Microalgae Bioremediation and Biorefinery for sustainable production of high-value-added products: A Brief Review.

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Abstract. Conventional wastewater treatment methods often struggle to effectively remove hazardous, recalcitrant, and emerging contaminants. In addition, these methods are notorious for not utilizing the full spectrum of nutrients present in the waste stream. These problems are addressed by the integration of microalgal bioremediation, which not only efficiently utilizes each nutrient, but also treats the wastewater to produce biofuels and value-added products. The robust and efficient metabolism of microalgae enables simultaneous pollutant removal and biomass growth. In addition, microalgae serve as a sustainable feedstock for biorefinery applications, which work together for an integrative approach using bioremediation and biorefinery to increase the financial feasibility of the plant. This increase occurs because the key challenges facing biorefineries are the excessive cost of operation and significant consumption of fresh water. However, by using nutrient-rich wastewater for microalgal cultivation, these challenges can be mitigated. This integrated approach of bioremediation and biorefinery not only facilitates pollutant removal and resource recovery, but also enables the production of energy and high-value products. As a result, it promotes a circular economy model and improves overall sustainability.

Keywords. Microalgae, Bioremediation, Biorefinery, Bioenergy, Circular Economy.

1. Introduction

A major current concern with respect to water resources is the continued growth of the world's population and its demand for clean water, which is severely impacted by global climate change and the improper discharge of industrial and urban wastewater [1]. Currently, these wastewaters are treated with conventional wastewater treatment (CWWT) methods that involve chemical, physical, and biological methods [2].

The main challenge is to treat hazardous, recalcitrant, and emerging contaminants and reuse each nutrient following the circular economy principle. In addition, these conventional methods are time-consuming and costly due to their low efficiency and high energy consumption, making the treatment unsustainable [2].

Therefore, microalgae bioremediation is emerging as a replacement technology for CWWT because of its ability to recycle nutrients that would be disposed of in conventional methods and reduce energy consumption. In addition, microalgae bioremediation can be attached to a biorefinery system, a concept for converting biomass into high-value products and energy, which increases the feasibility of the process and contributes to the concept of circular economy [3].

This review aims to explore the potential of an integrated approach using microalgae for bioremediation and biorefinery purposes, with the goals of reducing costs, increasing efficiency, promoting a circular bioeconomy, and strengthening environmental sustainability.

2. Microalgae bioremediation

Microalgae are photosynthetic organisms that can grow in a variety of substrates, including wastewater. This ability, combined with their strong environmental adaptability, makes them useful for bioremediation. Wastewater can contain heavy metals, pharmaceuticals, and other environmentally hazardous compounds that microalgae can treat [3–5]. The mechanisms by which microalgae process organic and inorganic substances are discussed in the following topics. The cultivation systems for microalgae are also discussed in this section.

2.1 Bioremediation mechanisms

Microalgae evolved to have a massive tolerance to various pollutants. The main mechanisms used by microalgae to tolerate these pollutants are biosorption, bioaccumulation, and biodegradation (Fig. 1).

Biosorption occurs in different passive manners, such as absorption, surface complexation, adsorption, and electrostatic interaction. Some cell wall compounds of microalgae such as glucans, peptidoglycans, and pectin function as sorbents, attracting and binding pollutants from wastewater. Biosorption involves the movement of pollutants from the liquid phase to adhere to a solid surface through mass transfer. Microalgae additionally secrete extracellular polymeric substances (EPS), which can contribute to the biosorption of pollutants. The effectiveness of EPS in this process varies based on factors such as the species of pollutants, the structure of EPS, and the operating conditions.

On the other hand, bioaccumulation is active. Microalgae can accumulate the pollutants adsorbed in their wall inside their cell for wastewater detoxification. This happens mainly because when the concentration of polysaccharides formed in the cell during photosynthesis decreases, pores can be formed in the cell wall, allowing pollutants with hydrophobic properties to enter the cell through diffusion. For the hydrophilic pollutants, their accumulation is due to the phenomenon of depolarization and hyperpolarization of the microalgae membrane or the use of energy to go against the gradient [2].

