harmon et al., 2021). Concerning the raceway, this method is uncomplicated and does not cost all that much money, but it has a number of drawbacks, including the fact that it needs large tracts of land, it has a problem with contamination, it has a high evaporation rate, and it has a low productivity rate (Baldev et al., 2022). It was discovered that the operation of open systems such as circular and raceway ponds is responsible for approximately ninety percent of the annual production of microalgae. These are the methodologies that are utilized in the industrial sector most frequently. The vast majority of microalgae, however, are unable to endure extended periods of time in open pond conditions due to the fact that they are prone to contamination by microorganisms that grow rapidly (Assunção and Malcata, 2020). As a result, closed systems based on photobioreactors have been developed in order to satisfy the growing demand. The high cost of constructing a large-scale closed photobioreactor system is one of the drawbacks of using such a system (Sirohi et al., 2022). In spite of this drawback, closed systems have the ability to overcome the major challenges that open systems face. These challenges include a poor mass transfer of CO₂, an inability to control culture conditions, a high possibility for contamination, and the requirement for a large space for cultivation. Closed systems also have the ability to meet the space requirements of open systems (Hosseini et al., 2018).

In recent years, a great number of improvements have been made to the photobioreactors in terms of light transfer, hydrodynamics, the efficiency of photosynthesis, and the rate at which algae grows (Ahmad et al., 2022; Dange et al., 2022). When it comes to increasing the amount of mass transfer in a photobioreactor system, mixing is the most important parameter. Photobioreactor systems are designed to transport microalgae cells in a cyclical manner from dimly lit regions to bright regions

surrounding the photobioreactor walls. Thus, the microalgae cell is able to receive a balanced amount of light, which results in an increase in the performance and productivity of the photobioreactor (Laifa et al., 2021; Karemore et al., 2015). Pumping, airlift, and mechanical stirring are the three methods that are typically used in photobioreactor systems as part of the mixing technique for the purpose of enhancing CO₂ transfer (Fig. 3E&F). Pumps or air spargers are typically utilized as aeration systems in automated vertical photobioreactor columns. Flat plates are applied to the walls of these columns in order to enhance upward mass transfer. This type of agitation system makes use of a high amount of kinetic and mechanical energy, as opposed to mechanical agitation systems that require paddles or impellers. In this context, a development would be the combination of mechanical and non-mechanical approaches to problem solving. In reactors, mixing can be significantly improved through the utilization of baffles or static mixers. The use of static mixers guarantees a good circulation flow direction, and as a result, microalgae cells will reap the benefits of normal light flashing effects (Yang et al., 2016). Moreover, there has been discussion regarding the creation of photobioreactor systems (Assunção and Malcata, 2020). In addition to these advancements, the application of nanotechnology makes a significant contribution to the cultivation of microalgae (Nguyen et al., 2019; Lau et al., 2022; Safarik et al., 2016).

6. Application of microalgae in wastewater treatment: Bioremediation

The term “wastewater; WW” refers to water that has been used for domestic purposes as well as water that has been used in industrial settings and is one of the primary streams of human waste. The treatment of wastewater (WWT) has always been a topic of concern for the government due to the harmful effects of WW's direct emission, which harms aquatic life, acidifies or alkalizes the soil near water sources, and even endangers human health (Ding et al., 2020; Zheng et al., 2020). There are various types of WWT, including physical, chemical, and biological (Li et al., 2022c; Jin et al., 2021; Shen et al., 2021). In recent years, scientists have increasingly advocated for and recommended biological treatment of WW over chemical WWT. Despite the fact that chemical WWT is the quickest method, the artificial chemical substances have negative impacts on the environment and living organisms (Wu et al., 2021; Al-Tohamy et al., 2022). In addition, biological treatment of WW is the method that has the least negative impact on the surrounding ecosystem (Al-Tohamy et al., 2022; Li et al., 2021; Chen et al., 2022). The process of using microorganisms to break down large particles or remove pollutants from water is known as biodegradation (Darwesh et al., 2020; Al-Tohamy et al., 2020a,b). This method has been put into practice for several decades. The most common form of biodegradation is called aerobic biodegradation, and it is characterized by the need for oxygen by the degrading organism (Ali et al., 2021f,d,c). The removal of pollutants such as nitrates (NO₃⁻), phosphorous (P), and sulfates (SO₄⁻²) using technology that is based on biological processes has involved the use of a wide variety of microorganisms (Abascal et al., 2022; Sharma and Malaviya, 2022). In the field of WWT, microalgae are becoming an increasingly popular option. Microalgae were found to be a promising option in municipal WW bioremediation, pharmaceutical waste streams, and waste streams from personal care products (Rempel et al., 2022; Sousa et al., 2022).

An emerging form of biotechnology that is beneficial for the environment is a process that treats WW using microalgae. The WW that is produced from agricultural practices and food processing typically contains a significant amount of nutrients, including organic carbon, phosphorus, nitrogen, and potassium. As

it contains an adequate amount of the nutrients necessary for the plant's growth, the nutrient-rich WW can be utilized as a source of irrigation for microalgae plants (Goswami et al., 2022). The term "fertigation" refers to this type of watering method (Hu and Chen, 2021). This will ensure that the resources are used in an appropriate manner, that the land is not contaminated or flooded, and that natural water is protected from turbidity, pesticides, salinity, and other hazardous pollutants of WW. Recent research has resulted in the development of an integrated green technology for the production of microalgal biomass through the biofixation of CO₂ using industrial WW and flue gas (Yadav et al., 2019). In this study, *Chlorella* and *Chlorococcum* were used to operate using an integrated approach. The growth of the microalgae improved, the rate of CO₂ fixation increased, and organic nutrients could be removed from WW (Yadav et al., 2019). Microalgae that were cultivated in industrial WW showed a high level of efficiency in the removal of P, in addition to the capture of CO₂ (Maurya et al., 2022). In addition, microalgae use both inorganic and organic nitrogen compounds, which results in a reduction in the amount of nitrous oxide (N₂O) that is emitted from WWT plants (Sutherland and Bramucci, 2022). In this regard, it has been found that WWT with microalgae resulted in emission factors that were 1000 times lower than the N₂O emission factor that is typically observed in conventional WWT plants. This was found in the context of the fact that conventional WWT plants emit between 5 and 6 times 10³ gN-N₂O per gram of nitrogen input (Alcántara et al., 2015). *Desmodesmus* spp. and *Scenedesmus obliquus* are able to treat WW and leachate because, in addition to being able to tolerate ammonia concentrations greater than 167 mg/L, they are also able to remove nitrogen and P through abiotic and biotic mechanisms. This allows them to treat both WW and leachate (Hernández-García et al., 2019).

Microalgae have also been utilized in the treatment of WW from dairy production (Kumar et al., 2019). Both the biological oxygen demand (BOD) and chemical oxygen demand (COD) levels in dairy WW are significantly higher than normal. The WW from dairy industry contains a variety of inorganic nutrients, such as nitrogen and phosphates. In addition, the WW is difficult to treat because it contains high concentrations of fats, oils, and dissolved particles (Lutzu et al., 2021; Khan et al., 2022). New technologies for treating dairy WW are currently being developed with the intention of overcoming this challenge (Mehrotra et al., 2021; Choudhury et al., 2022; de Mendonça et al., 2022). The advanced pond system, also known as the high rate pond, is currently one of the most widely used technologies. It successfully treated and improved the quality of the water (Leong et al., 2021; Craggs et al., 2012). It has been reported that marine water and freshwater microalgae were used for the treatment of dairy WW (Daneshvar et al., 2018). This demonstrates the versatility of microalgae for the treatment of WW, the removal of tetracycline, which is a contaminant in water, and the enhancement of lipid production.

Combining biological processes with adsorbents can improve the operational stability of WWT while also increasing the removal efficiency of pollutants (Anderson et al., 2022). It was demonstrated that the addition of zeolite and granular-activated carbon to the microalgal-bacterial system resulted in an increase in the amount of pollutants that were eliminated during the HTLWWT (Han et al., 2021). When biological processes are performed with an adsorbent present, it has been demonstrated that the adsorbent is capable of capturing pollutants even when the organic load is high. The adsorbent is able to release nutrients to the medium and ensure microbial growth even in an environment in which nutrients have been removed to the point where microorganisms are able to survive, as opposed to an environment in which there are not enough nutrients (Ibrahim et al., 2021; Baig et al., 2021). Scientists have been encouraged to use microalgae as biosorbent due to their resistance and flexibility to polluted water.

6.1. Mechanism of wastewater microalgae-based bioremediation

The use of microalgae in bioremediation is a method that is both profitable and efficient (Rosli et al., 2020; Carraro et al., 2022). Mixotrophic microalgae utilize both organic and inorganic nutrients for growth, which results in a significant reduction of these substances in the WW when they are used in WWT. This makes the application of mixotrophic microalgae for WWT an effective technique (Almomani and Omar, 2022; Koul et al., 2022). The production of oxygen, which is essential for heterotrophic bacteria to break down carbonaceous materials, is the primary benefit that comes from incorporating photoautotrophic microalgae into WWT systems (Perera et al., 2022). Microalgal cultivations that are phototrophic or mixotrophic are both capable of performing CO₂ biofixation in an effective manner (Almomani et al., 2019). It takes 8.4 to 2000 m³ of water, 45 kg of nitrogen, 4 kg of P, and 1.8 tons of CO₂ to produce one ton of algal biomass (Daneshvar et al., 2021; Mantzourou and Ververidis, 2019). Additionally, producing one ton of algal biomass requires a biomass concentration of between 0.5 and 120 g/L in suspension and non-suspension culture (Lu et al., 2021b). Because of its high production volume as well as its abundance of nitrogen, P, and organic matter, WW is, fortunately, a potentially useful source of nutrients for the growth of microalgae (Ravikumar et al., 2021).

Fig. 4 depicts the overall mechanism of WW microalgae-based bioremediation. The growth of microalgae in WW is at its core a symbiotic interaction with bacteria for the purpose of exchanging oxygen and CO₂ and making use of organic and inorganic nutrients. In this interaction, bacteria oxidize organic materials to inorganic forms (e.g. NO₃⁻, NO₂⁻, NH₄⁺, P, and CO₂), which are then consumed by microalgae in the presence of light for phototrophic production of biomass and oxygen (Khoo et al., 2021). Heterotrophic bacteria in WW oxidize the complex organic matter by using the oxygen that is produced by microalgae as a fuel source (Almomani and Omar, 2022). A number of different microalgae are able to grow in a mixotrophic manner when exposed to photon irradiation (Gao et al., 2021). This means that they take in both organic and inorganic sources of carbon. A relatively small number of microalgae are also capable of utilizing organic carbon in the dark in order to build their biomass and produce CO₂ in the same manner as bacteria (heterotrophic) (Jareonsin and Pumas, 2021). When microalgae are cultured in WW that contains a high concentration of organic carbon, abundant heterotrophic development is observed (López-Sánchez et al., 2022). On the other hand, phototrophic and mixotrophic growth of microalgae is predominant in WW that contains a low concentration of organic carbon.

7. Microalgae for biofuels production

The search for a reliable alternative to carbon-based energy sources has become increasingly important in light of growing concerns about the potential consequences of GHGs stemming from the use of fossil fuels as energy sources. Over the course of the past few decades, biofuel that is derived from algae has emerged as one of the most prominent examples of contemporary renewable energy sources. It is now widely accepted that algae can function effectively as a feedstock for the production of biofuels on a commercial scale. During the cultivation process, algae, like other plants, go through the process of photosynthesis, which converts the energy from the sun into chemical energy. During the phase known as "growth", biomass is produced as a result of the interaction of solar energy, phosphorus, nitrogen, CO₂, and water as illustrated in Fig. 5A.

Microalgae have the ability to absorb approximately fifty percent of their weight in CO₂ and store it (Iglina et al., 2022).

