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Review

Phycoremediation of Synthetic Dyes Laden Textile Wastewater and Recovery of Bio-Based Pigments from Residual Biomass: An Approach towards Sustainable Wastewater Management

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Abstract: The textile industry is a growing sector worldwide and has immense opportunity in terms of providing employment and boosting a nation's economy. However, there exist severe environmental risks associated with textile effluents that impact the surrounding ecosystem. This review offers an approach for sustainable water management using phycoremediation to treat dye-laden wastewater and recover bio-based pigments from the residual biomass. Microalgae such as *Chlorella*, *Scenedesmus*, *Phormidium*, and macroalgae like *Sargassum*, *Enteromorpha*, and *Codium* has been extensively used in several phycoremediation-based studies, and their residual biomass could be a potent source for extraction of bio-based pigments. This review also recommends studies involving the algal-bacterial consortia approach for treating dye-laden wastewater as an alternative to conventional, biobased methods. The outcome of this study will provide policymakers and researchers with new insight to manage water and wastewater resources sustainably. Furthermore, this review also enhances our understanding of nature-based decontamination approaches for treating dye-laden wastewater through algal-based technologies.

Keywords: textile wastewater; dye degradation; phycoremediation; bio-based pigments; algal-bacterial consortia

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1. Introduction

Rapid urbanization and an increase in global demand for textile apparel due to fast fashion has made textile industries a major source of the global economy, especially in developing countries like India, Bangladesh, Pakistan, Malaysia etc. [1]. Apart from being a major sector providing significant employability and economic growth to these countries, they are also a major pollution-emitting sector. The textile industry is water-intensive and requires massive amounts of water to run its unit operations. A typical textile industry requires around 230–270 tons of water to process 1 ton of product [2]. According to World Bank Report, approximately 20% of the total effluent generated from the industries is discharged from the textile industry [3]. Most textile industries comprise a range of wet processes such as de-sizing, scouring, bleaching, mercerization, dyeing, and washing units [4]. The water footprint is very high in all these wet processes, leading to a huge volume of effluent generation and discharge. These industries use a wide range of synthetic dyes in their dyeing operations [5]. The highly colored effluent inhibits light penetration in the water bodies and further inhibits the primary producers photosynthetic activities, adversely affecting the aquatic food web [6]. Introducing synthetic dyes into the aquatic environment has resulted in mutagenic, carcinogenic, genotoxic implications and aesthetic harm to waterbodies [7].

To overcome the threats caused due to textile effluents, several physicochemical treatment approaches have been applied. Some generally used methods are flocculation, coagulation, oxidation, precipitation, and membrane filtration [8,9]. All these methods have some significant flaws like sludge generation, overconsumption of energy, expensive, requirement of expertise to use them and their applicability on a large scale [10]. Hence, there is a need for a sustainable and eco-friendly approach to the remediation of dyes in the textile industry to overcome the problems faced while applying traditional methods while treating the textile effluent.

Bioremediation and phycoremediation could prove to be a very effective strategies for tackling pollution of significant environmental concern. The process of bioremediation entails the utilization of living organisms, including bacteria, fungi, or plants, to decompose or decontaminate harmful substances. Microorganisms can degrade or convert pollutants, making them safe for discharge into the environment. Bioremediation has been utilized in diverse contexts, encompassing the mitigation of soil and water pollution caused by petroleum derivatives, heavy metals, pesticides, and organic substances [11–15]. For instance, in the case of textile wastewater treatment, specific bacterial strains like *Pseudomonas aeruginosa* and *Bacillus subtilis* have been employed to degrade azo dyes commonly found in textile wastewater [16]. These bacteria produce enzymes called azoreductases that catalyze the reduction of azo bonds, leading to the degradation of dyes. Fungi is also utilized in bioremediation. Species like *Trametes versicolor* and *Phanerochaete chrysosporium* are known for their ligninolytic enzymes, which can efficiently degrade dyes through oxidative reactions [17,18].

