



Review

# Recent Progress in Microalgae-Based Technologies for Industrial Wastewater Treatment

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Abstract: The water resource crisis and concerns with environmental pollution prompt the necessity to upgrade conventional wastewater treatment processes. The microalgae-based wastewater treatment process has shown many advantages that can fulfill the stricter demands for improved wastewater treatment. Microalgae cultivation can be carried out in different photobioreactors and under different operational conditions. The cultivation of the microalgae biomass provides the bioremediation of some targeted pollutants through uptake/digestion or biosorption, resulting in treated effluent and the production of biomass. This paper reviews the progress in microalgae-biotechnology for industrial wastewater treatment. A brief overview of microalga types/classification, the cultivation photobioreactors type, and conditions was first provided. Next, a comprehensive review of the bioremediation of industrial wastewater, including distillery, heavy metals, textiles, and emerging contaminants, was provided. Finally, perspectives on the potential scale-up of the technology and some critical considerations were also discussed.

Keywords: microalgae; wastewater treatment; bioremediation; biodegradation



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#### 1. Introduction

Water is the core resource for every living organism and a significant feedstock for any industry [1]. The utilization of freshwater generates many effluents or contaminated water that might be directly disposed of and cause significant health and ecological risks. The contaminated wastewater may contain various hazardous materials. In addition, a vast number of inorganic and organic nutrients are released into the environment, reflecting high COD and BOD [2]. It was reported that 50% of the population faces energy shortages, 70% need food, and 50% need water, with more than 75% wanting to decline CO<sub>2</sub> emission [3]. One of the most challenging issues is surface water pollution (i.e., hypertrophication), because the globe faces a water shortage. The available reservoir also contaminates wastewater (such as sewage, industrial, non-industrial, medical, and laboratory wastewater). In addition, hypertrophication is caused by the excessive loading of N and P and causes solid waste generation and unwanted emissions into the air [4]. It also leads to supporting pathogenic microbes that become a significant threat to aquatic life as well as the associated organisms [5].

Another class of heavy metal pollutant might be directly inhaled, ingested, or in contact with the skin, causing major health issues and escalating the risk of cancer [6]. The

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unexplored or partially explored contaminates named emerging pollutants (EP), which were still not appropriately addressed and had severe danger, received attention during the last five years. The scientist focused on EPs [6–10], their hazards, and processing to eradicate these contaminants.

When water treatment is a concern, adopting the most effective technique fulfills the purification objective. The conventional methods for addressing the purification process, such as physical, chemical, physio-chemical, membrane technology, and hybrid processes, are commercially used. Still, these processes have some flaws or disadvantages [11] and shall be evaluated thoroughly before their implementation. The most effective process is the one that has been commercially used on a large scale to alter the water characteristics using chemical dosing, which alters the turbidity, pH, TDS, and TSS. Some other processes include chlorination, coagulation/flocculation, ultraviolet light, and ozonation. However, all these technologies also have economic, recycling, and maintenance issues. The most common technology for water and wastewater treatments applied on a large scale is the biological method that depends on the metabolic activities of microorganisms to decompose and convert pollutants (including toxins) to biomass and associated gases (CH<sub>4</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, and SO<sub>2</sub>) [12–15].

The biological approach involves biodegradation with various microorganisms among bacteria, fungi, yeast, and microalgae. This process is not quite simple, involving the metabolic activity to utilize the toxins [16]. However, biological processes are considered more cost-effective, despite of several restrictions such as a huge area, long retention time, low biodegradation rate, limited design flexibility, and limited ranges of operation conditions [17].

Biological treatment is typically categorized as the secondary treatment for eliminating mainly biodegradable pollutants that remain after the primary process. Various microalgae genera such as *Scenedesmus*, *Chlorella*, *Botryococcus*, *Phormidium*, *Limnospira*, and *Chlamydomonas* have been reported as remarkable agents for bioremediation. *Scenedesmus*, *Chlorella*, *Euglena*, *Oscillatoria*, *Chlamydomonas*, and *Ankistrodesmus* have shown effective growth and tremendous tolerance against toxins [17].

Bioremediation is a process that uses the living organism to target the toxins and transform them into safe ends [18], whereas the biosorption process is the one used to target the toxins via electrostatic attraction on the surface of microalgae [19]. The microalgae-based technique utilizes both processes, as such gained significant attention for treating diversified wastewater [20]. Microalgae can reduce hypertrophication by converting it into biomass mass in the presence of sunlight [21]. Additionally, the microalgae collected from various ponds can be a food source for multiple products [22]. Another optimized version of biological treatment is the microalgae coupled with any other microbes to speed up the remediation process [23]. Hence, it can be said that microalgae utilization for wastewater treatment is a big challenge for conventional approaches if the limitation mentioned above is addressed and resolved.

#### 1.1. Classification of Algae

The tiered group of life into empires, *phyla* (divisions), groups, etc. precedes the concept of progression [24]. The grouping triggers dilemmas with classification of monophyly, specifically of the "lower" or less-complex uni- and multicellular types [25]. In spirit, numerous researchers have endeavored to reclassify the algae, but no effort has been adequate, resulting in numerous distinct categories that are currently available [26]. The continual retitling and moving of genes from one tier to another do not solve the issue without adequate representation (i.e., phylogenies) [27]. Currently, it is difficult to create a comprehensive catalog that accurately represents the monophyletic lineages of the *Protista* and *Chromista* kingdoms. Rather than attempting to create hierarchically-organized catalogs, it may be more beneficial to encourage the development of consortia that can easily be distinguished and added to as necessary [28].

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## 1.2. Major Phyla/Class Characteristics of Commercial Microalgal Genera

## 1.2.1. Chlorophyta

It is a systematic group consisting of green algae that survive in marine contexts, but few are also present in freshwater and on land [29]. Some microbes can still live in harsh atmospheres such as deserts, saline water, and arctic regions [30]. These algae appear green due to the huge availability of *chlorophyll*, which consists of a *paraphyletic* group. Few might appear in colonies consisting of *chlorophyte cells* and *apical flagella* that engaged during locomotion.

These algae might be asexual or sexual. Asexuality could occur by fission or fragmentation. In comparison, sexuality occurs by exchanging nuclei via conjugation tubes of two identical gametes referred to as *isogamy* and *oogamy* [31]. The gametophyte phase is the haploid phase, and the sporophyte phase is the diploid phase. When both the gametophyte and sporophyte phases involve multicellular forms of the species, then it is described as diplobiontic. When only the gametophyte generation is multicellular, it is described as haplobiontic [32].

# 1.2.2. Haptophyta

The *Haptophyta* or *Prymnesiophyta* have 50 genera with more than 500 identified living species [33]. They are unicellular, live via photosynthesis [34], and are primarily found in marine and tropical regions, but some are found in freshwater. These algae generally appear to have a golden-brown color due to the presence of *diadinoxanthin* and *fucoxanthin*, which are yellowish-brown pigments [35].

#### 1.2.3. Stramenopiles

It is a group of *eukaryotic* creatures, occasionally considered as signifying the *phylum* (division) of *heterokontophyte*, which is proposed based on the latest indication from molecular systematics [36]. The *stramenopiles* include diverse forms, ranging from unicellular (e.g., diatoms) or colonial forms to large multicellular forms, such as brown algae [37]. Many have been classified into separate *phyla*, including the diatoms, brown algae (*Phaeophyta*), oomycetes (*Oomycota*), golden-brown algae (*Chrysophyta*), and yellow-green algae (*Xanthophyta*) [38].