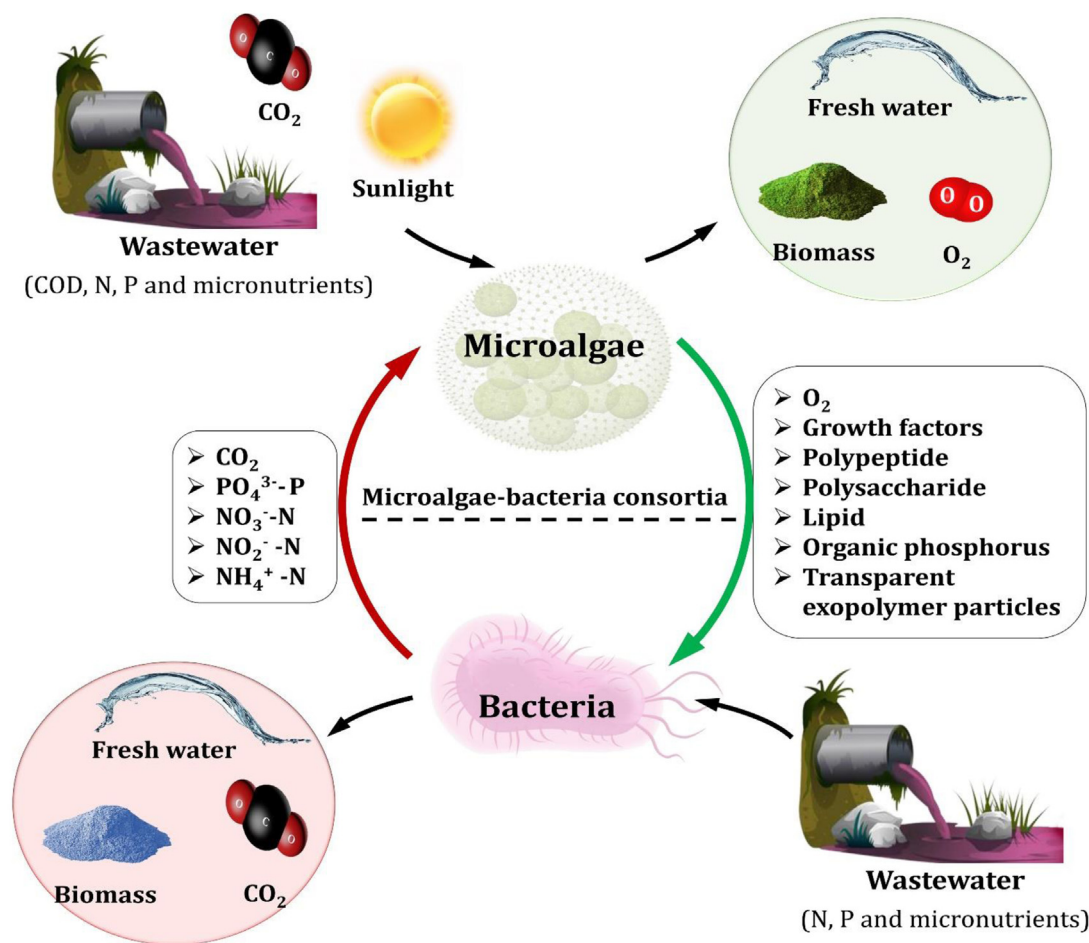


Fig. 4. Mechanism of wastewater microalgae-based bioremediation.

As a result of photosynthetic reactions, microalgae take in CO₂ from the atmosphere during the day and then release it into the atmosphere at night, just like other plants. The production of biofuels through the biological fixation of CO₂ is illustrated in Fig. 5B. Microalgae have the potential to sequester up to 90% of CO₂ when grown in closed cultivation conditions, and between 25% and 50% when grown in raceway ponds (Paul et al., 2021). When growing in an open environment, it can be challenging to keep environmental conditions stable. The optimal range for the concentration of CO₂ for the growth of microalgae is 5%–10%, as an increase in CO₂ results in a decrease in biomass productivity (Tang et al., 2011). The CO₂ fixation rates of *Scenedesmus obliquus* and *Chlorella vulgaris* are, respectively, 130 and 141 mg/L day (Chaudhary et al., 2018). The rate of CO₂ conversion that was achieved by *Chlorella vulgaris* was 14.9%, while it reached 13.85% for *Scenedesmus obliquus*. These qualities of microalgae contribute significantly both to the reduction of GHG and to the concurrent development of an endless supply of feedstock for biofuels (de Mendonça et al., 2022; Moshood et al., 2021).

7.1. Biodiesel

The production of lipids in microalgae is influenced by the conditions of cultivation, the capture of CO₂, and the organic carbon sources (Farooq et al., 2022). The fatty acids that are present in biomass are broken down to produce triglycerides (TGA), cholesterol, and lipids (Mimouni et al., 2018). Due to microalgae's ability to store a significant amount of lipids even

when exposed to adverse environmental conditions, the transesterification process can be utilized effectively in the production of biodiesel (Devi and Parthiban, 2020). As a consequence of this, lipid is one of the most important biological compounds required for the production of biodiesel (Adekunle et al., 2020; Aragonés et al., 2022). Distinct stages that make up the production of biodiesel from microalgal biomass are illustrated in Fig. 6. With the application of the appropriate processing methods, biodiesel that is produced from microalgal biomass can be converted into environmentally friendly biofuels. The cultivation parameters, such as WW composition, CO₂ concentration, temperature, and aeration rate, all have an effect on the biological composition of microalgal lipids. The most effective technique for obtaining biodiesel from microalgal biomass is illustrated in Fig. 7.

The use of waste from WWT plants in the cultivation of microalgae can significantly increase the amount of resources that are recycled efficiently while also significantly reducing emissions of GHGs (Vadiveloo et al., 2021). Lipid is an important source for the production of biodiesel because it is one of the most important metabolites that microalgae produce during their growth and reproduction (Ma et al., 2022). Table 2 summarizes the effects of carbon sources on microalgae lipid accumulation (Tian et al., 2020; Chen et al., 2020; Khanra et al., 2021; Lakshmikanandan et al., 2020; Tan et al., 2021; Bouzidi et al., 2020; Mondal et al., 2016; Liu et al., 2021; Nayak et al., 2019). It is possible for the lipid content of microalgae, which normally makes up between 1 and 70% of the dry cell weight, to reach up to 90% under certain conditions (Yamada et al., 2019). Because they

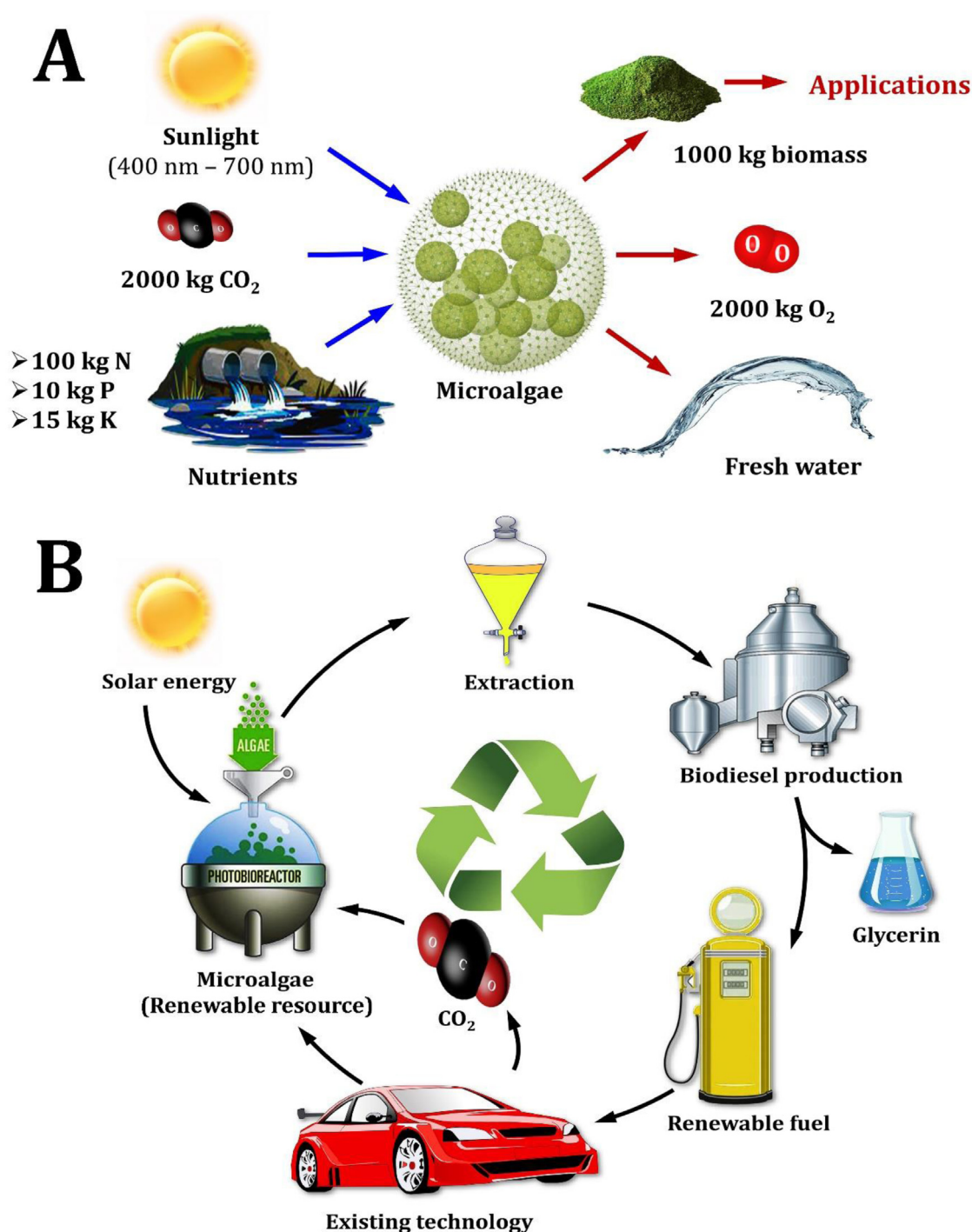


Fig. 5. Microalgae for biofuels production. Microalgal photosynthesis (A) and their role for future renewable energy production based on CO₂ capture (B).

contain a high percentage of lipids, microalgae are an excellent choice for use as a feedstock in the production of biodiesel. The production of biodiesel through the cultivation of microalgae is therefore considered as a promising strategy to the depletion of resources, the lack of availability of energy, and the pollution of the environment.