Phycoremediation is a distinct type of bioremediation that utilizes the capabilities of algae to eliminate or break down contaminants. Algae exhibit distinctive metabolic capacities and can remediate contaminants via diverse mechanisms such as biosorption, bioaccumulation and degradation [19–21]. The efficacy of phycoremediation has been evidenced in treating wastewater, eliminating nutrients, sequestration of carbon, and remediation of contaminants, including heavy metals, organic compounds, and surplus nitrogen and phosphorus [22–24]. The utilization of algae in phycoremediation offers several benefits, such as their swift growth, elevated capacities for pollutant removal, and adaptability to diverse environments such as wastewater ponds or bioreactors. Moreover, the utilization of algae in phycoremediation can enhance nutrient assimilation and reinstate equilibrium within the ecosystem—algal species such as *Sargassum* sp. *Ulva* sp., *Spirogyra* sp., *Spirullina* sp., *Scenedesmus* sp. and *Phormidium* sp. have shown the ability to accumulate dyes through the mechanism of biosorption, where dyes adhere to their cell surfaces [25–32]. Some algae can also metabolize dyes through enzymatic reactions, leading to their degradation and detoxification. For example, *Chlorella vulgaris* has been demonstrated to remove dyes like Congo Red effectively, Brilliant Blue R and Remazol Brilliant Blue R from wastewater [33,34]. Hence, phycoremediation presents a potentially viable method for the remediation of textile industry effluent. Algae possess distinctive metabolic capabilities that facilitate the efficient elimination or degradation of pollutants, such as dyes [35,36]. The studies have demonstrated that the algal biomass could generate value-added products like biofuels, biofertilizers, single-cell proteins, astaxanthins, etc., from its generated biomass [37]. However, pigment extraction from algae after bioremediation is an untapped area of research and needs to be explored more for its ground-scale applicability.

In recent time, chemical-based dyeing of textile apparel has been widely preferred in the textile industry [38]. Although these chemical-based dyes have several industrial benefits such as cost-effectiveness, reproducibility of shades, easy applicability etc., but when released into the environment, they pose a severe threat due to their toxic nature [39,40]. Hence, the natural dye could be an alternative solution to this problem. Plant-based extraction of natural colorants could be an option for obtaining natural pigment. However, the over-exploitation of any plant species for pigment recovery could bring it to the verge of extinction and can disrupt the ecological balance [41]. So, to avoid this, the strategy of using algal biomass for pigment extraction must be explored widely. The algae could be a suitable candidate because of its higher regenerative capacity, wide pigment diversity, and its application as a bioremediating agent for nutrient recovery and wastewater treatment.

In this regard, using algae to produce eco-friendly dye is gaining importance among researchers. Several studies have explored using algal species to produce natural dyes for the textile industry. Mir et al. [42] utilized the green algae *Cladophora glomerata* to obtain a natural colorant for the textile process. El-Khatib et al. [43] also reported using green algae *Spirogyra* sp. to produce a natural colorant for dyeing wool fabric. Similarly, Njiru et al. [44] explored the applicability of macroalgae for its potential to be utilized as a green dye for the textile sector. Hence, algal biomass generated after the phycoremediation of textile wastewater could be further explored for its applicability in producing these green dyes from biobased pigments acquired from residual algal biomass after the treatment.

Considering the challenges of wastewater treatment in a sustainable way, this review brings forth an in-depth study on algal-based treatment technologies as nature-based solutions for handling dye-laden wastewater. Further, a better understanding of bio-based pigment extraction from residual algal biomass after the treatment has also been comprehensively discussed in this review. This approach for producing bio-based pigments would form a sustainable treatment approach for dye-laden wastewater treatment through value addition of the entire phycoremediation process.