# 1.3. Microalgae and Their Organization

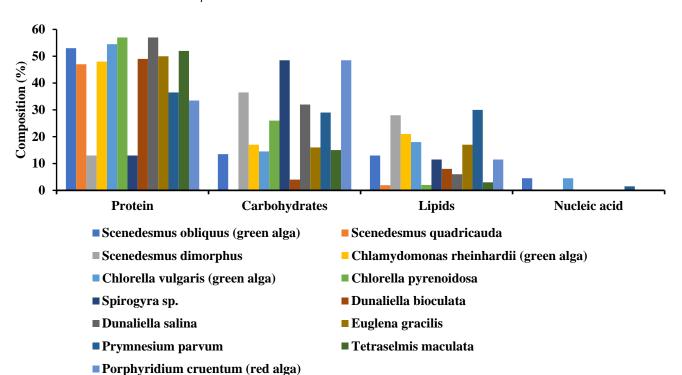
Algae can survive in diversified regions, from harsh deserts to favorable freshwater lakes, but they need some optimal conditions to grow [39,40]. Microalgae have been a source of multidisciplinary products, from pharmaceuticals to daily eating products [41]. The most impactful utilization of microalgae is effluent treatment and CO<sub>2</sub> eradication [42]. Its complex structure and cell organization consist of polysaccharides, lipids, pigments, proteins, vitamins, bioactive compounds, and antioxidants [43]. Algae are composed of organic contents such as protein, lipids, nucleic acid, and carbohydrates, but their proportion may vary with the variation in species (See Figure 1).

#### Difference between Micro- and Macro Algae

Microalgae and macroalgae are the two main kinds of algae based on cellularity. Microalgae are a unicellular algal genus that may be solitary or live in colonies [44]. Macroalgae are multicellular algal species [45]. They are commonly called "seaweeds" because they can grow profusely anywhere. Microalgae include the dinoflagellates, the diatoms, and other single-celled algal species [46].

Both microalgae and macroalgae are essential contributors to atmospheric oxygen through photosynthesis [47]. They do not have true stems, leaves, and roots. Macroalgae, though, are similarly multicellular, and the cells may function together, forming an organ. The *macroalgal thallus* is comprised of the following major parts: (1) the *lamina*, (2) *stipe*, and (3) *holdfast* and *haptera*. The *lamina* (also called the *blade*) is the leaf-like structure, the *stipe* is the stem-like structure, and the *holdfast* is the root-like structure [48]. It helps macroalgae to

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stay afloat. Another floatation-assisting organ is *float*. It is located between the *lamina* and the *stipe*.

Figure 1. Organic composition of some selected microalgae.

Microalgae are microscopic, single-celled, and mostly photosynthetic. While unicelled, a few can create colonies, such as strands or spheres with a similar genus. Their capability to photosynthesize is due to the existence of photosynthetic colorants [49]. The prevalent colorants inspire the shade of the algae in an algal cell. Thus, they are categorized based on green, red, or brown shades [50].

Algae are morphologically simple, chlorophyll-comprising, non-flowering, and typically aquatic plants of a large family with members including seaweeds and a range of uni- to multicellular organisms [51]. They are either *prokaryotes algae* with single standard deoxyribonucleic acid DNA in their formation or *eukaryotes* with double standard DNA in their makeup and are equipped with a nucleus and chloroplast. Microalgae exist in solitary or chain/group/colony contexts, depending on the species. Their sizes are 3–30  $\mu$ m, whereas those of the cyanobacteria are 0.2–2  $\mu$ m [52].

#### 1.4. Microalgae Cultivation

Microalgae cultivation can be accomplished in open ponds, tanks, raceway ponds, and controlled closed systems [53]. Extensive research has been conducted on microalgae cultivation [54–56]. From the literature, it has been explored that contamination with unwanted microalgae, high bacterial loads, and grazers is common in commercial-scale open-pond systems [57]. It has also been reported that the damaging impacts of rotifers on the culture *Tetraselmis*, *Chlorella*, *Nannochloropsis* and *Scenedesmus*, and *Amoeba* also damage diatoms. It is challenging to control the propagation parameters such as evaporation, culture temperature, etc. [58]. Those are the inherent challenges in implementing large-scale microalgae cultivation in an open-pond system.

Closed cultivation techniques, also called photobioreactors (PBRs) are the most promising approach for achieving quality cultivation because of the highly controlled parameters. This process can be optimized for genes. The extensive light availability decreases the contaminants concerns [54].

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The needs and demands can alter the basic principle of cultivation system design. An open pond is usually built with a circular shape or a gravity-driven flow, whereas the PBRs design has been improvised to accumulate the maximum light. There is limited literature available regarding the two-stage hybrid cultivation system. This cultivation system has been proposed to separate biomass growth from the lipid accumulation phase [56].

Researchers comparatively investigate an open and closed cultivation process. They used the same algal culture to cultivate. The airlift-driven, low-cost PBR was designed as a closed system. Open raceway ponds were designed as open systems. Critical parameters such as light intensity, nutrients, CO<sub>2</sub>, and water supply were examined. The investigation revealed that light accumulation is good in PBR, whereas in the race pond open system, the accumulation is relatively low due to hyperthropication. Fewer nutrients are required in PBR in comparison with the open system. The comprehensive outcomes are presented in Table 1 [59–63].

Table 1.	Compariso	n of differen	t microalgae	cultivation s	vstems
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System	Reactor/Vessel	Cons	Pros
	PBR (vertical)	Sophisticated construction design to address the hydrodynamics stress; tube diameter enhancement causes a decline in the exposed surface area	It has a smaller area, a high mass transfer rate, and less stress; low energy utilization; the potential to scale up; easy sterilization; reduced photooxidation and photoinhibition
Close	tPBR (Horizontal)	pH, DO, and CO <sub>2</sub> fluctuation among the pipe length; the wall might be foul, but it depends on many other parameters such as the mixing of the system; requires a	Large exposed area; viable for outdoor culture; good productivity
	PBRp	huge area for installation  No chambers are required if the reactor size needs to increase with a supporting structure; complicated to maintain the culture temperature; wall might be foul; hydrodynamic stress	Huge exposed area; viable for outdoor culture; fine algae immobilization; effective light penetration with good productivity; easy maintenance
Open	RPR	Difficult control and optimization of culture conditions; complex long-term cultivation; requires a huge area; low productivity; low light penetration	Very economical and simple; easy for cleaning and maintenance; can be large in volume.

PBR—Photobioreactor, tPBR—Tubular Photobioreactor, PBRp—Photobioreactor Plate, RPR—Round Ponds Racetrack.

# 2. Utilization of Microalgae for Wastewater Treatment

# 2.1. Distillery Waste

Distilleries are among the top industries based on the volume of discharged wastewater. It has been reported that manufacturing a unit liter of ethanol through a distillery process produces more than 10 L of effluent [64]. The ethanol produced from the distillation step is 8–12% pure, and the residue of this step is called vinasse/spend wash, which is organic. The cleaning and cooling water of the fermenter mixed with the spent wash produces the effluents. The distillery process has been improvised recently, but the economic aspects of effluent treatment are still not appropriately considered.

The effluent consists of rich organic constituents, including polyphenols, organic acids, and recalcitrant compounds such as melanoidins. The Environmental Protection Agency suggests limits for COD and BOD. There is a need for an effective effluent treatment design that is cost-effective to attain the recommended value. The specific properties of reported distillery effluents are summarized in Table 2. Many traditional approaches have been reported, but here, we focus on biological techniques (involving microalgae) used for effluent treatment.