Finally, biodegradation is the most effective method microalgae utilize for pollutant treatment. In this process, the contaminant is mineralized by metabolic degradation or co-metabolism. The former is used when the pollutant function as carbon source or electron donor/acceptor for microalgae. In the latter, microalgae use the contaminant for both purposes [6].

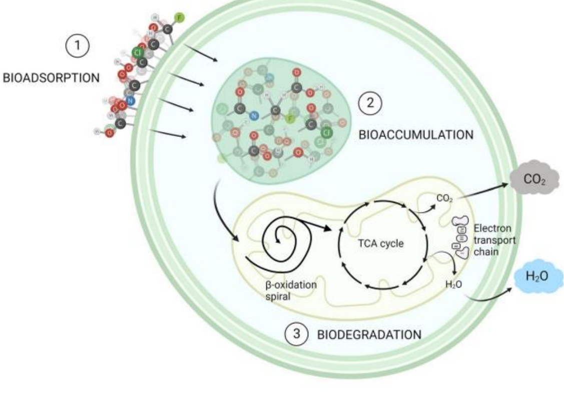


Fig. 1 – Bioremediation mechanisms [7].

2.2 Microalgae cultivation systems

Fig. 2 and Fig 3 illustrate some systems utilized for microalgae cultivation. The main types of systems utilized are open and closed systems. The former includes ponds, tanks, lakes, and open raceway ponds (ORPs) and they are widely used for microalgae cultivation [4]. Among them, ORP is the most widely used due to its low capital cost and ease of operation, despite the difficulties of controlling contamination, pathogen attack and variables related to environmental conditions such as pH, temperature, and dissolved oxygen (OD) which impacts in productivity [8]. Low biomass productivity is a characteristic of this system when compared to the closed system. Despite that, less energy is required for this system and scaling-up its easier than closed systems[9].

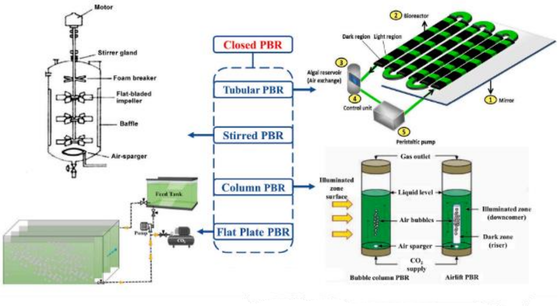


Fig. 2 - Microalgae cultivation closed systems. Adapted from [10].

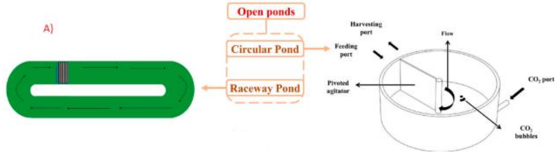
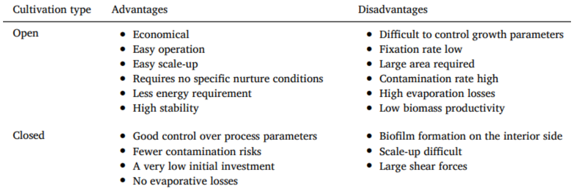


Fig. 3 - Microalgae cultivation open systems. Adapted from [10].

On the other hand, closed systems productivity is much higher because of the controlled parameters during the process such as pH, temperature, and OD. The closed system, also called photobioreactor (PBR), is divided in classes according to their shape: tubular PBR, stirred PBR, column PBR, and flat plate PBR and they usually are made of glass [10]. Tubular PBR is characterized for having closed tubing systems placed vertically or horizontally divided in two parts: one light region where microalgae grow, and the other is a dark region where there is a controlling step for the culture variables and oxygen removal [11]. Flat plate PBR have closed cuboidal shape chambers commonly designed as two parallel panels with a thin layer of microalgae suspension in the middle. They are difficult to scale-up, but their light utilization efficiency is high. Column PBR comes in two different forms depending on the gas injection: bubble column and airlift, and both have good mixing efficiency and gas exchange. Therefore, mass transfer and biomass production is increased. Although their energy consumption is low, their capital and maintenance requirements are high [12].