2. An Overview of the Textile Industry

The textile industry is one of the world's most influential and rapidly developing sectors [45]. These textile industries have a global market share of around $2000 and offer employment to ~120 million people across the globe. In India textile industry is one of the oldest industries and the second largest producer of textile apparel which shares around 5% of total global exports and contributes to 27% of Nationals Gross Domestic Product (GDP) [46]. Unfortunately, this sector employs a significant amount of water for its various wet processing activities and generates vast amounts of highly hazardous wastewater with a wide range of characteristics [47–49]. It is estimated that, on average, to create 8000 kg of textile fabric each day, a typical textile industry uses 1.6 million liters of groundwater, of which 30–40% is utilized in the dyeing process, 60–70% in the washing stage and 10–50% of unwanted dyes are discharged into water resource together with the produced effluent [50,51]. A typical textile industry is estimated to produce 5.2–6.6 MLD of textile wastewater through different unit operations [52]. The wastewater from these industries is generally characterized by high COD, color, and total dissolved and suspended solids, which make its treatment difficult [53–55]. Although the makeup of textile effluents varies considerably depending on the methods employed and the kind of fibers used, it generally includes a variety of unutilized organic and chemical components, such as dye waste, color residues, acids, alkalis, starch, various kinds of surfactants, cleaning solvents, inorganic salts [56]. When these complex wastewaters comprising the toxic cocktail of numerous types of dyes and chemical reaches the water bodies, it threatens the ecological balance of the aquatic ecosystem. Hence, they should be adequately treated before releasing them into the environment.

2.1. Varieties of Dyes and Fabrics Used

Dyes are compounds that have the property to absorb light radiance in the visible spectra (400–700 nm). The chromophoric group in the dye structure is responsible for the selective absorption of the incident light, and reflected light provides specific color to the dyes [57]. There are mainly two types of dyes such as natural and synthetic dyes, used in tie and dye sectors. Natural dyes are mainly derived from plants, animals, microbes, and minerals. They are considered less toxic to nature and can easily be degraded microbially. Some important sources of natural dyes are henna (*Lawsonia inermis* L.), Indigo (*Indigofera tinctoria*), Turmeric (*Curcuma longa*), Safflower (*Carthamus tinctorius*), Saffron (*Crocus sativus*) and Pomegranate rind (*Punica granatum*) [58]. However, due to rapid growth and market demand, the industry's demand for synthetic dyes continuously increases. Chandanshive et al. [5] reported that around 7 × 10^7 tons/year of synthetic dyes are produced worldwide for the textile industry. ~10% of the dyes are discharged into the waste stream. The dyes are characterized based on chromophore structure, which provides specific color to the dye. The most common chromophores are azo group (N=N), nitro (-NO_2), nitroso (-N=O), and carbonyl (-C=S) [47]. These chromophores absorb the incident electromagnetic wave due to the excitation of electrons to the higher orbit. The auxochrome group is also an important structure present in the dye structure, which is responsible for the fixation of dye to the fabrics. Various auxochromes exist, such as -COOH, -OH, NH_2, NR_2, etc. [57]. The textile industry fabrics are divided into two major categories: natural fabrics (cotton, hemp, wool, silk) and synthetic fabrics (nylon, polyester, polypropylene). Table 1 shows the list of industries using various dyes for specific fabrics.

Table 1. List of various dyes used by the textile industry for different fabrics [59–61].

Fiber's Categories		Dyes Used
Natural fiber	Cellulose fibers: Cotton, hemp, rayon, ramie, lyocell, and linen	Reactive dyes (remazol red and remazol blue), direct dyes (congo red and direct brown 116), naphthol dyes (fast yellow GC, and indigo dyes (indigo white and indigo carmine)
	Protein fibers: Wool. silk, cashmere and mohair	Acid dyes (azo dyes and anthraquinone dyes) and lanaset dyes (Bordeaux B)
Synthetic fibers	Synthetic fibers: Nylon, polypropylene, polyester, acrylic and acetate	Dispersed dyes (disperse red and disperse navy blue), basic dyes and direct dyes,

2.2. Effluent Characteristics

The qualities of the textile wastewater emitted vary by industry depending upon the machinery, processing unit and the nature of fabric and dyes required for desirable fabric production [62]. However, most textile industries comprise a range of wet processes such as de-sizing, scouring, bleaching, mercerization, dyeing, and washing [59]. The water footprint is very high in these wet processes, leading to a huge volume of effluent discharge. The steps are commonly known as the pre-treatment range units and are required to remove the starch and other impurities (like salts, enzymes, dust, etc.) from fabrics and provide white color to the fabric material. The main purpose of the de-sizing unit is to detach the starch from the fabric through hydrolysis or oxidation. This leads to the direct discharge of enzymes, starch, and hydrogen peroxide into the waste stream, making effluent rich in organic content.