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Source	Wastewater Generation (L/L Ethanol)	BOD (mg/L)	pН	Color	COD (mg/L)	Suspended Solids (mg/L)
Bottling plant	14	10	7.6	Hazy	250	150
Spent wash	14.4	36,500	4.6	Dark brown	82,080	615
Fermenter cooling	0.4	105	6.3	Colorless	750	220
Condenser cooling	2.88	45	9.2	Colorless	425	400
Floor wash	0.8	100	7.3	Colorless	200	175
Fermenter cleaning	0.6	4000	3.5	Yellow	16,500	3000
Other	0.8	30	8.1	Pale yellow	250	100

**Table 2.** Distillery Wastewater Characteristics.

Distillery wastewater treatment is challenging due to its very high organic content and recalcitrant compounds. Due to its recalcitrant and toxic nature, physicochemical processes were initially preferred for the treatment. However, the sludge generation and the cost were found to be the setbacks.

On the other hand, anaerobic, fungal, and thermophilic bacterial treatments were widely preferred. The raw distillery effluent treatment by biological processes was limited due to temporal variations in the loading rate and the inhibitive nature of phenolics and melanoidins constituents. Algal treatment has been emerging as an alternative to conventional treatment. The mixotrophic algal treatment requires less oxygen than other aerobic treatment technologies due to photosynthetic oxygenation.

Distillery waste contains beneficial constituents such as carbon, nitrogen, micro, macronutrients, and vitamins to aid microalgae growth [65]. Hence, it can be treated by simply growing microalgae, as demonstrated by numerous works reported earlier, summarized in Table 3. Some scientists isolated more than 25 algal strains from the distillery effluents. The algal strains included *Pediastrum* sp., *Scenedesmes* sp., *Perinidinium* sp., *Navicula* sp., *Chroococcus* sp., *Gloeocapsa* sp., *Merismopedia* sp., *Oscillatoria* sp., *Phormidium* sp., *Calothrix* sp., *Syctonema* sp., *Westiellopsis* sp., *Nitzschia* sp., *Spirulina* sp., *Anabaena* sp., and *Cylindrospermum* sp. [66].

In a diluted distillery effluent, the *cyanobacterium* growth was enhanced compared to a raw distillery effluent. It has been reported that when the effluent is diluted with inorganic media, the maximum biomass of 1.4 g/L was obtained during an algal growth [67]. This result was also authenticated during the growth of *Chlamydomonas reinhardii* in the appearance of vinasse [68]. The triacetylphosphate media with 1% of vinasse were observed to reach a biomass concentration of 0.543 g/L, whereas without vinasse, it was 0.093 g/L. *Micractinium* sp. and *Chlamydomonas biconvexa* growths were examined in raw, diluted, and purified vinasse in an Airlift Flat Plate Photobioreactor. It was noticed that the crude vinasse was not helpful for non-axenic algal growth due to fungal contamination and lesser light penetration [55]. The hydraulic retention time was 74 h with pH 8 to overcome the fungal contamination. The light penetration was increased via dilution or clarification using coagulation [69].

During the growth, biomass generation was reported at around 0.1 g/L/d in raw vinasse for an axenic culture. In a 50% dilution, the biomass generation in both genes increases to 0.177 g/L and 0.182 g/L, respectively, whereas in a clarified vinasse, it becomes 0.164 g/L and 0.222 g/L [55].

Chlorella vulgaris was employed in an Anaerobic Fluidized Bed Reactor (AFBR), in which the effluent consisted of 17 g/L of COD and a BOD/COD value of 0.22. OLR was set to  $0.14 \, \text{kg/m}^3$ , with a hydraulic retention time of 10 d [70]. The removal of COD, BOD, and Phosphorous was 98%, 98%, and 90%, respectively. The recommended source of N for anaerobic digestion was emitted NH<sub>3</sub> during digestion [71].

Krishnamoorthy et al. attempted to combine membrane technology with a biological approach. They located the microalgae unit of *Oscillatoria* sp. among the anaerobic digestor and reverse osmosis (RO) and found that the COD declined up to 55%, reducing the load on RO [70].

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System	Conditions	COD Removal (%)	Productivity or Biomass Conc. (g/L)	BOD Removal (%)	References
Stirred tank batch reactor	HRT = 30 h		101.1 mg/L/d	36.2	[72]
Bubbled column photobioreactor	$T = 30 ^{\circ}C$ , $I = 1 ^{\circ}k$ Lux	16	0.155 g/L/h		[73]
Cycle tubular photobioreactor	Flow = 110 mL/min, I = 3 k Lux, T = 27 °C, pH = 6	3.5–3.7	0.61 g/L/d	72–76	[74]
Algal pond	0.14 kg/m <sup>3</sup> /pond/d, HRT = 10.9 d, DO = 1.3–1.7 mg/L, T = 27–32 °C	98.2	0.01/d	98.8	[75]
Semi batch photoreactors	pH = 7, Aeration = $0.1 L/min$ , COD = $4 g/d$ , T = $27 °C$	>4		92	[76]

**Table 3.** Distillery effluent treatment using various reactor types in the presence of microalgae.

#### 2.2. Heavy Metals

Toxins biosorption and bioremediation, which engages a range of microbes involving yeasts, fungi, microalgae, and bacteria, has developed progressively as a replacement for conventional remedies owing to its ecological and economic advantages [77]. Microalgae-based bioremediation is an alternative to traditional treatment techniques for cleaning up contamination. The produced biomass has a varied assortment of microalgal biomass utilizations. The production of microalgae has long been utilized to remediate urban effluent [78].

Some microalgae species, which have extraordinary biologic traits involving high photosynthetic effectiveness and clean composition, can grow well in severe ecological conditions involving intense temperature, nutritional stress, the existence of metallic toxins, and high salinity. Among all microbes, owing to their high binding affinity, the accessibility of a vast number of binding sites, and their enormous surface area, microalgae are rapidly being utilized in the physio-redress of risky toxins [78,79].

The most straightforward approach to eradicating metallic toxins is biosorption. Biosorbents can be created from both living and non-living microalgae biomass [80]. Toxic metals can be carefully eliminated from the ecosystem by using microalgae for bioremediation. Microalgae have an additional benefit over higher plants because they grow rapidly and can be utilized to make biofuels and fertilizers [81]. Microalgae can also retrieve precious metal ions containing thallium, silver, and gold. The results of some of the literature data, detailed in Table 4, reveal the ability of algae to eradicate metallic toxins.

Microalgae	Toxins	Toxins Conc. (mg/L)	Biosorbent Formation Approach	Condition	Q (mg/g)	Removal Efficiency (%)	Isotherm	Reference
	Hg <sup>+2</sup>	100	Cells gathered from	pH = 6	72.2		Freundlich biosorption model	
Chlamydomonas reinhardtii Cd <sup>+2</sup>	100	logarithmic phase cultures	pH = 5.0	42.6		Freundlich biosorption model	[78]	
	Pb <sup>+2</sup>	100		pH = 6	96.3		Freundlich biosorption model	
Chlorella sp.	Cd <sup>+2</sup>	10	Algae immobilized in water hyacinth-derived pellets			92.45		[82]
Chlorella minutissima	Cd <sup>+2</sup> , Cu <sup>+2</sup> , Mn <sup>+2</sup> Zn <sup>+2</sup>	0.2–0.6 mM 0.2–0.6 mM 0.2–0.6 mM 0.2–0.6 mM	Dead (lyophilized) biomass		35.36 3.28 21.19 33.71			[80]
Chlorella Vulgaris	Cd <sup>+2</sup>	100	Live biomass		16.34	96.8	Pseudo-first-order model	[81]
Chlorella vulgaris	Cd <sup>+2</sup>	100	Isolated Green Algae	Dose = $1 \text{ g/L}$ , time = $2 \text{ h}$ , $T = 25 ^{\circ}\text{C}$ .	65.3	97.43	Langmuir isotherm model	[83]

Table 4. Metallic Toxins Eradication Using Algae.

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Table 4. Cont.