Microalgal fatty acids, which serve as the primary intermediate of lipid, are typically made up of hydrocarbon chains that range anywhere from 4 to 36 carbons in number and end with a carboxyl group. The degree of saturation and unsaturation in the carbon chain is used to categorize microalgal fatty acids into three primary groups: saturated fatty acids (SFAs), monounsaturated

fatty acids (MUFAs), and polyunsaturated fatty acids (PUFAs) (Sajjadi et al., 2018). Polar lipids contain a high proportion of PUFAs, while neutral lipids are primarily composed of SFAs. The production of biodiesel calls for microalgae cells that are abundant in SFAs and MUFAs; on the other hand, the accumulation of PUFAs is primarily used for the production of high-value products (Liang et al., 2019). For the production of biodiesel, microalgal species that are rich in C16–C18 fatty acids, including palmitic acid (C16:0), palmitoleic acid (C16:1), stearic acid (C18:0), oleic acid (C18:1), and linoleic acid (C18:2) are regarded as suitable feedstock. The

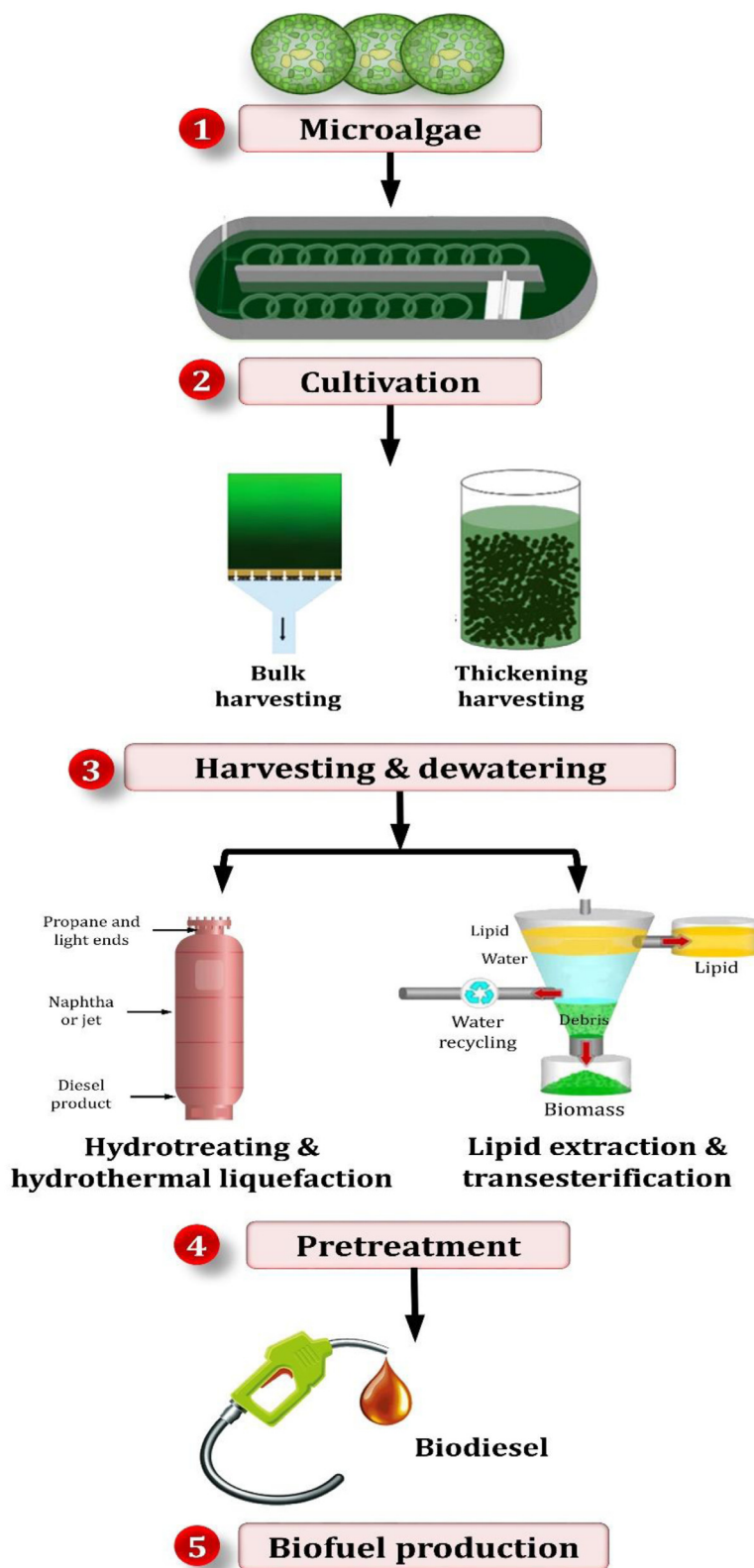


Fig. 6. Distinct stages that make up the production of biofuel from microalgae.

most common types of fatty acids found in microalgae are summarized in Table 3 (Hernández-García et al., 2019; Lakshmikanandan et al., 2020; Shen et al., 2020; Maheshwari et al., 2020; Lu et al., 2021a).

Biodiesel that is produced from microalgae can be used directly in diesel engines with minimal structural modification and can be blended with petroleum diesel in various proportions (Bukkarapu and Krishnasamy, 2021). Because it contains

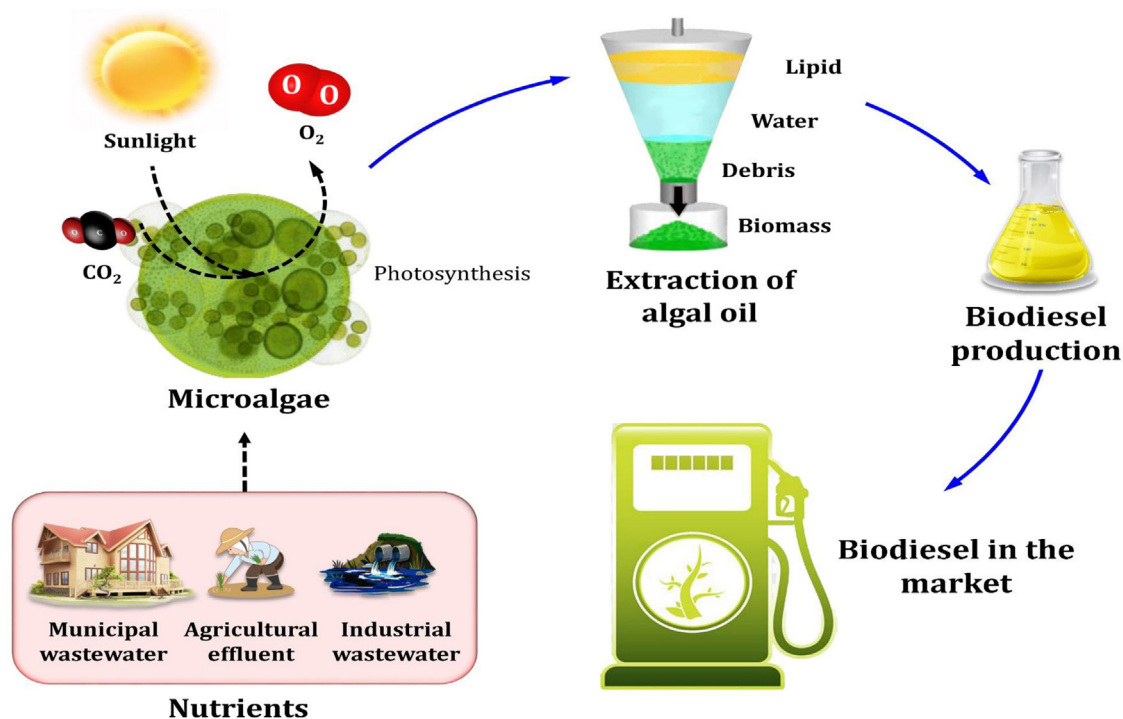


Fig. 7. Biodiesel from microalgal biomass.

Table 2
Effects of carbon sources on lipid accumulation in microalgae.

Carbon source	Microalgae	Culture type	Lipid content (%)	Reference
Glucose	<i>Chlorella pyrenoidosa</i>	Heterotrophic	26	Tian et al. (2020)
Glycerol	<i>Thraustochytrium</i> sp.	Heterotrophic	41.87	Chen et al. (2020)
Molasses syrup	<i>Chlorococcum</i> sp. SVF	Heterotrophic	80.34	Khanra et al. (2021)
Carbon dioxide	<i>Scenedesmus obliquus</i>	Autotrophic	20	Lakshmikandan et al. (2020)
Carbon dioxide	<i>Chlorella pyrenoidosa</i>	Autotrophic	15.3	Tan et al. (2021)
Sodium bicarbonate	<i>Halamphora</i> sp.	Autotrophic	25	Bouzidi et al. (2020)
Cheese whey permeate and carbon dioxide	<i>Chlamydomonas</i> sp.	Mixotrophic	38.66	Mondal et al. (2016)
Sodium acetate and carbon dioxide	<i>Micractinium reisseri</i> FM1	Mixotrophic	29.35	Liu et al. (2021)
Urea and carbon dioxide	<i>Chlorella</i> sp. HS2	Mixotrophic	36.7	Nayak et al. (2019)

Table 3
Composition of fatty acids found in a variety of microalgal species.

Microalgae	Carbon source	Culture type	C16–C18	SFAs (%)	UFAs (%)	Reference
<i>Scenedesmus obliquus</i>	Glucose	Heterotrophic	99.1	26.6	82.4	Shen et al. (2020)
<i>Chlorella vulgaris</i>	Carbon dioxide	Autotrophic	96.7	23.5	76.4	Lakshmikandan et al. (2020)
<i>Arthonema</i> sp.	Sodium bicarbonate	Autotrophic	74.1	34.4	65.6	Maheshwari et al. (2020)
<i>Spirulina platensis</i>	Sodium acetate	Mixotrophic	7.2	69.4	30.6	Lu et al. (2021a)
<i>Desmodesmus</i> spp.	Landfill leachate	Mixotrophic	95.4	30.4	69.6	Hernández-García et al. (2019)

SFAs, saturated fatty acids; UFAs, unsaturated fatty acids.

a greater proportion of PUFAs containing four or more double bonds than vegetable oil does, microalgal oil is more prone to oxidation during storage, which restricts its potential as a source of biodiesel (Koutra et al., 2018). The level of fatty acid unsaturation is an essential requirement for the production of microalgal biodiesel, and it can be easily altered through the utilization of a hydrogenation catalytic reaction (Yao et al., 2021). It is possible to produce microalgal biodiesel, which is a monoalkyl ester of fatty acid, by using TGA transesterification with alcohol. Since it possesses physicochemical properties that are comparable to those of conventional fuels, there has been a lot of interest in it. The lipid type and fatty acid composition of microalgae are influenced not only by the species of microalgae but also by the carbon sources and growth conditions (Shokravi et al., 2022).

A reliable source of carbon is necessary for the accumulation of lipids, the dissemination of lipid properties, and the production

of biodiesel (Alami et al., 2021). The consumption of organic carbon source by microalgae requires transportation systems, symbiosis systems, and ATP, whereas the utilization of inorganic carbon source involves the capture of photons and the fixing of dissolved inorganic carbon to biomass through photosynthesis. Investigations into the processes of synthesis and metabolism of lipids in microalgae are currently being carried out. According to research findings, the two primary processes that microalgae use to accumulate lipids are known as fatty acid synthesis and triacylglycerol (TAG) synthesis (Mulgund, 2022; Bibi et al., 2022). These processes are illustrated in Fig. 8. Microalgal biodiesel has emerged as one of the most promising forms of fuel for use in the aviation industry due to the fact that it has a low freezing point and a high energy density (Giwa et al., 2018). In addition to this, microalgal biodiesel meets the requirements of Standard EN14214 (Arguelles and Martinez-Goss, 2021). However, more