Similarly, the scouring and bleaching processes are required to remove the cotton wax and natural color substance from the fabric surface. These processes include using hot alkali, detergent, organic solvent, and hypochlorite (bleaching agent). Afterwards, mercerization must provide luster, increase strength, and improve dye uptake capacity [63]. The dyeing unit is the central process where a wide range of dyes or pigments are applied to the fabric to provide desirable shade. As discussed in the previous section, different dyes are used according to the fabric. In addition, various chemicals such as surfactants, salts, metals, sulfide, and organic chemicals might also be added to specific dyes to enhance the dye binding to the fabric. These chemicals and dyes are the key contaminants in the generated dye effluent. The primary metals responsible for environmental degradation are zinc, chromium, iron, lead, and mercury. Table 2 shows the reported physicochemical characteristic of actual textile effluent in different textile industries worldwide. Literature reported that the high chemical oxygen demand (COD), biochemical oxygen demand (BOD), TDS, and color of textile effluent were due to the presence of a large number of chemicals, salts, starch, fabric residue, and complex dyes [64–66]. Moreover, the effluent also has high pH and temperature. The range of organic content and other parameters in the effluent varies throughout the year as per the market demand for fabric.

Table 2. Physico-chemical characterization of real textile effluent.

Parameters	[67]	[68]	[69]	[65]	[66]	[70]	[64]
COD (mg/L)	350–700	1017	2200–2800	2200 ± 250	700–1250	3280	1000 ± 100
BOD (mg/L)	150–350	9.8	-	-	-	689	-
Colour (Hazen value)	-	-	-	2800 ± 300	500–1250	4225	6383 ± 100
pH	5.5–10.5	9	9.5–11.2	11.5 ± 0.5	8–9.5	8.6	9.2 ± 0.2
Total dissolved solids (mg/L)	1500–2200	-	1870	3200 ± 300	-	-	-
Total Suspended Solids (mg/L)	200–1100	535	-	150–250	200–450	1746	-
Chloride (mg/L)	200–500	38,600	745.5	-	800–1500	-	-
Sulphate (mg/L)	500–700	4500	-	350 ± 50	200–600	-	362 ± 100

3. Phycoremediation as a New Age Eco-Friendly Technology for Application in Textile Effluent Treatment

Phycoremediation refers to the biological method which employs algae as a bioremediating agent for the biotransformation and bioaccumulation of the contaminants from the polluted sites. Recently, phycoremediation has gained much attention due to its omnipresence and resistance to various environmental variations, making it a suitable candidate for bioremediation. Several studies have demarcated the potential of suitable algal strains to acclimatize and grow well in different kinds of wastewater in batches and pilot-scale studies. [23,71,72]. Apart from remediation of the contaminants, the algal biomass also sequesters the atmospheric CO_2 and can help secure carbon credits for industries [73]. Also, the algal biomass obtained after the bioremediation can produce value-added products like fertilizers, feeds, pesticides, pigment extraction, biofuels, etc. [74,75]. Along with the treatment, it has also been observed that the treated effluent tends to have higher dissolved oxygen content while releasing into back into the environment [76]. All these factors give the edge to phycoremediation-based treatment technologies over other treatment methods for handling textile wastewater.

3.1. Algal Mechanism of Dye Removal

Microalgae are unicellular organisms with a wide diversity and cosmopolitan distribution [77]. In an approximation, around 72,500 species of microalgae are available, among which around 44,000 species have been discovered to date [78]. Such a vivid diversity and omnipresence of these algal species develops the potential to achieve a wide array of metabolic diversity to produce several novel enzymes. These enzymes could help in the bioremediation of the contaminants in the environment. Other than the enzymes, the live or dead biomass produced can be used as biosorbing agents [79,80]. Hence, these microalgae could serve as potential candidates for decolorizing the dye from the textile effluents by reducing its toxicity significantly before its disposal.

These microalgal species could contribute to the decolorization of textile dyes through the mechanism of biosorption and biodegradation, which are briefly discussed in the below-given sections.