Microalgae	Toxins	Toxins Conc. (mg/L)	Biosorbent Formation Approach	Condition	Q (mg/g)	Removal Efficiency (%)	Isotherm	Reference
Chlorella vulgaris	Cd <sup>+2</sup>	100	Dead Biomass	t = 105 min,	16.65	95.2	Pseudo-Second-order model	[81]
Chlorella Vulgaris	Fe <sup>+2</sup>	30–300	Suspended cells		74.54			
Chlorella Vulgaris	$Zn^{+2}$	30–300	Suspended cells		69.19			
Chlorella Vulgaris	$Mn^{+2}$	30–300	Suspended cells		65.1			[84]
Chlorella Vulgaris	Fe <sup>+2</sup>	30–300	Immobilized cells	Dose = $0.4 \text{ g/L}$ , t = 300 min,	128		Langmuir and D-R	
Chlorella Vulgaris	$Zn^{+2}$	30–300	Immobilized cells	pH = 6.0, T = 25 °C	115.5		isotherm model	
Chlorella Vulgaris	Mn <sup>+2</sup>	30–300	Immobilized cells		105.25			
Nostoc sp.	Pb <sup>+2</sup>	100-800	Freshly collected from ponds, ditches, etc.; dried before use	t = 90  min, pH = 5.0, Dose = 0.5  g/L t = 70  min,	93.5		Langmuir Isotherm and second-order kinetics Langmuir Isotherm	[85]
Oedogonium sp.	Pb <sup>+2</sup>	100-800		pH = 5.0, $Dose = 0.5  g/L$	145.0		and second-order kinetics	
Parachlorella sp.	Cd <sup>+2</sup>	18–180	Biomass from cultured microalgae	pH = 7, T = 35 °C	96.2		Langmuir model Kinetics: pseudo-first-order	[86]
Parachlorella sp.	Cd <sup>+2</sup>	18-180	O	pH = 7, T = 35 $^{\circ}$ C	90.72		pseudo-mst-order	
Scenedesmus obliquus	Cd <sup>+2</sup>	2.5–7.5	Living cells immobilized in a loofa sponge	Flow = $15 \text{ mL/min}$ , t = $15.5 \text{ h}$	38.4			[87]
Scenedesmus obliquus CNW-N	Cd <sup>+2</sup>	25–200	Biomass harvested by centrifugation and concentrated by lyophilization	Aeration with $2.5\% \text{ CO}_{2}$ , $pH = 6$ , $T = 30 \degree \text{C}$	68.6		Langmuir model Kinetics: pseudo-second order	[88]
Scenedesmus quadricauda	Co+2	5-40	Living cultures		2.14-52.48			
Neochloris pseudoalveolaris	Cr <sup>+3</sup>	5–40	Living cultures		81.98			
Neochloris pseudoalveolaris	Pb <sup>+2</sup>	5–40	Living cultures		4.26			[89]
Neochloris pseudoalveolaris	Cd <sup>+2</sup>	5-40	Living cultures		2.96			
Neochloris pseudoalveolaris Neochloris	Ni <sup>+2</sup>	5–40	Living cultures		55.71			
pseudoalveolaris	Mn <sup>+2</sup>	5–40	Living cultures  Collected from a pond,		75.20		I an amazin igath anna	
Spirogyra sp.	Pb <sup>+2</sup>	200	sun-dried, and then oven-dried at 70 °C for 24 h	pH = 5.0, t = 100  min	140 mg/g		Langmuir isotherm Kinetics: pseudo-second-order Endothermic	[90]
Spirulina platensis	Cr <sup>+6</sup>	0-156.3	Freshly harvested biomass	pH = 6		90	Langmuir isotherm model	[91]
Spirulina platensis	Pb <sup>+2</sup>	100	Dead biomass	pH = 3.0, $T = 26 ^{\circ}\text{C},$ t = 60 min, Dose = 2 gm		>90		[92]
Spirulina sp.	Cd <sup>+2</sup> *	3.81	Cells lyophilizate	2000 - 2 gm	0.463			[93]
Spirulina sp.	Hg <sup>+2</sup> *	0.76	Cells lyophilizate Algae collected from irrigated water	t = 20 min,	1.340	\$00		
Ulothrix zonata	Cu'	5–50	channels; dried at 100 °C for 5–6 h	pH = 4.5		>80		[94]

<sup>\*</sup> Discharge from copper smelter and refinery, with high concentrations of Hg and Cd.

There are only a few reports on the use of microalgae for the biosorption of metals from actual industrial discharges. Freely suspended and restrained *Chlorella vulgaris* was shown to be effective in eliminating  $Fe^{+2}$ ,  $Mn^{+2}$ , and  $Zn^{+2}$  from palm oil mill effluent by biosorption [84]. It was stated that *Spirulina* sp. could eliminate residue components, specifically  $Hg^{+2}$  and  $Cd^{+2}$ , from industrial waste (copper smelter and refinery) by biosorption and bioaccumulation. El-Sheekh et al. [95] indicated that *Nostoc muscorum* and *Anabaena subcylindrical* could grow in discharge from salt and soda factories and sewage effluent, eliminating metals such as  $Cu^{+2}$ ,  $Co^{+2}$ ,  $Pb^{+2}$ , and  $Mn^{+2}$ .

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#### Insight into the Mechanism

Various heavy metals such as Cu<sup>+2</sup>, Zn<sup>+2</sup>, Ni<sup>+2</sup>, Fe<sup>+2</sup>, and many others are effectively utilized as micronutrients for microalgae. This metallic content is vital for microalgae cell metabolic activity. But some other heavy metals such as mercury, titanium, cadmium, silver, and gold are not helpful for microalgae growth and behave as toxins for metabolic activity. Microalgae are promising and effective in bioremediation due to outstanding attributes such as survival in harsh environments, the ease of growth, superb binding affinity, effective area, and ecologically friendliness, and dead microalgae can be used for many other purposes [96].

The microalgae mechanism has been elaborated in different dimensions such as gene regulation, chelation, and the desorption of microalgae boost with a decline in pH. The eradication of heavy metal with microalgae is done in a two-step process: (1) rapid, reversible, and passive adsorption onto the cell surface (metallic ions sorb due to electrostatic attraction to the functional group located at the cell wall), followed by (2) a slow, irreversible, active process, involving metallic ion mobility from the cell wall to the cell membrane rather than to *cytoplasm*. The initial step occurs in both alive and dead cells, whereas the second step only takes place in living cells [97]. The eradication mechanism of toxins by the microalgae mechanism is shown in Figure 2.

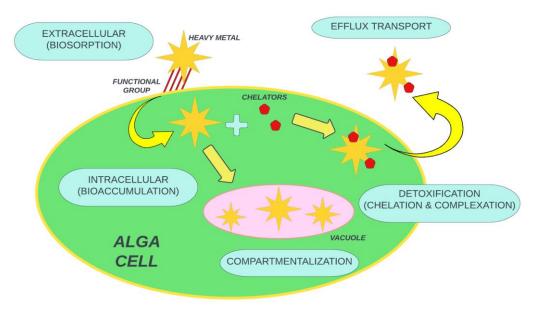


Figure 2. General eradication mechanism of toxins by microalgae.

#### 2.3. Textile Waste

Microalgae of unicellular and filamentous genera have been explored for biosorption to remove dyes, as summarized in Table 5. Most findings were accomplished utilizing non-viable algal biomass on a dye solution. In one study, the algal biomass of *Microspora* sp. after lipid extraction was noticed to be an effective biosorbent for methylene blue, eliminating up to 100% of the dye in 24 h under stirring of 150 rpm [98].