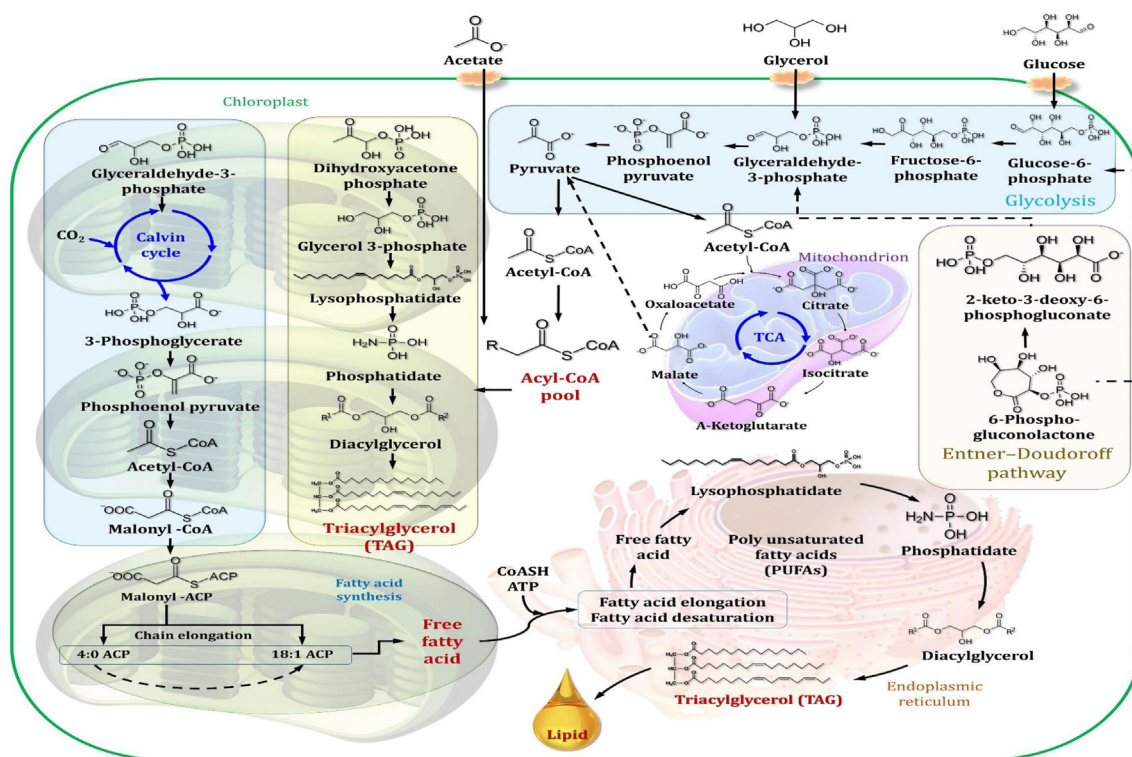


Fig. 8. Mechanism of carbon uptake and synthesis of fatty acid/triacylglycerol for lipid accumulation by microalgae.

research is needed to determine the location of TAG synthesis in the production of lipids by microalgae. It is essential to have an understanding of the lipid synthesis pathway in microalgae in order to improve the efficiency of biodiesel production through the testing of different species of carbon sources and genetic modification.

7.2. Bioethanol

In order to improve the octane rating of fuels derived from petroleum and reduce CO emissions, bioethanol is often combined with fuels derived from other sources of energy. Producing renewable second-generation bioethanol involves using agro-industrial lignocellulosic waste as a source of cellulose and hemicellulose (Ali et al., 2017b; Danso et al., 2022). The cellulose and hemicellulose are then hydrolyzed enzymatically to produce fermentable sugars (Wang et al., 2020a). Fermentation is another method for producing bioethanol from syngas, which can also be produced by the gasification of coal and biomass or municipal solid waste (Bidir et al., 2021).

Microalgae biomass can be successfully converted into bioethanol, which is the most popular type of third-generation alternative fuel (Tan et al., 2020). The production of bioethanol from the microalgae biomass has a number of benefits, including the fact that it does not require large areas of arable land and it lowers the levels of CO₂ in the atmosphere. The cell walls of microalgae are loaded with a variety of compounds, including lipids, carbohydrates, and proteins. Under anaerobic conditions, carbohydrates are first reduced to simple sugars via a chemical or enzymatic process, and those sugars are subsequently converted into bioethanol (Hossain et al., 2020). The production of bioethanol from microalgae involves a series of steps (Melendez et al., 2022; Elkatory et al., 2022). These steps include the selection and cultivation of algal biomass, pretreatment, liquefaction, saccharification, anaerobic fermentation, and distillation for bioethanol purification. The process of producing

bioethanol from microalgae is presented in Fig. 9. Ethanol in its purest form is a viable alternative to gasoline because it has a higher vaporization temperature and octane number than gasoline, thereby making it a more effective fuel. Moreover, the use of microalgae as feedstock for the production of bioethanol is more efficient than the use of traditional crops such as maize and sugarcane (Maity and Mallick, 2022; Beigbeder and Lavoie, 2022). It has been reported that the potential yield of bioethanol that can be produced from microalgae is nearly double that of sugarcane and five times that of corn (Vergara-Fernández et al., 2008). *Chlorella sorokiniana* was deemed the most successful hydrolyzate for the production of bioethanol (Constantino et al., 2021). There have been reports that enzyme-catalyzed hydrolysis results in high glucose conversion yields (90%) for marine red microalgae *Porphyridium cruentum*, whereas in freshwater *P. cruentum*, the conversion yield is only 85%. The production of bioethanol from freshwater *P. cruentum* was increased to 70% when simultaneous saccharification and fermentation were carried out, as opposed to the previous production rate of 65% when hydrolysis and fermentation were carried out separately. According to these findings, *P. cruentum* is capable of growing in freshwater environments and has the potential to be converted to bioethanol (Kim et al., 2017b).

7.3. Bio-hydrogen

The combustion of hydrogen results in the production of no CO₂ and only water as a waste product, making it exceptional among renewable energy sources (Asghar et al., 2021). The vast majority of hydrogen is produced by burning fossil fuels or other types of conventional fuels, despite the fact that hydrogen is currently utilized in a wide range of industrial applications (Fan and Tahir, 2022). Fig. 10 depicts the various pathways that could be taken in order to extract bio-hydrogen from microalgae. As a possible source of energy, bio-hydrogen has garnered a lot of interest due to the high calorific value it possesses as well as its clean oxidation properties. In comparison to thermochemical

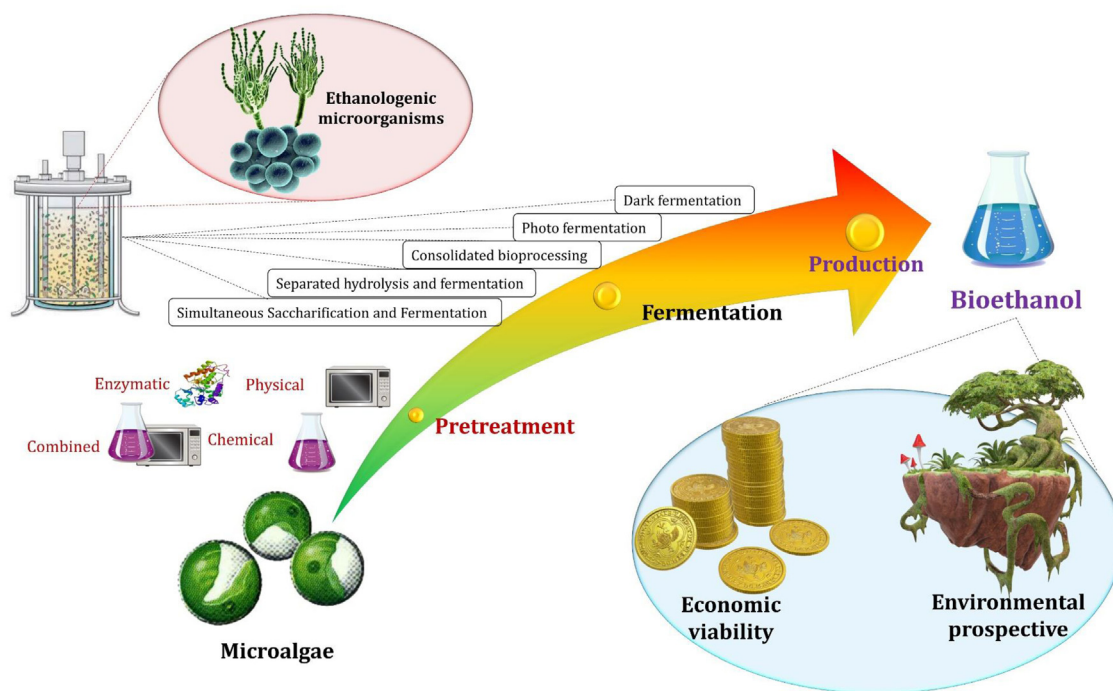


Fig. 9. Methods utilized for microalgal bioethanol production.

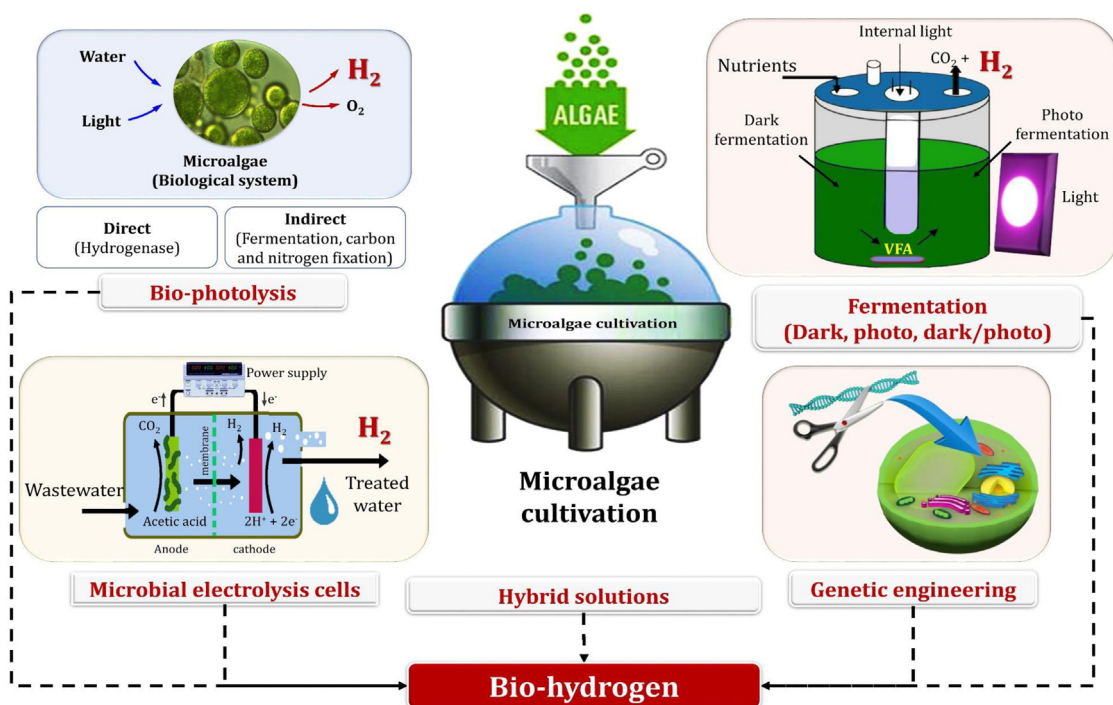


Fig. 10. Various strategies for extracting bio-hydrogen from microalgae.

methods, the production of bio-hydrogen through biological processes is less harmful to the surrounding environment, requires a lower amount of energy, and may be carried out in conditions that are found naturally (Sharma et al., 2021; Zheng et al., 2021).

The production of bio-hydrogen from microalgae has recently come to light as a potential option for the generation of environmentally friendly energy (Li et al., 2022a). As shown in Fig. 11, there are two different kinds of bio-hydrogen synthesis in

microalgae: the light-dependent and the light-independent (Batyrova and Hallenbeck, 2017). Microalgae and cyanobacteria, which belong to the first type, are responsible for the bio-photolysis of water, whereas photosynthetic bacteria are responsible for photo-fermentation. Anaerobic bacteria are responsible for the fermentation of organic molecules during the process known as

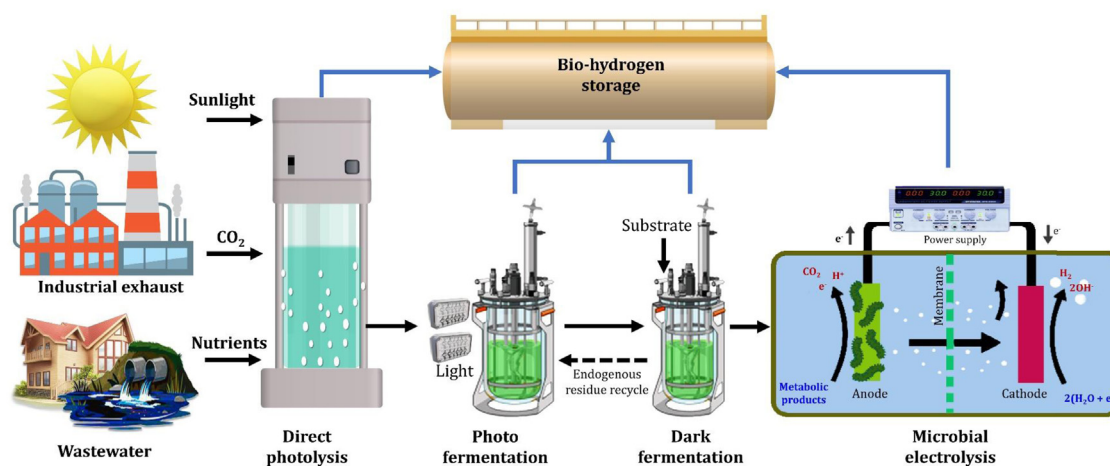


Fig. 11. Microalgae bio-hydrogen production using a hybrid bioreactor technique.