3.1.1. Biosorption

The sequestration of the pollutant through their passive binding on the surface of dead or live biomass is termed biosorption, as depicted in Figure 1. The adsorption could occur through the phenomenon of physisorption, in which the formation of weak Van der Waals forces or electrostatic forces could take place between biomass and pollutant, or it may take place through the phenomenon of chemisorption, which takes place through the covalent bond formation between the biomass and pollutants [81].

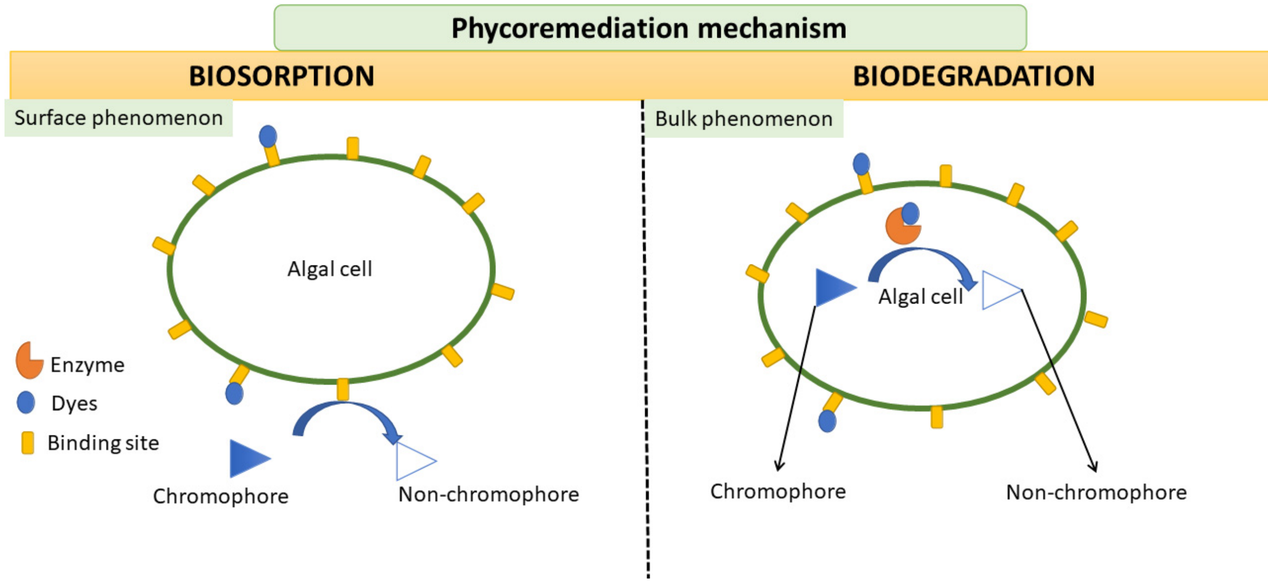

Figure 1. Schematic representation of phycoremediation through biosorption and biodegradation mechanism.

The benefit of using algal biomass as an adsorbent lies in the high surface area of their cell wall and the diversity of functional groups attached to them that give them desired electrostatic force and binding ability. This is because biosorption tendency mainly depends on the structure and composition of their cell wall. In the case of brown algae, alginate plays a crucial role in dye decolorization through adsorption by binding pollutant ions [30]. Table 3 shows the list of some recent studies done on the biosorption of dyes using algal biomass.

In recent trends, diatoms have also been found to be efficient biosorbing agents. Ref. [82] studied live and dead biomass of diatom *Phaeodactylum tricornutum*, which was explored for the biosorption of dye from seawater. It was found that both the live and dead biomass in a condition of very high ionic strength of seawater were able to remove color within 4 h from synthetic dye effluent. The study done by El-Ahmady et al. [83] has also shown that diatom *Gelidium corneum*, under optimized conditions, is capable of biosorbing mercury (Hg) and ramazol brilliant blue from the dye solution. Hence, these diatom-based biosorbents could also be utilized for their dual-action-based contaminant removal.

Table 3. Algal biosorption efficiency for various synthetic dyes.