Defatted *Scenedesmus dimorphus* was also assessed for its effectiveness in eliminating methylene blue by biosorption [99]. The maximum adsorption capacity was analogous to raw and acid-pretreated biomass. Waste residue from the algal biodiesel industry was effective as a biosorbent for dye removal. For instance, it has been testified that biochar derived from *Spirulina platensis* after oil extraction for biodiesel was noticed to be an inexpensive biosorbent for methylene blue [100]. In another analysis, Jing et al. [101] revealed that biochar derived from the residual biomass of *Ulothrix zonata* after pigment extraction might be treated as an affordable biosorbent for malachite green, quartz violet, and Congo red.

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**Table 5.** Dye eradication from textile wastewater using microalgae.

Dye	Microalgae	Concentrations (mg/L)	Conditions	Removal (%)	COD & BOD	Q (mg/g)	Isotherm	References
Malachite green	Chlorella sp.	2.0–20.0	T = 25 °C, pH = 3.0–11.0,			9.45–33.7	Pseudo-second-rate model Langmuir and	[102]
Methylene blue	Chlorella pyrenoidosa	10–60	Dry Biomass		BOD = 87%	7.2–29.2	Freundlich Kinetics Pseudo-second- order Langmuir and	[103]
Methylene blue	Chlorella pyrenoidosa	10–60	Wet Biomass		BOD = 80%	5.6–18.24	Freundlich Kinetics Pseudo-second order	
Remazol Black B (RB)	Chlorella vulgaris	800	$T = 39 ^{\circ}\text{C},$ pH = 2			419.5	Freundlich, Langmuir,	[104]
Remazol Red (RR)	Chlorella vulgaris	200	$T = 35 ^{\circ}C$ , pH = 2			52.3	Redlich-Peterson, and Koble-Corrigan	[101]
Remazol Golden Yellow RNL (RGY))	Chlorella vulgaris	200	$T = 25 ^{\circ}\text{C},$ pH = 2			33.5	O	
Lanaset Red 2GA	Chlorella vulgaris	0–60	F	44				[105]
(Supranol Red 3BW	Chlorella vulgaris	0–60		44				[100]
Supranol Red 3BW	Chlorella vulgaris	20		33	COD = 62%		Langmuir and Freundlich models	[106]
Methylene blue	Microspora sp.	20–2500	pH = 7, Dose = 7 g/L	94.8		139.11	F 11: 1 a	[107]
Malachite green	Pithophora sp.	20–100	Raw Algae			64.4	Freundlich & Langmuir Isotherm Model	
Malachite green	Pithophora sp.	20–100	Thermally Activated @ 300 °C for 50 min			117.6	Freundlich & Langmuir Isotherm Model	[108]
Methylene blue	Scenedesmus dimorphus	1–5	Raw Biomass			6.0	Pseudo Second-Order	[99]
Methylene blue	Scenedesmus dimorphus	1–5	Defatted Biomass			7.73	Kinetics	[22]
Methylene blue	Scenedesmus dimorphus	1–5	Acid-Treated Biomass T = 5 min,			7.8		
Methylene blue	Spirulina platensis	30–200	Biochar, 0.2 g/100 mL, pH = 7	85.2		57.80	Freundlich model Pseudo-second- order	[109]
Methylene blue	Spirulina platensis	30–200	T = 5  min, Raw Biomass, $pH = 7$	86.4		4.17	model	
Azo dye	Spirogyra sp.	15	$T = 30 ^{\circ}\text{C},$ pH = 7	35.3-64		5.8	Langmuir model	[110]
Reactive Yellow 22	Spirogyra sp.	100	t = 12 h			400		[111]
Synazol Red dye	Aspergillus Niger fungus	15	pH = 3, $T = 30 ^{\circ}C$ , Dose = 8  g/L,	88				[112]
	Spirogyra sp.		t = 18  h	85				
Methylene blue	Wet torrefied	200	Dose = 1 g/L, t = 120 h, pH = 3.7	91		113.5	Langmuir model	[113]
Congo red	Chlorella sp.	200	Dose = 2 gm/L, t = 4 h, pH = 3.7	90		164.3	zangmun model	[113]

Different studies highlighted the potential use of microalgae for the biosorption and bioremediation of textile wastewater and the removal of dyes [111]. Further, it can be added that marine microalgae are promising candidates for remediating inorganic and organic toxins due to their versatile metabolic activities and microalgae organization.

It has been proven that microalgae are impactful biosorbents for eradicating dyes and other contaminants present in textile waste such as COD, colors, and organic and inorganic toxins. This process has advantages such as economics, a green process, huge availability, and high removal rates with viable process parameters. The optimal result can be achievable by manipulating the parameters such as the microalgae dosing amount, the pH, the temperature, the pretreatment of microalgae, the residence time, and the pollutant concentration in the effluent.

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#### 2.4. Emerging Pollutant

EPs are identified as threats to the environment, health, and living beings. Many approaches have been utilized recently to eradicate EPs from the effluent, but adsorption is the most economical and easiest way to deal with such toxins. Recently, microalgae have received much attention due to their capability to eradicate many toxins, including EPs such as pharmaceutical contents, personal care products, and non-pharmaceutical contents present in effluent, due to the economic, easy, and innovative solution in comparison with traditional approaches [114]. Microalgal materials have been used to eradicate EPs. It was found that they were much better than other conventional processes.

#### 2.4.1. Pharmaceuticals

Pharmaceutical-based EPs eradication has become a significant concern, and researchers have focused on its remediation approach. Microalgae have been considered as an adsorption agent for removing these toxins. However, the research was mostly conducted on a lab scale with optimum conditions, but it is the demand of the current era to scale up this approach for the eradication of toxins commercially. However, the industrial application of microalgae for the remediation of EPs is still unclear because of a significant gap between lab outcomes and commercial applications. Therefore, the comprehensive data encapsulated in Table 6 show the potential of microalgae to eradicate these toxins via bioremediation, which will help to bring the lab data to scale up this process.

**Table 6.** Emerging Pollutant Removal using Microalgae.

Active Ingredients	Effluent	Microalgae Species	Removal%	Condition	Effluent Conc. (mg/L)	Reference	
sulfadiazine	synthetic	– <i>Chlamydomonas</i> sp. Tai03	35	$T = 25 ^{\circ}\text{C}$ , $CO_2 = 2\%$ , $I = 250 \mu\text{mol}$ $m^2 \text{s}$ 1, $t = 56$ d		[115]	
ciprofloxacin	synthetic	— Chumyuomonus sp. 14103	65	T = 25 °C, CO <sub>2</sub> = 2%, I = 250 μmol m <sup>2</sup> s 1, t = 5–6 d		[110]	
sulfamerazine			75				
sulfamethoxazole			60				
sulfamonomethoxine			47	_			
trimethoprim			40				
clarithromycin		H. pluvialis	-20			[116]	
azithromycin	synthetic		48	T = 25 °C, t = 40 d	0.02		
roxithromycin			35				
lomefloxacin			70				
levofloxacin			39	_			
flumequine			40				
paracetamol			41		25	- [117]	
salicylic acid	Mann and Myons	all II II I	93	$T = 25 ^{\circ}\text{C}$ , pH = $(7.5 - 0.5)$ ,			
paracetamol	Mann and Myers	Chlorella sorokiniana	69	t = 144 h			
salicylic acid			98		250		
sulfamethazine	Sterilized Bold's	Scenedesmus obliquus	62.3	T = 27 °C, t = 14 d	0.25	[118]	
sulfamethoxazole	Basal	Sceneuesmus obuquus	48.5	1 = 27 C, t = 14 u	0.25	[110]	
cefradine	synthetic	Chlorella sp. L166	97.7		5–100	[119]	
cerradine	synthetic	Scenedesmus quadricauda	98.5		5–100	[119]	
paracetamol			11.6				
ibuprofen	synthetic	Nannochloropsis sp.	12.1	t = 1 d	300	[120]	
olanzapine	symmetic		32.4				
ceftazidime		Escherichia coli	90	t = 7 h	100	_	

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Active Ingredients	Effluent	Microalgae Species	Removal%	Condition	Effluent Conc. (mg/L)	Reference
diclofenac		Nannochloropsis oculata CCAP 849/7	59–92	T = 25 °C,		[121]
	synthetic	Scenedesmus acutus UTEX 72	12.2–26.5	Aeration = $0.3 L/min$ , $CO_2 = 7\%$ , t = $25 d$	0.33	
		Scenedesmus obliquus CCAP 276/2	15–28			

#### 2.4.2. Non-Pharmaceuticals

Industrial effluent can contain substances that limit microalgae growth. When this issue persists, it becomes a challenge because the kind of effluent and its constituent can inhibit the eradication process; for example, olive mill effluent has antibacterial properties with phytotoxicity due to the high amount of phenolic content [122].