Table 4

Biogas and methane (CH₄) yield by some common microalgal species.

Microalgae	Biogas yield (mL/g VS)	CH ₄ yield (mL/g VS)	Time (day)	Reference
<i>Dunaliella salina</i>	505	323.2	32	Mussgnug et al. (2010)
<i>Arthrospira platensis</i>	481	293.4	32	Mussgnug et al. (2010)
<i>Scenedesmus obliquus</i>	287	177.9	32	Mussgnug et al. (2010)
<i>Chlorella kessleri</i>	335	217.7	32	Mussgnug et al. (2010)
<i>Chroococcus</i> sp.	487	267.4	30	Prajapati et al. (2013)
<i>Chlorella pyrenoidosa</i>	464	264.7	NA	Prajapati et al. (2014)
<i>Chlorella minutissima</i>	340	195.6	NA	Prajapati et al. (2014)

NA, Not available.

“dark fermentation”, which belongs in the second category (Budi-man and Wu, 2018). Microalgae are capable of producing bio-hydrogen under anaerobic environments when given the opportunity to do so in the presence of light and water. Because it only creates water as a byproduct and does not release any GHG emissions, bio-hydrogen is regarded as an effective and efficient energy source (Li et al., 2022a).

Bio-hydrogen is the most efficient fuel because it has the highest energy density and the best conversion efficiency of all fuels. Its energy density is 142 MJ/kg (Cuellar-Bermudez et al., 2015). Hydrogenase is a proton-lowering enzyme that was first discovered in microalgae. It is responsible for the splitting of water, which leads to the production of hydrogen under the conditions of anaerobic fermentation (Bhatia et al., 2021). However, due to the creation of oxygen, which swiftly deactivates the hydrogenase enzyme, this strategy only allows for a short amount of time for the reaction to take place. Therefore, additional technological developments are necessary in order to increase the oxygen tolerance of the hydrogenase enzyme. The technique of dark fermentation is one that is both inexpensive and friendly to the environment. It also results in easily marketable byproducts, such as acetic and lactic acids. This technique does not require the use of a light source or aeration, which results in a reduction in the additional expense. The production of 2.87 mmol H₂/g of *Chlorella* sp. resulted from the dark fermentation of *Chlorella vulgaris* with *Clostridium butyricum* under anaerobic conditions (Lunprom et al., 2019). Therefore, the combined algal and bacterial system provides an increased and cost-effective technique for enhancing the efficiency of bio-hydrogen generation through dark fermentation.

7.4. Biomethane

Microalgae can be used to produce biogas in order to generate electricity, fuel cells, and liquid fuel (Venkiteshwaran et al., 2022). Because it contains a relatively low amount of lignin and

cellulose, microalgal biomass is a promising feedstock for the production of biogas through the anaerobic digestion (AD) process (Gavaldà et al., 2022; Zabed et al., 2020). Combustible gases and gases that cause corrosion are both components of biogas (Ali et al., 2019a). In addition to trace amounts of hydrogen sulfide (H₂S), biogas is made up of methane (CH₄), CO₂, hydrogen, and ammonia (Ali et al., 2019c, 2021g, 2020c). It is possible to be powered by any type of organic waste biomass, such as municipal solid waste, lignocellulosic biomass waste, microalgae, and other organic wastes (Ali et al., 2020b, 2021e; Koutra et al., 2021; Saratale et al., 2018; Roy and Pal, 2015). Due to their enhanced carbohydrate and lipid concentrations, absence of lignin, and low cellulose content, microalgae are an efficient producer of biogas. Moreover, AD results in the production of solid waste, which can later be incorporated into the soil as a fertilizer (Itskos et al., 2016; Saqib et al., 2013). The production of biogas from microalgae has a significant amount of untapped potential. Several different types of microalgal species, including *Scenedesmus*, *Spirulina*, and *Chlorella* have been exploited in the production of biogas (Nagarajan et al., 2017). The weakening of the cell walls of microalgae is a unique strategy that improves the efficacy of pre-treatment as well as the substrate's ability to be degraded anaerobically. The cell wall of the microalgae *Chlorella vulgaris* is more resilient and resistant to anaerobic biodegradability compared to other substrates (Kavitha et al., 2019). Fig. 12 depicts the effect of microalgal cell wall weakening and disintegration on biogas yield. Table 4 summarizes the biogas and CH₄ yield of various common microalgae biomass (Mussgnug et al., 2010; Prajapati et al., 2013, 2014).

It is anticipated that Europe's population would expand by 1.7% between the years 2016 and 2080, which equates to a gain of 8.5 billion people by 2080 and, as a result, an increase in the amount of wastewater generated (Kouis et al., 2021). In this sense, the European Union is confronted with a serious problem management, which requires the development of cutting-edge

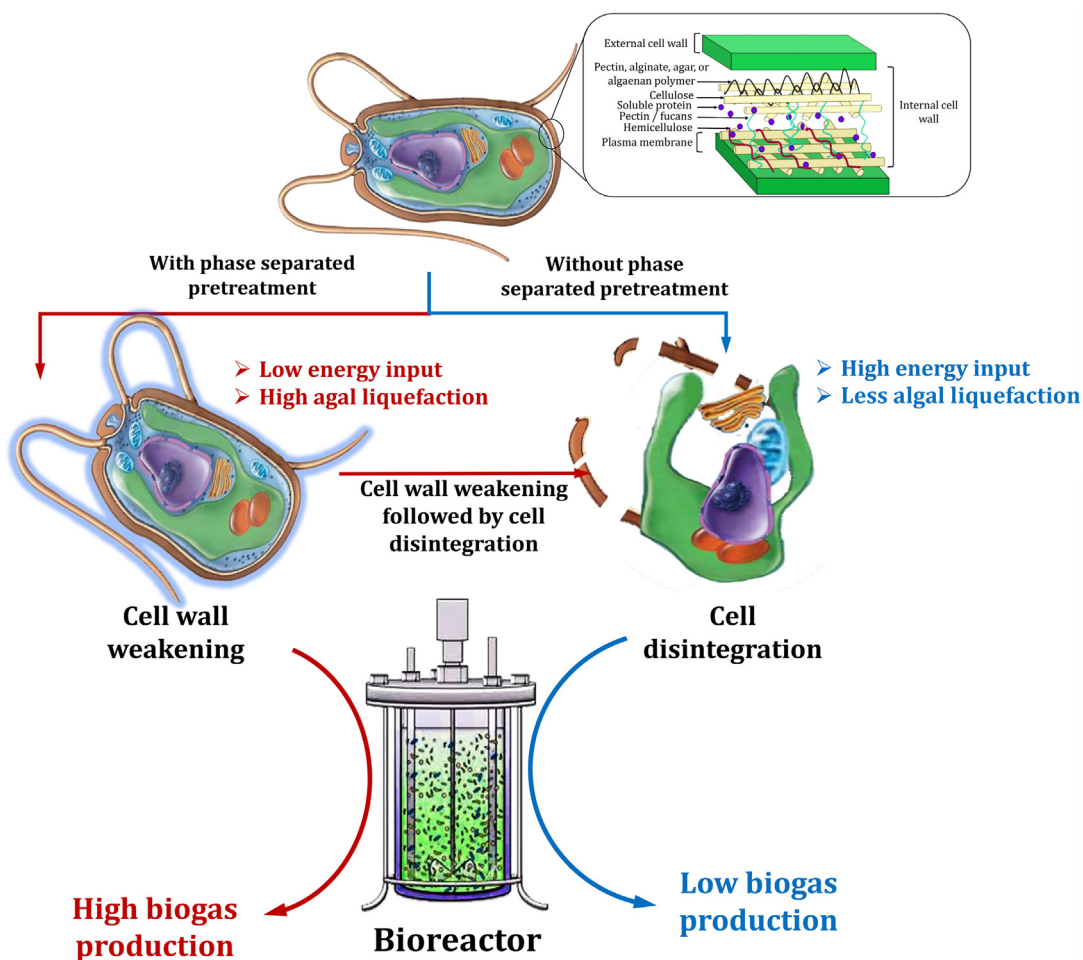


Fig. 12. Effect of microalgal cell wall weakening and disintegration on biogas yield.

technologies that lead to increased efficiency and lower costs. In this regard, WWT systems that are based on microalgae and very high-density algal ponds are fascinating alternatives in contrast to activated sludge WWT plants of the usual kind (Arashiro et al., 2018). Fig. 13 presents a representation of the equilibrium of the chemical oxygen demand (COD) for the microalgal-based WWT from the first raw sewage that is received to the discharge of the final effluent.

8. Processes for converting microalgal biomass into energy

Three distinct processes are used to convert microalgal biomass to energy: chemical (transesterification), biochemical (fermentation and anaerobic digestion), and thermochemical (liquefaction, pyrolysis and gasification). These processes convert biomass into three major types of products: biofuels, heat, and electricity (Fig. 14). The selection of an appropriate process is linked to the product's economic feasibility and application. Thermochemical processes do not necessitate the extraction of lipids or carbohydrates. Therefore, these biomass conversion processes are a more promising option for valorizing microalgae than chemical and biochemical processes (Ayub et al., 2022).

8.1. Transesterification

Microalgae are a promising feedstock with scalability that has the potential to be used in the production of biodiesel,

which is the most important renewable liquid biofuel for transportation (Branco-Vieira et al., 2020b,a; Shomal et al., 2019). The synthesis of biodiesel is most frequently accomplished by a process known as transesterification. This involves the utilization of methanol and a catalyst to convert lipids and TGAs into fatty acid methyl esters (FAMEs) (Pham et al., 2022; Panchal et al., 2020). The microalgal biomass that is separated from oil and FAME is abundant in carbohydrates and is an excellent candidate for the production of bioethanol (Ma et al., 2020). The leftover biomass that is left behind after biodiesel and bioethanol synthesis can be used to make biogas if it is digested in anaerobic conditions and biogas is produced (Laurens et al., 2017). The microalgal biomass that is left over after primary fuels have been extracted can be used to make biochar, biosorbent, and nutritious digestates/hydrolyzates (Rashid et al., 2013). Fig. 15 depicts the cascade flow of microalgal bioenergy generation through transesterification and biochemical reactions. When considering microalgae as a biodiesel feedstock, it should be noted that microalgae are capable of accumulating lipid moieties during late development or stationary phase, especially when subjected to a stressful environment. The direct conversion of microalgal biomass that already contains lipids into FAME is known as reactive transesterification (direct/in-situ process), whereas the conversion of lipids that have been extracted from microalgal biomass and then converted into FAME is known as extractive transesterification (indirect process) (Park et al., 2015) (Fig. 16).