Algae	Degraded Dye	Efficiency	Incubation Time	pH	Temperature (°C)	Reference
Codium decorticatum	Crystal violet (CV) & Congo red (CR)	96.9% Color removal 89.8% Color removal	60 min	10 4	25	[84]
Chlamydomonas variabilis	Methylene blue (MB)	98% Color removal	30 min	7	25	[85]
Ulva lactuca	Congo red	97.89% Color Removal	120 min	6	30	[29]
Ulva lactuca	Methylene blue (MB)	91.92% Color Removal	110 min	8	25	[31]
Enteromorpha flexuosa	Crystal violet (CV) Methylene blue (MB)	90.3% Color removal 93.4% Color removal	1 min	1.7–5.2 1.8–5.4	-	[86]

Table 3. *Cont.*

Algae	Degraded Dye	Efficiency	Incubation Time	pH	Temperature (°C)	Reference
Enteromorpha intestinalis	Malachite green	99.63% Color removal	38.5 min	9.92	28 ± 2	[87]
Spirulina platensis	Malachite green	94.12% Color removal	52.43 min	7.57	-	[27]
Spirogyra sp.	Acid Orange 7 (AO7), Basic Red 46 (BR46), Basic Blue 3 (BB3)	6.2 mg dye/g biomass 13.2 mg dye/g biomass 12.2 mg dye/g biomass	60 min	4 10 10	30	[28]
Laminaria digitata	Methylene Blue Reactive Blue 19	95% Color removal 60% Color removal	15 min	5.6 1	25	[88]
Ulva fasciata	Reactive Yellow 2 Reactive Red 195 Rective Blue 19 Reactiv Black 5	82.75% 83.23% 100% 100% Color removal	8 h	2	25	[32]
Bifurcaria bifurcata	Acid Orange 7 Basic Red 5	88.8% Color removal 94% Color removal	120 min	7.5	25	[89]
PDA modified *Oscillatoria princeps*	Reactive Red 120	260.3 mg dye/g biomass	120 min	3	25	[90]
Fucus vesiculosus	Methylene Blue Rhodamine B	98.71% color removal 96.68% color removal	420 min	8	45	[91]
Microalgae	Crystal Voilet	243 mg dye/g biomass	5.2 min	9.8	30	[92]

3.1.2. Biodegradation

Biodegradation or bioconversion is the breaking down of contaminants and changing them into smaller molecules, as depicted in Figure 1. Microalgae break down the pollutants into smaller molecules and further utilize them for nutritional purposes [93]. The degradation of dyes through microalgae is mainly based on the release of enzymes. These enzymes break the bond in the dye's chromophore groups during their metabolic process, decolorizing the dye effluents. Some of the most common types of enzymes reported for treating textile dye produced by algal systems are azoreductase, laccase peroxidase, polyphenol oxidase, etc. [94,95]. The most common mode of the dye degradation pathway is through the activity of the azoreductase enzyme. These are the oxidoreductase enzymes that cleave azo linkages in the dye, leading to the formation of aromatic amines. Further, the algae catabolize these aromatic amines into CO_2 and H_2O [96]. In the presence of reductase enzymes, algal cells can convert complex dye molecules into smaller, less harmful compounds. The critical biochemical conversion of dyes into inorganic compounds through catalysis by enzymes, referred to as mineralization, is pivotal to mitigating the detrimental effects of these pollutants on the environment [97]. The process can occur through either direct or indirect mechanisms. In the direct method, electrons are transferred between the enzyme and the dye, enabling the enzymatic cleavage of the dye into simpler aromatic compounds.

However, the indirect technique necessitates electron carriers, namely FAD, NAD+, and flavin, which enable the conveyance of electrons from the enzymes to the dyes via an indirect route. These coenzymes act as electron carriers, mediating degradation [98,99]. The presence of reductase enzymes in algal cells highlights their inherent capacity to mitigate the harm caused by complex dyes. By employing enzymatic pathways, algal cells contribute to transforming dyes into less harmful compounds, minimizing their impact on the ecosystem.