Researchers have attempted to deal with such challenges, and it was noticed that genetically adaptive microalgae could survive in harsh effluents such as herbicides, mining effluent, antibiotics, and many other toxins [20]. Studies reveal that preliminary microalgae exposure could eradicate cefradine better than wild genes [123]. In other findings, it has been reported that acclimated microalgae strains could be favorable to raw effluent. *Chlorella luteoviridis* and *Prachorella kessleri* were acclimated to municipal effluent within an acclimation duration of 2 months [124]. The acclimation to effluent tolerance was interlinked with an accumulation of carotenoid pigments. It was enhanced with ascorbate peroxidase activity. Isolated *P. kessleri* from effluent revealed good capabilities to survive in a diversified atmosphere [125].

The major problem faced during EPs eradication was the appearance of EPs in tiny concentrations. It was observed that the  $EC_{50}$  (the concentration of ECs at which 50% of microalgae growth is inhibited) was very high and had a magnitude greater than the ECs concentration in the effluent [126]. It was authenticated previously in 2016 by a group of researchers when they employed *Chlorella vulgaris* inhibited by diazinon with a maximum eradication of 94% at 20 mg/L [127]. Table 7 reveals the findings of different researchers at a glance, which show the ability and viability of microalgae in eradicating non-pharmaceutical Eps.

**Table 7.** Non-pharmaceutical emerging pollutant removal using microalgae.

Toxins Origin	Active Pollutant	Microalgae	Medium	Condition	Initial Conc. (mg/L)	Removal%	Ref.
	Methylisothiazolinone	Scenedesmus sp. LX1	BG 11	$T = 25 ^{\circ}\text{C},$ $I = 50-60 \mu\text{mol m}^{-2} \text{s}^{-1},$ t = 4 d	3	100	[128]
	Triclosan	Nannochloris	Milli-Q water	(12/12 h) light/dark cycle, t = 7 d		100	[129]
Personal care products	Triclosan	Chlorella pyrenoidosa	Acetate carbon source	T = 22 °C, I = 4000 Lux, (8/16 h) dark/light cycle, t = 6 d	0.1-0.8	72.2	[130]
	Triclosan	Microalgal consortium		t = 5 d	8	74.68	[131]
	Nonylphenol	Chlorella vulgaris	Bristol	$T = 25 ^{\circ}\text{C},$ $I = 40.1 \text{mol m}^{-2} \text{s}^{-1},$ t = 168 h	0.5–1	80	[132]
Surfactant	4-Nonylphenol	Arthrospira maxima and Chlorella vulgaris	BG11	Aeration = $1.5 L/m^2$ , T = $21  ^{\circ}C$	9.29	96	[133]

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Toxins Origin	Active Pollutant	Microalgae	Medium	Condition	Initial Conc. (mg/L)	Removal%	Ref.
	Para-xylene	Rhodomonas sp. JZB-2	F/2	$I = 60 \mu mol m^{-2} s^{-1},$ 14/12 h cycle (light/dark), $t = 6 d$	9.682	100	[134]
Industrial chemicals (aromatic hydrocarbons)	19 different chlorinated phenolic compounds (9–90)	Scenedesmus obliquus	Liquid culture medium	$I = intensity:$ $50-60 \ \mu mol \ m^{-2} \ s^{-1},$ $(light/dark)$ $cycle = 12/12 \ h$ $light/dark, T = 30 \ ^{\circ}C,$ $t = 6 \ d$		90	[135]
	Phenanthrene			I = 2500 Lux, (light/dark)		90	
	Fluoranthene Rhodomonas baltica	Conway medium	cycle = 12/12 h		70	[126]	
	Pyrene	Pyrene	dark/	dark/light, T = $18 ^{\circ}$ C, t = $6 ^{\circ}$ d			[136]
	Neonicotinoids	Scenedesmus sp.		$I = 100 \ \mu mol \ m^{-2} \ s^{-1}$		71.24	

Biperiden and Trihexyphenidyl were eradicated by *Coelastrella* sp. with 92% and 94% effectiveness, respectively. Bioremediation/biosorption took place due to the biotransformation of complexes into simple units. Compared with biosorption or bioaccumulation, the biodegradation process can deal with such complex EPs by facilitating the complexes inside the algal cells [137]. Hence, it can be assumed that the EPs eradication using microalgae species is quite time-consuming, with huge algal sludge formation and sensitive parameters control. Besides all these concerns, there is a chance to compete with the conventional approaches of eradicating EPs due to the cheaper, economical, viable, and limited utilization of hazardous chemicals for treatment.

#### 3. Parametric Evaluation of Bioremediation and Biosorption

Algae utilization for any toxin's removal needs its cultivation process intact. The cultivation process depends on the light intensity, mixing, nutrient, gas exchange, temperature, pH, etc. It can be carried out by adopting any metabolic methods, including mixotrophic, photoautotrophic, and heterotrophic methods, along with any cultivation system. Some of the essential factors that impacted the process are discussed in this section.

#### 3.1. Temperature

Microalgae growths are strictly dependent on temperature. Each microalgae species has its own optimal growth temperature; for example, the upper temperature of *eukaryotic microalgae* is 62 °C and above 75 °C. No photosynthetic microbes' growth was reported due to chlorophyll sensitivity toward high temperatures. Optimal temperature conditions are necessary because they are linked with carbon preoccupation. After all, a higher temperature will cause an increase in CO<sub>2</sub> and sorption, but it can inhibit the metabolic respiration system of microalgae and imbalance cells' energy. The cell size of microbes also shrinks with the temperature increment, limiting the algal growth [138].

Many studies revealed that with an elevation in temperature up to  $40\,^{\circ}$ C, the metabolic activity of microalgae could fluctuate, which leads to fluctuation in the toxin's eradication process. Therefore, it has been recommended for the bioremediation process that the optimal temperature condition would be ambient. The ambient condition is cost-effective and eases the process design when dealing with wastewater [139].

Even though various authors indicated a rise in metallic ion abstraction with rising temperatures, others have asserted a lessened uptake. For instance, the extent of Ni<sup>+2</sup> adsorbed to dry biomass of *Chlorella vulgaris* raised with increasing temperatures [140], but there was a decrease in Cd<sup>+2</sup> sorption by *Oedogonium* sp. at elevated temperatures [82]. Other studies reported no impact of temperature on metal sorption.

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## 3.2. Light

Light is vital in algal growth, cultivation, and toxins eradication. This is because the light directly impacts the photosynthesis process. Light energy is converted into chemical energy as chlorophyll absorbs photons to produce ATP and NADPH. Similarly, the light intensity decline causes photoinhibition and photooxidation, which adversely impacts microbes' cells [141].