Cultivation type	Advantages	Disadvantages
Open	• Economical • Easy operation • Easy scale-up • Requires no specific nurture conditions • Less energy requirement • High stability	• Difficult to control growth parameters • Fixation rate low • Large area required • Contamination rate high • High evaporation losses • Low biomass productivity
Closed	• Good control over process parameters • Fewer contamination risks • A very low initial investment • No evaporative losses	• Biofilm formation on the interior side • Scale-up difficult • Large shear forces

Fig. 4 – Open and closed systems comparison. Adapted from [9].

3. Integrating microalgae bioremediation and biorefinery

The concept of biorefinery is new and related to petroleum refineries, which is different from the raw material it uses to produce commercial products and energy. By integrating microalgae bioremediation into the biorefinery process, high-value products are generated in addition to wastewater treatment, increasing the plant's profit and fitting into the concept of circular economy [13]. The simplified process is illustrated in Fig. 5.

The significant benefit of incorporating microalgae into wastewater for biorefinery purposes lies in its dual capacity to address environmental concerns while simultaneously generating biofuel alongside additional value-added compounds [14].

The essential components within the value chain of an integrated model for wastewater microalgal bioremediation and biorefinery consists in two main phases: upstream and downstream. The former comprehend cultivating microalgae and bioremediation discussed in the sections above, and the latter comprehend drying, cell disruption, fractionation, and conversion process for production of value-added compounds [15].

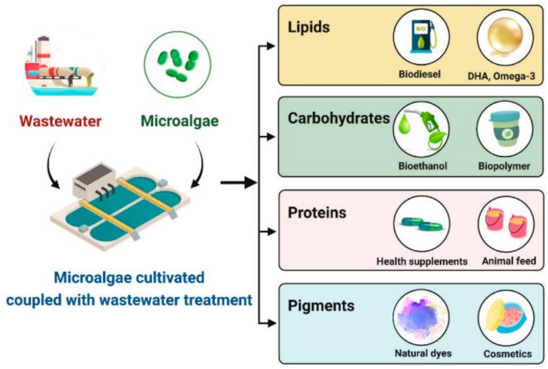


Fig. 5 –Integrating microalgae bioremediation and biorefinery [14].

3.1 Downstream

After cultivation microalgae using wastewater for bioremediation the harvesting phase will take place. There are several harvesting methods that will be chosen according to the plant scale and microalgae type. This part of the process comprises 20-30% of the total cost of the plant, therefore it is an important phase [16]. The most popular methods are filtration, centrifugation, flotation, flocculation, electro flocculation, gravity sedimentation, electrophoresis, and magnetic separation. Also, these methods can be combined with each other to maximize efficiency [13].

After harvesting, drying processes are used to maintain the stability of the microalgae for further use in extraction or storage. The most common methods used at this stage are solar, convection, spray and freeze drying. These processes are energy intensive and use techniques that can damage the microalgae structure, which has a major impact on post-treatment [10].

Cell disruption is the next phase of the process and is divided into main two general types: non-mechanical and mechanical which are illustrated in Fig. 6. These methods are important to maximize yields of microalgae's fractions, reduce operating costs and increase the process efficiency [17].

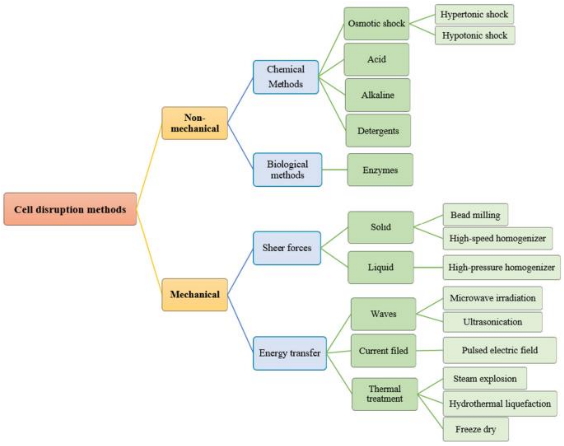


Fig. 6 – Methods of cell disruption [17].