The chemical composition of dye and algal species are the two most important factors deciding the dye degradation rate in the phycoremediation based approach. Studies based on the remediation of dyes through the degradation mechanism by algae have been illustrated in Table 4. There are several microalgae that have been reported to show such dye-degrading characteristics. Some of them include *Chlorella vulgaris*, capable of degrading Congo Red dye [34], *Phormidium autumnale*, capable of complete degradation of indigo, red dye [100], *Oscillatoria* sp. effective against acid black 1 dye and basic fuchsin dye [95,101].

Table 4. Algal degradation efficiency for different types of textile dyes.

Algae	Degraded Dye	Efficiency	Incubation Time	pH	Temperature	Reference
Oscilltoria sp.	Malachite Green (5 mg/L) Methylene Blue (5 mg/L) Safranin (5 mg/L)	93% 66% 52%	5 Days	-	25 °C	[102]
Haematococcus sp.	Congo Red (10 mg/L)	98%	15 Days	7	24 °C	[103]
Hydrocoleum oligotrichum and *Oscillatoria limnetica*	Basic Fuchsin (5 mg/L) Methyl Red (20 mg/L)	92.44% 90.23% 53.23% 50.18%,	7 Days	7.4	25 °C	[101]
Scenedesmus obliquus	Methyl Red (20 mg/L) Congo Red (20 mg/L)	55.45% 62.05%	10 Days	7.4	25 °C	[104]
Spirogyra sp. (*CKW1*) and *Cladophora* sp. (*PKS33*)	Reactive Blue (100 mg/L)	~90% ~88%	7 Days	7	30 °C	[105]
Phormidium autumnale UTEX1580	Indigo dye	91%	14 Days	7	25 °C	[100]
Chlorella vulgaris	Reactive Black 71 (200 mg/L) Disperse Red 1 (200 mg/L) Direct Blue (300 mg/L)	80% 84% 78%	10 Days 10 Days 10 Days	5 8 8	40 °C 40 °C 40 °C	[106]
Blue-green algal biofilm	Acid Orange (100 mg/L)	>95	12–24 h	7	25 °C	[107]

4. Phycoremediation of Real Textile Effluent

Microalgae utilize textile industrial wastewater as a media from which it utilizes dye molecules as a carbon source, and other nutrients are obtained from nitrate, phosphate and other mineral components present in the dye wastewater, which leads to the promotion of cell proliferation of algal biomass [108]. In this way, nutrient removal and decolorization are achieved during the phycoremediation of dye wastewater. Some studies demonstrating phycoremediation on real textile industrial wastewater are presented in Table 5.

Several algae like *Chlorella*, *Scenedesmus*, *Phormidium*, *Oscillatoria* etc. [109] have shown to be promising for the dye degradation and treatment of textile industrial effluent. Currently, these algal species could be utilized for the phycoremediation-based treatment of dye wastewater, but the cocktail of toxic chemicals and synthetic dyes could hinder the algal growth significantly, affecting the overall performance of the phycoremediation process. Tolerance to such toxic wastewater and the phycoremediation potential is attributed to the environmental conditions and the type of algal species employed during this treatment approach [110]. Hence a detailed characterization of textile effluent is an important step based on which the algal species should be selected and employed for phycoremediation of dye wastewater. Some studies have demonstrated that employing native algal species could perform better with textile wastewater as these species have already been acclimatized to the dye-laden environment and could perform better [111,112]. Also, genetic engineering of algal species could further enhance their dye degradation potential [113].

It can be seen from different studies that *Chlorella* sp. is the most commonly used microalgal species for phycoremediation due to its robustness and its high tolerance to synthetic dyes during the treatment process [34,112,114]. A phycoremediation-based study done by Sinha et al. [99] on the dye-laden wastewater with Direct Red 31dye has shown that a resistant strain of *Chlorella vulgaris* could be employed for complete decolorization of the dye wastewater, and significant contaminant removal could be achieved. The mechanism involved in decolorization was rapid biosorption followed by degradation with the help of the azoreductase enzyme.

Apart from the microalgal strains, several other factors like pH, temperature, light, the composition of textile wastewater, reactor configuration etc., can affect the phycoremediation potential of dye wastewater [115]. External factors like pH, temperature, light, and reactor configuration can be optimized based on the requirement for microalgal growth. But the composition of textile wastewater cannot be changed as it depends on textile operations in those industries from which these effluents are released.