During the bioremediation process, light intensity is not the only reason to manipulate the eradication process. Some other factors are also associated with it. The literature reveals that the light intensity majorly increases the removal rate of toxins, but some species might show a reverse process. The  $CO_2$  uptake enhances by increasing the light intensity. Raeesossadati et al. employed light intensity from 100– $300 \, \mu mol/m^2 s$  to study the impact of light. They found that the maximum eradication of toxins from real industrial effluent using algal biomass was achieved at  $200 \, \mu mol/(m^2 s)$ . When the intensity increases to  $300 \, \mu mol/(m^2 s)$ , it leads to a photoinhibition [142].

#### 3.3. Nutrients

Microalgae culture needs macronutrients, vitamins, and trace elements. The literature revealed that the optimal cultivation media for any microalgae species would be Redfield (C: N: P = 106:16:1), but it is flexible to metabolism requirements with various environmental situations [143]. The most impactful nutrient is discussed below.

#### 3.3.1. Carbon

Microalgae biomass has the primary element carbon up to 65%, but in some species and culture situations, it does not exceed 18%. Most microalgae species consist of 50% of C, but it rigidly bound this limit for other nutrients [144]. Most of the inorganic carbon is utilized by microalgae cells via the Calvin Cycle. This uptake is achieved due to the membrane diffusion of CO<sub>2</sub> into microalgae cells. The CO<sub>2</sub> uptake depends on the media pH; carbon is metabolized due to active transport rather than diffusion. At a high pH, CO<sub>2</sub> is obtained due to calcification, which consists of the precipitation of CaCO<sub>3</sub>. It has been noticed that the CO<sub>2</sub> uptake to fixate the C into algal units boosts the process of eradication.

# 3.3.2. Nitrogen

N is the second main constituent; a significant amount is in microalgae. It has been noticed that the amount in dry microalgae was 1–14%, which is also a vital part of DNA, RNA, proteins, and pigments [145]. The N requirement is fulfilled by dosing ammonium salts, nitric oxide, nitrogen dioxide, and organic sources, such as urea [146]. Microalgae cells can bear up to 100 mM, but a higher concentration adversely impacts microbes' growth. It was noticed that the culture *Botryococcus braunii* reached the optimal concentration of 4 mM in 10 d, but it was inhibited when the concentration was increased up to 8 mM. The CO<sub>2</sub> uptake also boosts the N uptake. Similarly, the high pH value is effective and favorable for nitrogen uptake for microalgae growth [147].

#### 3.3.3. Other Nutrients

Other constituents also help cultivate microalgae such as  $Mg^{2+}$ , which is present in culture media from 0.35% to 0.7%. It helps to activate various enzymes; a pH higher than 11 supports microalgae flocculation. Some other minerals such as  $Fe^{+2}$ ,  $Ca^{+2}$ , and P also help with algal growth [148].

## 3.3.4. PH

Microalgae metabolic activity depends on pH because it can regulate ions uptake, enzyme activity, and microalgae growth. The effective pH for marine contexts is 7.9-8.3, and for freshwater, it is 6.0-8.0. Many microalgae can also survive beyond this pH range; for example, *Chlorella vulgaris* can tolerate elevated pH, i.e., pH =  $10 \, [149]$ . Finally, research shows that a high pH inhibits the cell cycle and triggers lipid accumulation.

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The pH is one of the most important parameters that affect the the biosorption efficiency of algae for heavy metal eradication and EPs removal [16]. The pH impacts both microalgae growth as well the eradication of toxins. It also affects the color and the solubility of some dyes. The interface between the sorbate and biosorbent is affected by the pH of an aqueous solution. The biosorbent surface has numerous functional groups such as carboxyl, hydroxyl, amino, and phosphates. As such, the net charge of the biosorbent is dependent on pH [150].

If the pH decreased, the biosorbent surface posed more positively charged sites favorable for the adsorption of anions via the electrostatic attraction. At lower and higher pH values, the biosorbent surface becomes a net positive charge and net negative charge, respectively [120]. Therefore, at lower pH values, the biosorbent surface binds with anionic ions and dyes, while at higher pH values, the biosorbent surface is attached to cationic dyes or cations. It has been observed that the uptake of Sandocryl Golden Yellow C-2G by green seaweed *Caulerpa scalpelliformis* increased from 17 to 27 mg/g with an increase in pH from 3.0 to 8.0. The initial pH of the solution appreciably influenced the biosorption of dyes due to a change in the surface properties of the adsorbent [151].

The pH of the medium affects the  $CO_2$  chemical equilibrium species and hence the alkalinity of the medium. Each species of microalgae has a pH range in which growth is optimal, depending on which chemical species are more accustomed to assimilating. The pH in most microalgae is between 7 and 9, with an optimum between 8.2 and 8.7 [152].

# 3.4. Nutrient Recovery in the Form of Valuable Biomass

Microalgae require various nutrients for their growth. It has been observed that nitrogen and phosphorus are vital parts of nutrients for growing microalgae successfully. By observing this, various researchers used fertilizer to grow microalgae, but this leads to uneconomical consequences. Various process industries' effluent is rich in microalgae nutrients, which was alternatively used for microalgae biomass generation, as per life cycle analysis [152,153]. It has been reported that microalgae production increases in such effluent where the concentration of phosphorus and nitrogen is present in abundant quantities. Biomasses (generated microalgae) can be used in biofuel production, biofertilizers, animal feed additives, and cosmetic products.

## 3.4.1. Nitrogen Recovery

Nitrogen is essential content for amino acid, nucleic acid, and pigment synthesis. It has been noticed that in the wastewater treatment plant aided by microalgae, thew assimilation of Nitrogen is the major mechanism rather than ammonia stripping or denitrification. The assimilation process needs active transport to incorporate Nitrogen forms into the cell [154]. The presence of bacteria in wastewater shows various benefits; for example, when microalgae is used for wastewater remediation, aerobic bacteria oxidize proteins and nucleic acids to  $NH^{4+}$ . However, when the  $NH^{4+}$  concentration exceeds 100 mg/L and the pH value exceeds 8, some portion of  $NH^{4+}$  turns to  $NH_3$ , which leads to toxicity for algae. The nitrogen uptake rates reported in the literature varied from 0.1 to 65 mg of TN/L of pBR [155].

#### 3.4.2. Phosphorus Recovery

Phosphorus is the key element for microalgae for metabolic activity, energy transfer, phospholipids, and DNA synthesis. In traditional wastewater systems, phosphorus is chemically removed via precipitation. Moreover, under specific conditions, microalgae can be induced to polyphosphates inside the cell independently of biomass productivity. When microalgae are exposed to higher energy (light), this allows for elevated phosphorous removal. On the contrary, microalgae grow in limited phosphorous, which results in the enhancement of carbohydrates and lipids [156].

The accumulation of one or more compound depends on microalgae species rather than on operational conditions. Species such as *chlorella*, *spirulina*, and *Scenedesmus* accu-

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mulate lipids inside the cell. Phosphorous uptake was noticed to be up to 40 g of soluble phosphorous per kg of produced biomass. However, the general demand of phosphorous is in the range of 10–15 g/kg of microalgae. The optimization of the reactor configuration can lead to maximizing the uptake rates of nutrients [157,158].

#### 3.4.3. Energy Savings

The microalgae-based technique is associated with the production of feedstock for biofuel production or many other valuable products. Therefore, the energy consumption and production cost are related to these processes. Very limited work has been carried out to investigate the energy consumption and production costs of microalgae biomass (during cultivation, harvesting, and drying) in a full-scale setup. It has been reported that the energy production from microalgae was only viable if the microalgae aided wastewater treatment coupled with a biorefinery. Microalgae-based systems' feasibility is highly related to their energy demand and majorly focuses on biomass production for valorization [159].

However, the microalgae-based technique for wastewater treatment remediation cannot compete with conventional processes, as the energy demand for these systems is approximately 500 Wh/m³ of the wastewater treated, two magnitude higher than the conventional process of 1.5–8 Wh/m³ [160]. Therefore, there is a need for a comprehensive and extensive economical evaluation of microalgae-based systems for wastewater treatment coupled with the biorefining process and to compare this with the conventional one to optimize the process and make it viable for a large scale.