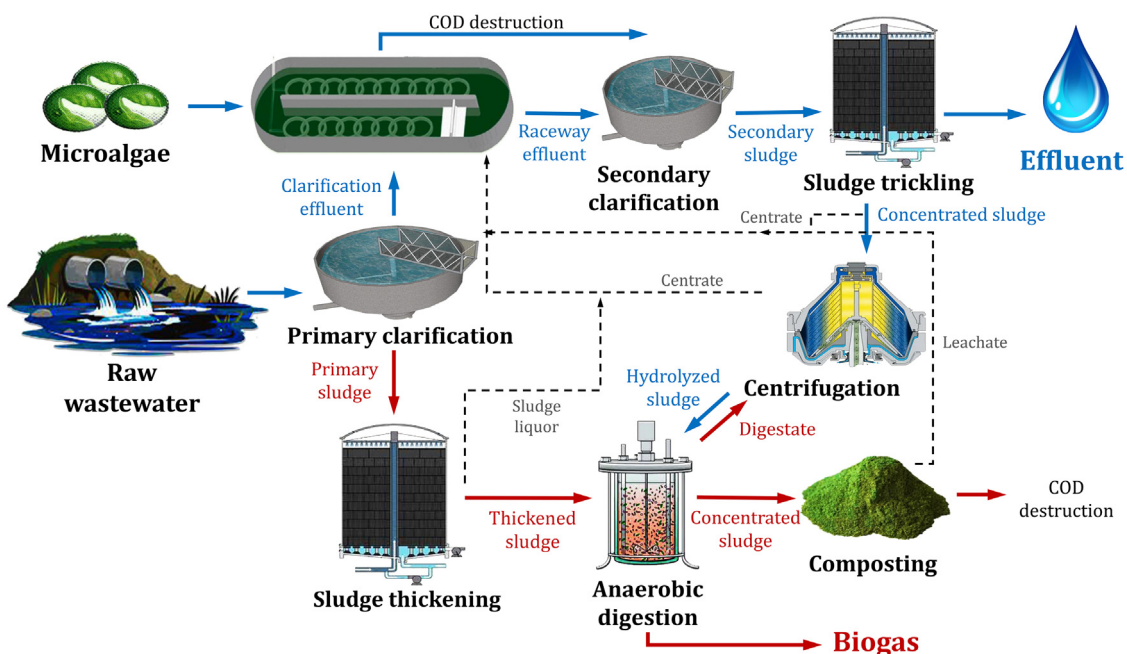


Fig. 13. Chemical oxygen demand (COD) of the microalgal-based wastewater treatment: Biogas, composting, and effluent.

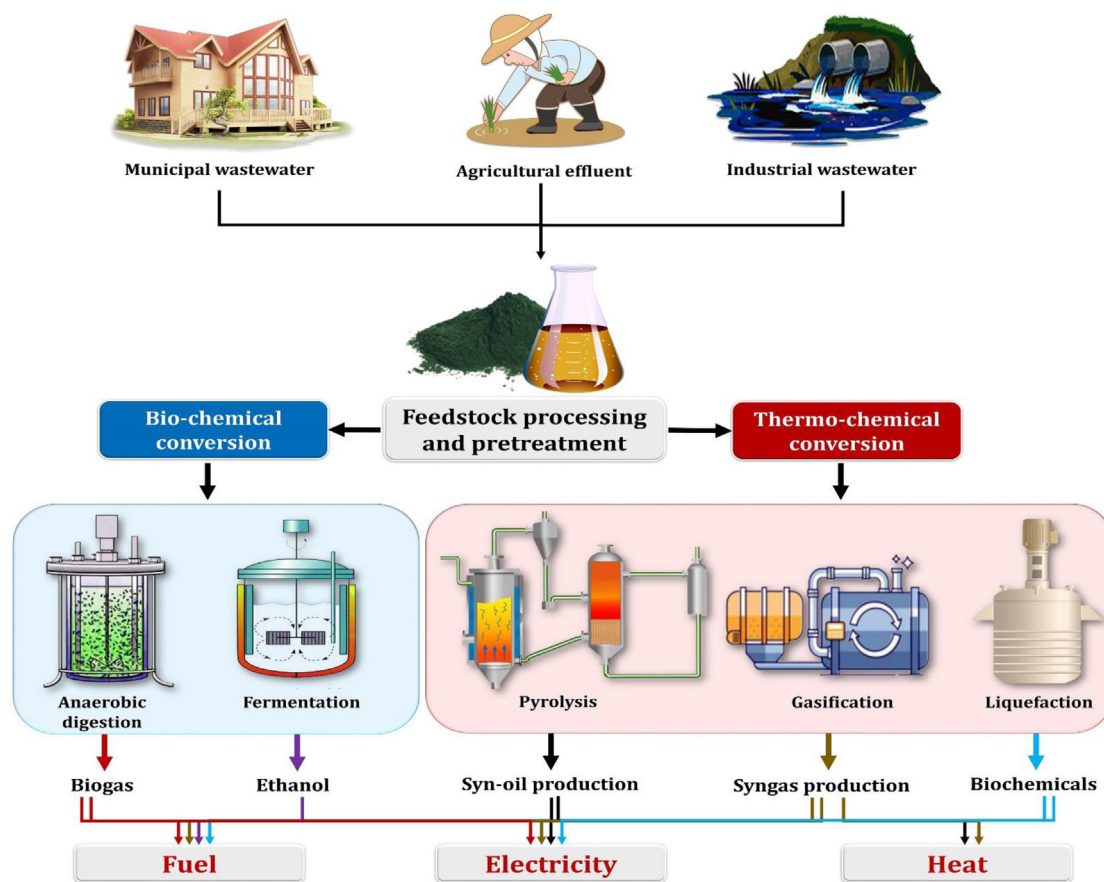


Fig. 14. Industrial and domestic waste conversion into three major types of products: biofuels, heat, and electricity.

It is possible to transesterify either the oil from microalgal biomass or the biomass itself in two steps. In order to reduce the amount of free fatty acid (FFA), the acid esterification process is carried out in two stages (Dong et al., 2013). The first phase of transesterification of algal oil by acid transesterification

reduced the FFA content from 6.3% to 0.34% by using optimal conditions. In the second phase, the highest biodiesel production of 90.6% was obtained via base transesterification under optimal conditions (Suganya et al., 2013). Even though the vast majority of in-situ transesterifications were completed as a single-step

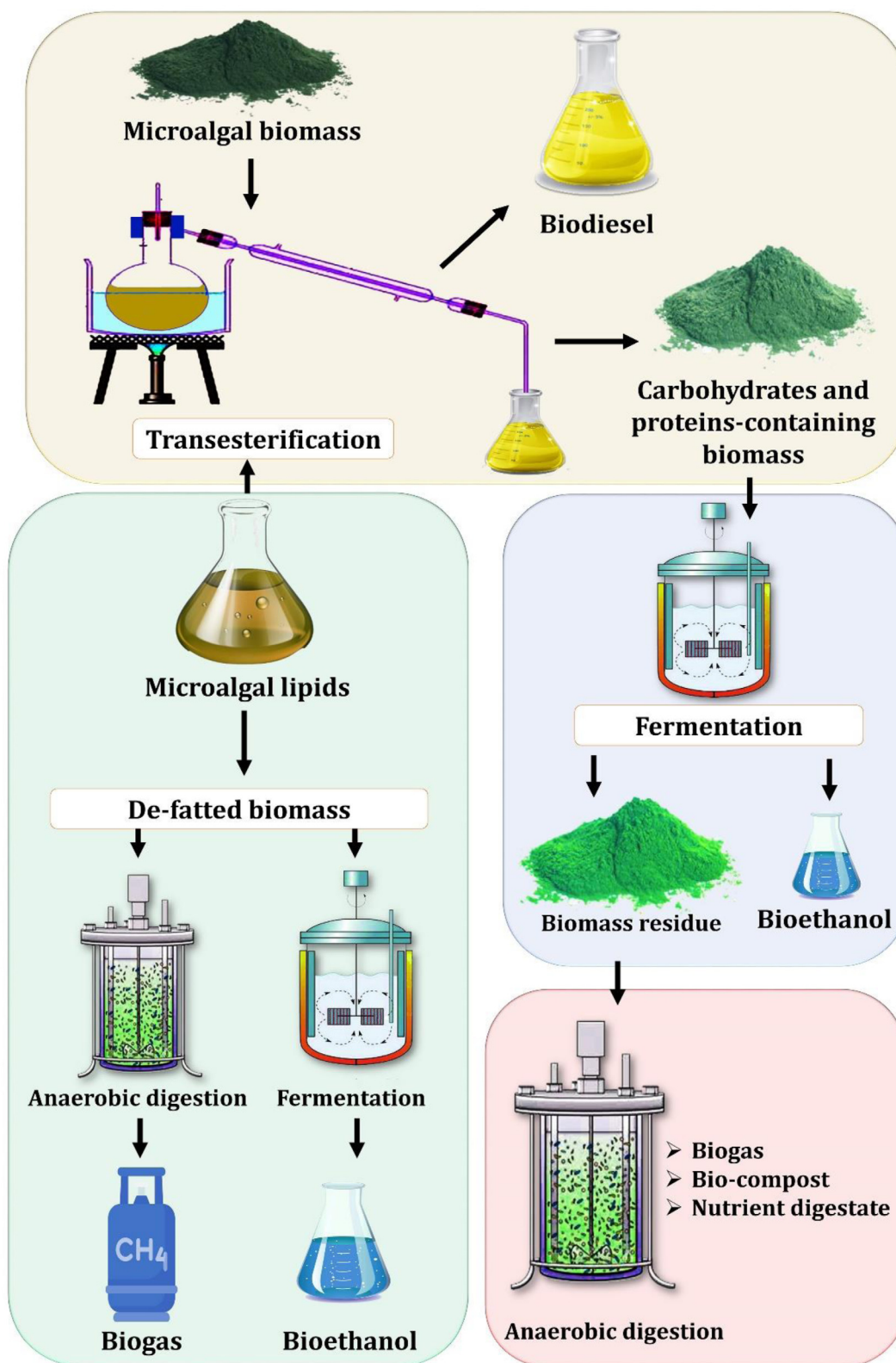


Fig. 15. Microalgal bioenergy synthesis in a cascade flow via transesterification and biochemical reactions.

reaction (Ghosh et al., 2017), in-situ transesterification can also be carried out in a two-step process (Ma et al., 2015). In-situ transesterification is becoming an increasingly popular method for the production of biodiesel in microalgae due to the fact

that it eliminates the need for costly processes such as biomass drying and lipid extraction, hence reducing the overall number of processing steps (Ghosh et al., 2017; Mandik et al., 2020).