The choice of which method to use will depend on the final product and the difficulties of the separation of contaminants due to the costs involved in this final process. Also, the intracellular products recovery from the microalgae is complex due to the rigid cell wall structure [15]. Enzymatic cell disruption plays a key role in solving this problem because it is highly selective for the intracellular compounds of microalgae and does not require elevated temperatures during the process, which is usually responsible for the loss of valuable products [17].

Fractionation of microalgal biomass is essential for the correct distribution of each component to its production line (biofuels or high-value products) increasing the economic feasibility of the biorefinery [15]. The composition of microalgae can include 8-69.7% carbohydrates, 5-74% proteins, and 7-65% lipids, and the following topics will discuss the use of these components for biofuel production and value-added products [13].

3.2 Biofuels

Biofuels are renewable energy sources derived from biomass as a feedstock and can be produced from microalgae biomass by various processes such as biochemical and thermochemical. Some examples of these biofuels are biodiesel, bioethanol and biomethane [18]. In the biochemical route, biodiesel is usually produced through a transesterification process that converts the lipids from the microalgae cell into biodiesel. In addition, bioethanol and biomethane can be obtained by fermentation and anaerobic of carbohydrates and anaerobic digestion of microalgae biomass, respectively. It is worth noting that the efficiency of these processes depends immensely on the disruption of microalgae cells due to the availability of substrate during the fermentation process [13]. The summary of these process is illustrated in Fig. 7.

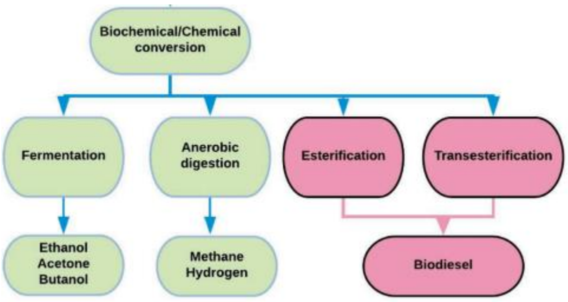


Fig. 7 – Biochemical route for biofuels production [13].

3.3 High-value products

Proteins, pigments, and polyunsaturated fatty acids (PUFAs) are some of the compounds of microalgae biomass which composition varies a lot from each species. Microalgae-based proteins are valuable sources of nutrition because of the essential amino acids content in their chain which can be used as health supplements. Commercial species of *Chlorella* and *Arthrospira platensis* are used for this production [19].

Pigments can be used in health care for their antioxidant, antimutagenic, antimicrobial and neuroprotective properties and they are also used in the formulation of cosmetics, food, and animal feed, namely, β-Carotene from *Dunaliella salina* [20].

PUFAs such as omega-3, omega-6, and docosahexaenoic (DHA) fatty acids are extremely important for human nutrition as they are part of the group of essential amino acids that humans need to obtain from diet. Research on PUFA from microalgal biomass is increasing due to the efficient production in some species such as *Chlamydomonas variabilis*, *Chlorella vulgaris*, *Haematococcus pluvialis, and Spirulina platensis*, the high potential for scale-up and the environmentally friendly aspect.

4. Conclusion

CWWT strives to remove hazardous, recalcitrant, and emerging contaminants while reusing all the nutrients present in the waste. Microalgal bioremediation promotes the efficient use of each nutrient, treats wastewater, and produces biofuels and value-added products in the process. This process is made possible by the robust and effective metabolism of microalgae, which can remove pollutants and grow. In addition, microalgae serve as a sustainable feedstock for biorefinery applications. The sustainability challenges of high operating costs and significant freshwater consumption in biorefineries can be addressed by using nutrient-rich wastewater for microalgal cultivation. This integrated bioremediation-biorefinery approach offers significant benefits, including pollutant removal, resource recovery, energy production, and carbon sequestration, thereby promoting a circular economy and enhancing sustainability.

5. References

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