# 3.5. Comparative Analysis of Microalgae Remediation and Other Processes

Toxins eradication has also been carried out by various chemicals and physical, physicochemical, hybrid, microwave-assisted, electrostatic-assisted, biosorption, biodegradation, and phytoremediation processes. Every process has some advantages and disadvantages. Some are economical, some are easier, some are complex, and some are green processes. The bioremediation process is a hot topic due to its simplicity. It has many advantages; for example, it reduces the use of chemicals and makes the process green. The comparative investigation is presented in Table 8.

Table 8. Comr	parison of Conv	entional to C	Green Processes	for toxins e	eradication
Table 0. Comp	Janison Of Conv	critioriar to c	JICCII I IOCCOOCO	ioi toanis t	.iauicauoii.

Process	Advantages	Disadvantages:	
Carbon Filtration	Economical and easy maintenance. Effective for organic and inorganic toxins	Not affected by toxins that attract carbon; needs the replacement of the filter when the active sites are fully accumulated; ineffective for pathogenic bacteria and viruses	
UV light	A harmless non-chemical process; simple maintenance and installation; economical and energy-efficient; effective for the eradication of microbes	It can eliminate microbes, but does not eradicate other toxins	
Oxidative	Easy to operate	Oxidizing agents need to be activated	
Fenton's Reagents	Deals with diversified toxins	Huge sludge generation	
Ozonation	Ozone can be utilized in a gaseous form, with no effluent volume increment	Short half-life, i.e., 20 min	
Photochemical	No sludge formation	By-product formation	
Electrochemical Destruction	No chemical utilization; No sludge generation	Requires high flow rates to cause a decline in toxins removal	
Decolorization of white rot fungi	Able to degrade dyes using enzyme	Unreliable enzyme activity	

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Table 8. Cont.

Process	Advantages	Disadvantages:
Microbial culture	Decolorized in 24-30 h	Cations are not metabolized
Sorption by living and non-living organisms	Some toxins have an affinity for binding microbes	Not effective for all toxins
Anaerobic	Allows some toxins to eradicate	The breakdown process yields ${ m H_2S}$ and ${ m CH_4}$
Adsorption AC	Good removal of toxins	AC production needs a lot of energy, making the process uneconomic
Membrane filtration	Removes toxins; low use of chemicals	High CAPEX, sludge formation, and membrane fouling
Ion Exchange	Deals with only some toxins	Needs regeneration
Electro-Kinetic Coagulation	Economically feasible	High sludge formation
Chemical Precipitation	Simple, economical, and leads to all toxins	High sludge formation
Chemical Coagulation	Sludge settling with dewatering	Cost-ineffective; slow process; cannot deal with all toxins

#### 4. Conclusions and Perspectives

This review covers the bioremediation of wastewater involving microalgae as biological agents. Bioremediation can be practical for organic, inorganic, metallic, textile effluent, distillery effluent, and emerging pollutants, as demonstrated by the literature. Microalgae-based bioremediation has emerged as a promising option for handling diversified toxins as part of EPs. Microalgae utilization for toxins eradication reveals the CO<sub>2</sub> sequester and has been proven effective. However, various issues are still not adequately addressed. Many abiotic and biotic parameters can alter the microalgae growth and eradication capability. It is essential to design a parametric condition of every gene of microalgae for the cultivation and eradication process because every species has its metabolic activity. The process design and equipment organization for microalgae utilization are under consideration. The optimization of existing bioreactors and new bioreactor development will take place soon to minimize the flaws of current reactors. Finally, the coupled processes of bioremediation might be effective, viable, innovative, and economical.

Microalgae-based biotechnology for wastewater treatment is not mature enough yet. It has been evident that these processes require optimum growth conditions and sufficient nutrients. They are vulnerable to cross-contamination and involve complex operation and controlling systems. Some major shortcomings are detailed below:

- Most of the reported research focuses on the pilot or lab scale under strictly controlled conditions. They did not operate in a scaled-up system treating real wastewater that typically exposes microalgae to adverse conditions, including the weather condition and variable toxins concentration. This is because both conditions can change the effectiveness of toxins removal.
- Detailed metabolic engineering studies are needed to measure the actual capabilities
  of microalgae for biotechnology. The information can also guide in increasing the
  probability of modifying the microalgae cells for the improvement and enhancement
  of microalgae's ability to survive under realistic conditions.
- The difficulty in the separation of microalgae biomass—microalgae harvesting—from
  the treated effluent after the bioremediation. The treated wastewater must be free
  from the microalgae biomass.
- Economic feasibility must be comprehensively assessed and compared with existing traditional processes. Very few economic studies have been conducted to elaborate the microalgae-based effluent treatment process.

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 A large-scale wastewater treatment plant aided with microalgae technology needs very sensitive and complicated operation monitoring and control because the process is highly sensitive to pH, temperature, BOD, COD, and DO. This challenge should be addressed by adopting a new advanced monitoring and controlling system.

The toxicity eradication process using microalgae has been widely employed due to its cheaper cost. Due to water shortages, many countries focus on bioremediation and biological processes. Microalgae growth depends on its cultivation media and optimal parametric conditions. It was discussed in detail how to deal with eradicating different toxins. The comparative evaluation of its techno-economical aspects is summarized in Table 9.

<b>D</b> .	Minister Production Production	Conventional		
Parameters	Microalgae-Based Eradication Process	Physical	Chemical	
Pollutants	Dyes, Metals, and EPs	Dyes, Metals, and EPs	Dyes, Metals, and EP	
Modification Possibility	Yes	Yes	Yes	
Process Capacity	Moderate to High	Low	Moderate	
Removal Efficiency	Low to Moderate	Moderate	High	
Quantity Required	Huge	Huge	Huge	
Time	High	Moderate	Low	
Sludge Formation	Moderate to High	Moderate	High	
Economically Feasible	High	Moderate	Low	
Ecologically Feasible	High	Moderate	Low	
Commercially Feasible	Low	High	High	
Waste generation	Moderate to High	Low	High	
Availability	High	Moderate	Low	
Examples	Bioremediation, biosorption using E. Coli, Scenedesmus sp. LX1, Nannochloris sp., Chlorella pyrenoidosa, microalgal	Adsorption using activated carbon, zeolite, ion exchange, coagulation/flocculation, UV, etc.	Fenton's, oxidation chlorination, etc.	

Table 9. Techno-Economical Aspects of Green and Conventional Processes.

Table 9 reveals that bioremediation is economical, feasible, and viable, but commercially, it needs serious attention, mainly due to a long retention time relative to other physical and chemical processes. Finally, it can be stated that bioremediation can be utilized as a commercially adopted process in a hybrid configuration.

Effluent treatment by microalgae has many advantages. The deployment of a PBR on a commercial scale is a viable option. Most bioremediation processes were evaluated on a lab scale, and some considerations on scale-up have been identified as follows.

- Microalgal-based processes might be restricted to an elevated concentration of toxins such as phenolic compounds and many other organic contaminants.
- Melanoidins in distillery effluent can reduce light penetration, slowing photosynthesis and growth.
- Antimicrobial agents and antioxidants inhibit the eradication process.
- Effluent that contains a low concentration of organic toxins can be effectively removed by bioremediation.
- Immobilization of algae also aids in overcoming toxic load or shock load.
- Decolorizing effluent can effectively increase the exposed area and light intensity.
- The optimal parametric condition should be incorporated to deal with any toxins.

Thus, the scale-up of this approach is still very challenging in achieving a maximum eradication rate. The process needs very in-depth consideration to deal with all the major highlights.

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