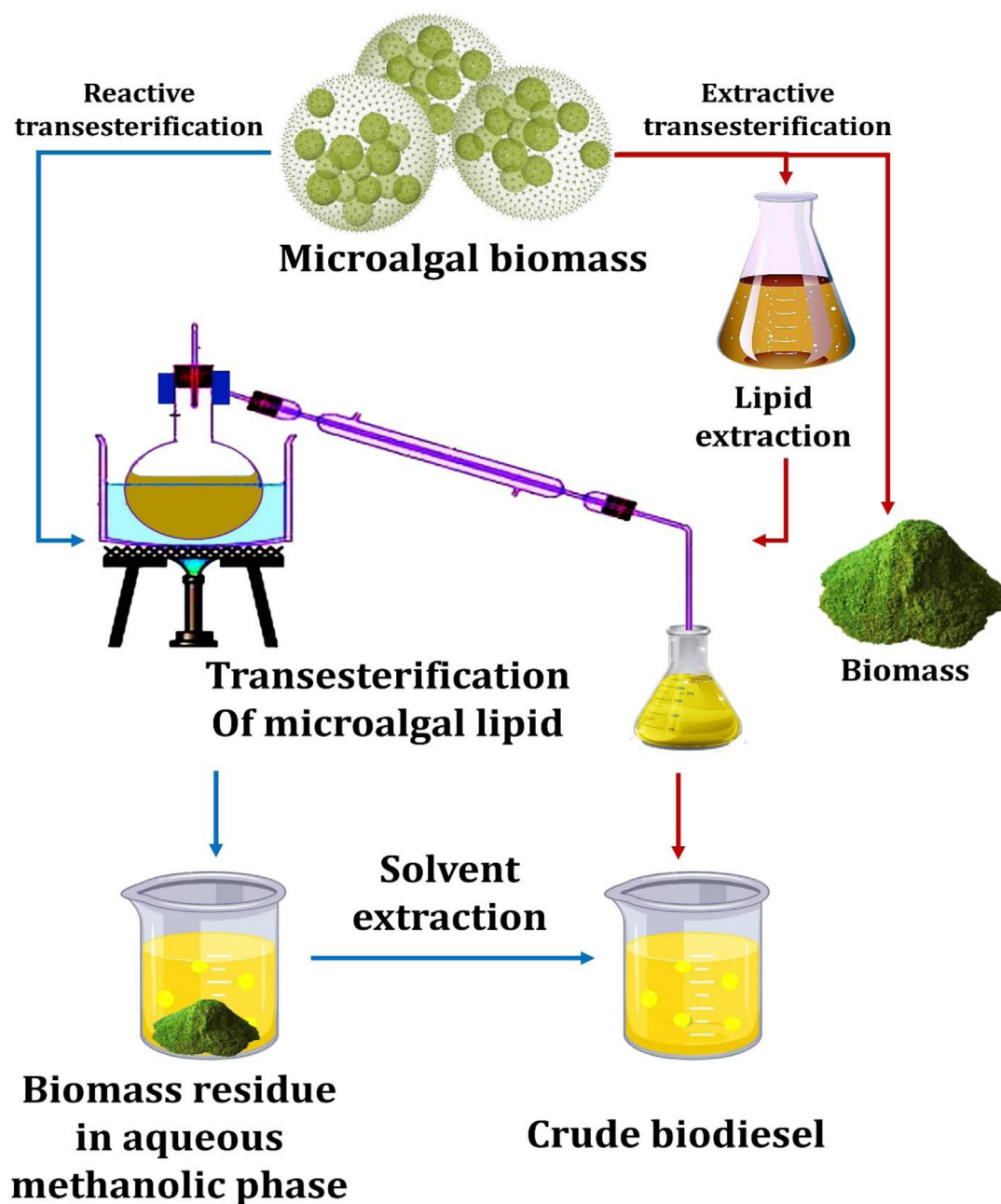


Fig. 16. Routes for converting microalgal biomass fatty acid methyl ester through transesterification.

8.2. Fermentation

The economic viability of producing biofuels and their availability are directly correlated, making the cost of feedstock one of the most important factors. Because of this, each generation of bioethanol has developed into the next in order to overcome the difficulties that were linked with the feedstock used in the previous generation. Fig. 17 provides a listing of the different feedstocks that are utilized by each generation. Over 70% of the earth's surface is covered by water, which serves as the habitat for a variety of marine microalgal species (Chauton and Størseth, 2018). Green algae and cyanobacteria are the types of marine microalgae that receive the greatest attention. They are considered a viable feedstock for research on bioethanol due to their vast diversity, singular evolutionary history, and great photosynthetic efficiency (Maeda et al., 2018). During the process of photosynthesis, microalgae are capable of absorbing 10–50 times more

solar energy than terrestrial plants. Additionally, microalgae can fix ambient CO_2 directly into their cells, making them an ideal candidate for CO_2 mitigation (Onyeaka et al., 2021). Therefore, microalgae have the potential to produce a significant quantity of carbohydrates, which range anywhere from 20 to 40 percent and serve as the principal substrate for the synthesis of bioethanol. Starch and cellulose together make up the vast majority of the carbohydrates that are found in green microalgae. In contrast, cyanobacteria store their carbohydrates mostly in the form of glycogen (Arias et al., 2021). Polysaccharides found in microalgae and cyanobacteria are easier to degrade than those found in terrestrial plants and lignocellulosic biomass. This is because neither of these organisms contain lignin (Maity and Mallick, 2022). In addition to this, these tiny photosynthetic organisms are less difficult to work with compared to other feedstocks (Arias et al., 2021). During the manufacture of biofuel, marine microalgal biomass can be converted into a number of useful byproducts in

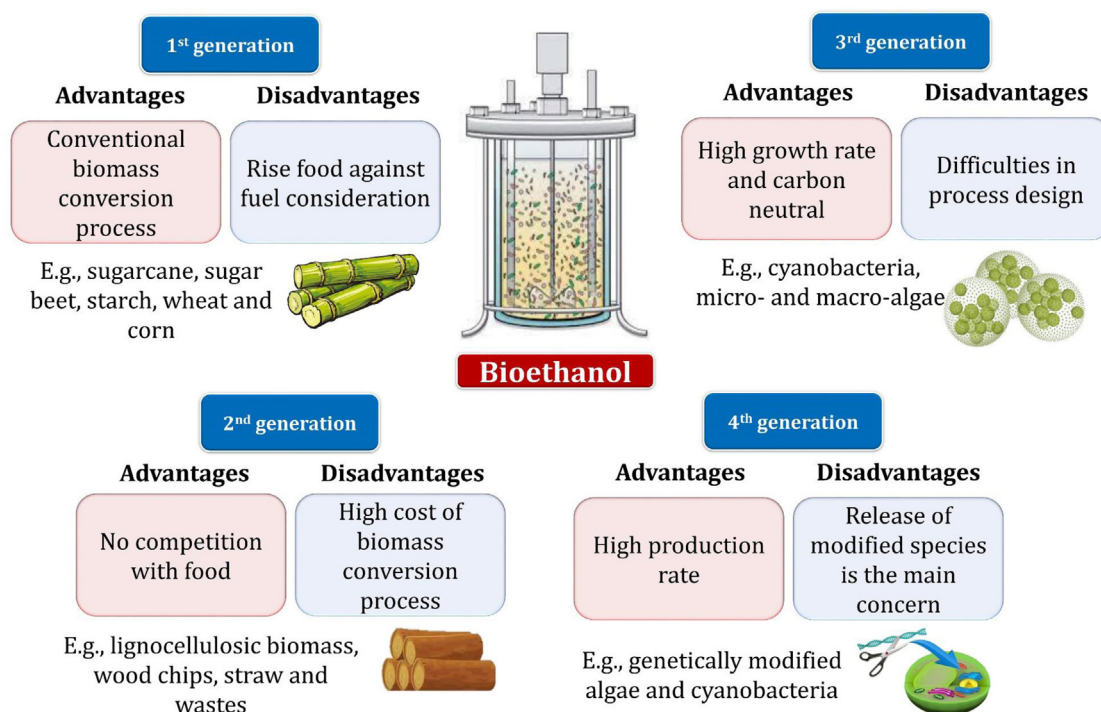


Fig. 17. Bioethanol among various feedstock generation: advantages and disadvantages.

Table 5

Advances in bioethanol production by some common marine microalgal species.

Microalgae	Pretreatment method	Fermentation condition				Bioethanol yield (g/g DCW)	Reference
		Temp (°C)	pH	Time (h)	Centrifugation (rpm)		
<i>Porphyridium cruentum</i>	Cellulase & Pectinase Enzymes	37	4.8	9	NR	0.60	Kim et al. (2017b)
<i>Scenedesmus dimorphus</i>	Acidic (2.5% H ₃ PO ₄) & Thermal (Autoclave)	30	NR	24	120	0.30	Chng et al. (2018)
<i>Scenedesmus abundans</i>	Acidic (3% H ₂ SO ₄) & Enzymatic (glucoamylase, amylase).	30	5.5	48	200	0.10	Guo et al. (2013)
<i>Tetraselmis suecica</i>	Alkaline (0.75% NaOH)	30	NR	48	150	0.70	Reyimu and Özçimen (2017)
<i>Synechococcus</i> sp.	Mechanical (Sonication) & Enzymatic (Lysozyme)	34	NR	48	160	0.22	Möllers et al. (2014)

NR, Not Reported.

Table 6

Advances in bioethanol production by some common marine microalgal species.

Microalgae	Pretreatment method	Biogas or CH ₄ yield	Reference
<i>Nannochloropsis salina</i>	Freezing (−15 °C, 24 h)	0.233 L biogas/g VS	Schwede et al. (2011)
<i>Scenedesmus</i> sp.	Thermal (70 °C, 15 min)	0.085 L CH ₄ /g COD	González-Fernández et al. (2012)
<i>Spirulina maxima</i>	Ultrasound (10 min)	0.17 L CH ₄ /g VS	Samson and LeDuy (1983)
<i>Chlorella vulgaris</i>	High pressure heating (140 °C, 20 min)	0.226 L CH ₄ /g COD (0.131 L CH ₄ /g VS)	Mendez et al. (2014)
<i>Scenedesmus obliquus</i>	Microwave (21 800 kJ/kg TS)	0.2120 L biogas/g VS (68.5% CH ₄) (0.14 L CH ₄ /g VS)	Passos et al. (2013)
<i>Chlorella vulgaris</i>	Thermochemical (120 °C, 20 min)	0.180 L CH ₄ /g COD	Mendez et al. (2013)
<i>Isochrysis galbana</i>	Mechanical stirring with glass beads (1 min)	0.0127 L biogas (79.0% CH ₄)	Santos et al. (2014)
<i>Nannochloropsis oculata</i>	Thermal (90 °C, 4 h)	0.39 L biogas/g VS (74% CH ₄)	Marsolek et al. (2014)
<i>Scenedesmus</i> sp.	Mechanical, thermal and chemical (Extraction of aminoacids)	0.273 L CH ₄ /g VS	Ramos-Suárez and Carreras (2014)
<i>Scenedesmus</i> sp.	Mechanical, thermal and chemical (Extraction of lipids)	0.212 L CH ₄ /g VS	Ramos-Suárez and Carreras (2014)

addition to bioethanol. Some examples of these byproducts include biopolymers, medicines, and vitamins (Mastropetros et al., 2022). The fermentation parameters that are connected with the production of bioethanol from marine microalgal species are displayed in Table 5 (Kim et al., 2017b; Chng et al., 2018; Guo et al., 2013; Reyimu and Özçimen, 2017; Möllers et al., 2014).

8.3. Anaerobic digestion

The digestibility of the cell wall is a major factor that determines the quality of microalgal biomass (Wicker et al., 2021). Pretreatment with either physical, chemical, or biological agents can improve the digestibility of the cell wall. The proportion of cellulose, hemicellulose, and biopolymers in the cell wall that can

barely be broken down by bacteria is directly related to the cell wall's resistance to bacterial degradation. The microalgae biomass needs to be processed first in order to improve the digestibility of the microalgae cell wall, which must be done before the process can begin and hence boost methane potential. There are a variety of contemporary pre-treatment techniques that can be used for the production of biogas/CH₄ by microalgae (Schwede et al., 2011; González-Fernández et al., 2012; Samson and LeDuy, 1983; Mendez et al., 2014; Passos et al., 2013; Mendez et al., 2013; Santos et al., 2014; Marsolek et al., 2014; Ramos-Suárez and Carreras, 2014) as given in Table 6.

8.4. Liquefaction

The effect that ultrasonic pretreatment had on the amount of bio-oil that could be extracted from microalgae as well as its heating value when subjected to the HTL process at low temperatures has been investigated in recent (Ido et al., 2018). Because of this, the utilization of ultrasonic pretreatment is theorized to solve the HTL pressure and temperature reductions connected with bio-oil yield, which are responsible for the difficulty associated with large-scale commercialization. According to the findings of the study, ultrasonic-assisted high temperature liquefaction, also known as UHTL, may increase bio-oil output even at short sonication times while keeping the total energy value stable (up to 90 s). The second inference is that the amount of thermal energy added to bio-oil by UHTL is greater than the amount of electrical energy that is consumed during the sonication process. In order to demonstrate this, the oxygen content of the bio-oil produced via the use of UHTL reduced while its heating value increased when compared to bio-oil produced through the use of conventional HTL. In addition, a bio-oil yield of 28.9% was produced by sonicating the material for 90 s at 250 °C. The possibility of converting the biomass of *Chlamydomonas reinhardtii* into nitrogen-rich bio-char, bio-oil, and biodiesel has also been investigated (Grierson et al., 2009). This was probably due to the fact that the UHTL method did not have an effect on the nitrogen content on average. Table 7 summarizes the recent HTL processes on microalgal biomass (Kandasamy et al., 2020; Parsa et al., 2018; Cui et al., 2020; Shakya et al., 2017; Xu et al., 2019; Bravo et al., 2019; Arun et al., 2020b; Wang et al., 2020b).

8.5. Pyrolysis

The destruction of chemical bonds only through the application of heat is known as pyrolysis (Bai et al., 2021). It has applications in a wide number of fields, including forensics, biology, natural materials, synthetic polymers, and investigations of trace levels (Gao et al., 2022; Chi et al., 2021; Echaroj et al., 2021; Soongprasit et al., 2021). It is also used in the production of biofuels (bio-oil, biogas, and biochar) by heating biomass at a predetermined speed to a specified temperature, where it is maintained for a period of time before moving on to the next step in the process (Fu et al., 2022; Tarelho et al., 2020; Tursunov et al., 2020). There are numerous different pyrolysis technologies, including slow, fast, flash, microwave, and catalytic pyrolysis (Ju et al., 2021; Suntivarakorn et al., 2018). Because of its ease of use and relatively low cost, the process of slowly pyrolyzing microalgae is typically carried out in a reactor with a fixed bed. In most cases, biochar is made by heating biomass at a slow heating rate (10 °C per minute or less) to temperatures ranging from 350 to 600 °C while maintaining a vapor residence time of minutes or longer (Ribeiro et al., 2022). Fast pyrolysis of microalgae is often carried out in a fluidized bed reactor, although it can also be carried out in a fixed bed reactor on occasion. This is due to the fact that the product that is sought after being the

liquid fraction, which is known as bio-oil. By heating biomass to a temperature of up to 500 °C at a high heating rate and a short residence vapor time in seconds or milliseconds, fast pyrolysis is typically used to produce bio-oil (Suntivarakorn et al., 2018). Therefore, the method of fast pyrolysis is superior than the technique of slow pyrolysis in terms of its effectiveness in producing a higher percentage of liquid product (Chen et al., 2015). Microwave-assisted pyrolysis, in which heating is achieved with the assistance of microwaves, has found widespread application in industrial operations. One of the most promising new pyrolysis methods is called microwave-assisted pyrolysis. This is because it has a shorter residence time and more rapid chemical reactions than traditional pyrolysis (Ju et al., 2021). The process of heating biomass in the absence of oxygen with the assistance of a size-selective catalyst is referred to as catalytic pyrolysis. Another name for this process is catalytic cracking. In most cases, it takes place at temperatures ranging from 300 to 600 °C, and the ratio of catalysts to biomass might be anywhere from 0.2 to 9 (Chen et al., 2015). Table 8 summarizes the recent pyrolysis processes on microalgal biomass (Zainan et al., 2018; Jafarian and Tavasoli, 2018; Abd Rahman et al., 2020; Grierson et al., 2011; Harman-Ware et al., 2013; Beneroso et al., 2013; Norouzi et al., 2017; Aysu et al., 2017).

8.6. Gasification

Gasification is another thermochemical process that uses biomass as a fuel feedstock to produce energy-dense gaseous products at high temperatures (Ayub et al., 2022). After combustion, the primary products are syngas and fuel gas. Syngas production also results in the production of methanol and hydrogen, which are widely used as transportation fuels (Hassan et al., 2020). The two primary processes for converting microalgal biomass to energy are traditional and advanced gasification (Farooq et al., 2021). The traditional gasification process involves heating the algal biomass feedstock to a high temperature of between 800 °C and 1200 °C, which produces syngas composed of CH₄, H₂, CO, and CO₂ as well as other hydrocarbons such as char and tar (Ayub et al., 2020). However, commercial yields of syngas are low due to the high moisture content of algae and the production of tar. As an example of advanced gasification, supercritical water gasification involves heating the algal biomass feedstock at a low temperature range of 350 °C to 550 °C and under high pressure (20–26 MPa). The main disadvantage of this method is that it has not yet been commercialized (Ahmed et al., 2020). Table 9 summarizes the products and gas composition obtained from algal biomass feedstock via conventional or advanced gasification (Figueira et al., 2015; Raheem et al., 2017, 2015, 2018; Wang et al., 2018; Sanchez-Silva et al., 2013; Caputo et al., 2016; Stucki et al., 2009; Duan et al., 2018).

9. Conclusion

The utilization of microalgae as a resource for bioelectricity of the next generation offers an economic and eco-friendly alternative to GHG emissions. The greatest challenge posed by the excessive use of fossil fuels and the global industrial revolution is overcoming high energy demand and mitigating the negative environmental impact of industrial waste. In addition to waste from agricultural practices, waste from industrial processes is the primary contributor to water pollution. Water scarcity and pollution have attracted a great number of people who are looking for solutions because they are major environmental problems. The need for alternative forms of energy is steadily growing in tandem with the depletion of resources pertaining to fossil fuels. Microalgae are the most suited biological agents for the treatment of WW

Table 7
Recent hydrothermal liquefaction (HTL) processes on microalgal biomass.

Microalgae	Operation conditions			Bio-oil yield (%)	Reference
	Temp. (°C)	Time (min)	Catalyst		
<i>Arthrospira plantensis</i>	250	30	Water	9.0	Kandasamy et al. (2020)
<i>Gracilaria gracilis</i>	350	50	–	15.7	Parsa et al. (2018)
<i>Galdieria sulphuraria</i>	310	30	–	12.9	Cui et al. (2020)
<i>Nannochloropsis</i> sp.	320	30	–	66	Shakya et al. (2017)
<i>Nannochloropsis</i> sp.	320	30	–	57	Shakya et al. (2017)
<i>Chlorella</i>	340	30	H ₂ addition	22	Xu et al. (2019)
Natural consortia	350	120	–	16	Bravo et al. (2019)
<i>Scenedesmus obliquus</i>	300	60	Water	25.6	Arun et al. (2020b)
<i>Scenedesmus obliquus</i>	300	60	Clam shell-derived catalyst/water	39.6	Arun et al. (2020b)
<i>Arthrospira plantensis</i>	250	30	CeO ₂ /water	26	Kandasamy et al. (2020)
<i>Spirulina</i>	270	30	NiO–SAPO–34/water + ethanol	59.9	Wang et al. (2020b)
<i>Spirulina</i>	270	30	NiO–Al ₂ O ₃ /water + ethanol	55	Wang et al. (2020b)

Table 8
Recent pyrolysis processes on microalgal biomass.

Microalgae	Pyrolysis type	Operation conditions		Bio-oil yield (wt. %)	Gas yield (wt. %)	Biochar yield (wt. %)	Reference
		Temp. (°C)	Catalyst				
<i>Chlorella vulgaris</i>	Catalytic	300–600	Ni on Zeolite-Y	10.4	–	–	Zainan et al. (2018)
<i>Arthrospira plantensis</i>	Catalytic	400–700	Ce/HMS-ZSM5	36.4	28.6	31.8	Jafarian and Tavasoli (2018)
<i>Arthrospira plantensis</i>	Catalytic	400–700	Fe/HMS-ZSM5	38.2	58.9	30	Jafarian and Tavasoli (2018)
<i>Arthrospira plantensis</i>	Catalytic	400–700	Ce/HMS-ZSM5	36.4	28.6	31.8	Jafarian and Tavasoli (2018)
<i>Isochrysis</i> sp.	Catalytic	500	Li-LSX Zeolite	42.6	–	–	Abd Rahman et al. (2020)
<i>Tetraselmis chui</i>	Slow	500	–	27.9	–	–	Grierson et al. (2011)
<i>Scenedesmus</i> sp.	Fast	480	–	18.4	–	4.6	Harman-Ware et al. (2013)
<i>Scenedesmus almeriensis</i>	Microwave-assisted	400–800	–	15.6–41	–	27–44.5	Beneroso et al. (2013)
<i>Gracilaria gracilis</i>	Catalytic	500	–	38.6	–	35.5	Norouzi et al. (2017)
<i>Pavlova</i>	Catalytic	450–550	Ce/TiO ₃	15.5–21.7	37.1–46.3	36.4–47.7	Aysu et al. (2017)

Table 9
Conventional (CG) and supercritical water gasification (SWG) processes on algal biomass.

Microalgae	Gasification type	Operation conditions		Gas composition (%)				Reference
		Temp. (°C)	Catalyst	H ₂	CO	CO ₂	CH ₄	
<i>Chlorella vulgaris</i>	CG	850	Argon/water vapor	16.8	50.1	–	20.6	Figueira et al. (2015)
<i>Chlorella vulgaris</i>	CG	700–950	–	22.5–39.2	20.6–22.4	25.2–30.8	17.4–21.4	Raheem et al. (2017)
<i>Chlorella vulgaris</i>	CG	900	ZnO/NiO–CaO, air	42.9	8.7	–	18.7	Raheem et al. (2015)
<i>Chlorella vulgaris</i>	CG	700	Air	19.1	23	–	19.6	Raheem et al. (2015)
<i>Spirulina platensis</i>	CG	800	–	20	35	40	4	Wang et al. (2018)
<i>Chlorella vulgaris</i>	CG	700–900	ZnO–Ni–CaO	37.2	13.1	28.5	21.1	Raheem et al. (2018)
<i>Nannochloropsis</i> sp.	CG	850	–	45–55	33–35	12–15	2–5	Sanchez-Silva et al. (2013)
<i>Nannochloropsis gaditana</i>	SWG	663	Na ₂ CO ₃	52	–	–	10	Caputo et al. (2016)
<i>Nannochloropsis gaditana</i>	SWG	663	K ₂ CO ₃	55.4	0.2	–	13.7	Caputo et al. (2016)
<i>Spirulina platensis</i>	SWG	>400	Ru/ZrO ₂ and Ru/C	6–29	–	38–77	2–52	Stucki et al. (2009)
<i>Chlorella pyrenoidosa</i>	SWG	380–600	–	1.6–11	0.2–5.8	22–84	4.6–58	Duan et al. (2018)
<i>Nannochloropsis gaditana</i>	SWG	663	–	41–55	0.2–1.8	22–25	13–20	Caputo et al. (2016)

and the energy crisis when compared to other physical–chemical treatment approaches. This is because microalgae can convert sunlight into usable energy. Microalgae have the potential to grow quickly, treat WW, and produce biofuels in a manner that is more efficient and less expensive than other methods. Some types of microalgae are capable of growing heterotrophically, which results in the removal of nutrients from WW and the production of biofuels. Other types of microalgae are capable of growing mixotrophically, which captures CO₂ while also treating WW. The major concerns of water pollution and the energy crises can be handled by integrating WWT with the production of biofuels derived from microalgae. Therefore, microalgae are potential agents to be applied simultaneously for WWT and biofuels production. When it comes to all of the challenges that are associated with green technology, finding sustainable energy sources is always the most significant one. The use of microalgae in wastewater treatment is a new approach to biotechnology that is beneficial to the environment and helps treat wastewater while also lowering the amount of heavy metal contamination. The production of liquid hydrocarbons with a decreased oxygen content from microalgal biomass can be accomplished by HTL, pyrolysis,

and gasification processes. The production of environmentally friendly microalgae-based biofuels is also accomplished through the processes of transesterification, fermentation and methanation. The relationship between microalgae and green technologies is increasingly being researched, as was covered in this review. However, the identification and modification of microalgae that can tolerate variable conditions and stresses within the existing infrastructure of WWT can also be useful. In addition, the integration of existing WWT into a commercial scale production may reduce costs, which requires extensive research in order to benefit from this technology. Moreover, researchers in this discipline have a golden perspective to explore more bioenergy resources and value-added products that can generate revenues from microalgae.

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.

Data availability

Data will be made available on request.

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