To overcome this limitation, the strategy of diluting the textile effluent is performed to enhance the performance of the phycoremediation process. Diluting the dye wastewater further decreases toxicity and promotes algal cell growth. Also, the decrease in the color due to dilution will further enhance the light penetration, thus increasing the photosynthetic potential and enhancing the phycoremediation process.

However, trade-offs should be considered. Dilution requires substantial freshwater, posing challenges in water-scarce areas. Additionally, dilution requires extra space, which can be problematic for large-scale projects in densely populated or constrained areas. Recognizing these trade-offs is crucial for comprehensively understanding dilution's implications and guiding decision-making toward sustainable and efficient bioremediation strategies.

The study done by Oyebamiji [110] demonstrated that a 2% dilution of dye wastewater further enhanced the overall biomass production, heavy metal and color removal. The dilution required is based on the tolerance level of selected algal species for the phycoremediation process. Hence before starting the phycoremediation-based treatment amount of dilution required must also be explored based on the effluent characteristics and the microalgal species employed during the phycoremediation process.

Table 5. Phycoremediation based studies on real textile effluent.

Sr. No.	Microalgal Species	Pretreatment	Experimental Conditions			Treatment Efficiency	Reference
			Light Intensity	Temperature	Time		
1	*Chlorella vulgaris*	Algal cultivation in diluted textile effluent (5–30%) + 10 g/L sodium bicarbonate as a supplement	3000 lux	25 °C	15 Days	75.68% Decolorization; COD 69.9%	[112]
2	Mixed Algal Consortium	In 4 L of textile effluent 0.5 L of algal consortium	170 μmol m^{-2} s^{-1}	-	5 cycles for 95 days.	68–72% Decolorization; COD 50–70.7%; * TN 70.8–100%; * TP 88.5–100%	[116]

Table 5. *Cont.*

Sr. No.	Microalgal Species	Pretreatment	Experimental Conditions			Treatment Efficiency	Reference
			Light Intensity	Temperature	Time		
2	Mixed Algal Consortium	In 4 L of textile effluent 0.5 L of algal consortium	170 µmol m^{-2} s^{-1}	-	5 cycles for 95 days.	68–72% Decolorization; COD 50–70.7%; * TN 70.8–100%; * TP 88.5–100%	[116]
3	*Chlorella pyrenoidosa* NCIM 2738	Photobioreactor with 0.5 OD algal beads	-	28 ± 2 °C	10 days	100% Decolorization; COD 87.60%; Chloride 97.3%; Sulphate 56.06%; Phosphate 29.11%.	[99]
4	*Chlorella vulgaris* Wu-G22 and *Chlorella* sp. Wu-G23	Dilution rate (0%, 10%, 20%, 40%, 60%, 80%)	-	-	7 days	60% Decolorization; COD 75%; Ammoniacal nitrogen 90%	[114]
5	*Chlamydomonas* sp. TRC-1	-	100 µmol m^{-2} s^{-1}	27 °C	7 days	100% Decolorization; COD 83.08% Nitrogen 87.15% Phosphate 92.36%	[111]
6	*Chlorella sorokiniana*	Dilution (0.25–16.0%)	60 µmol m^{-2} s^{-1}	NA	14 days	70% Decolorization with 2% Dilution	[117]

* TN: Total Nitrogen; * TP: Total Phosphorus.

5. Algal-Bacterial Consortia for Dye Laden Wastewater

A single strain of bacteria, fungi, and algae effectively removes only a limited type of dye from the textile effluents. In contrast, a microbial consortium comprised of several microbial communities tends to produce a wide variety of dye-degrading enzymes, which could be the most suitable biological approach for treating raw textile industrial effluents [118].

In an algal bacterial consortium, there is a mutual relationship between them, as they help each other in their growth. In this microalgal bacterial synergism, the algal partner performs photosynthesis, and the end-product oxygen is utilized by the aerobic bacteria. These aerobic bacteria use this oxygen to mineralize nutrients and make them available for algae [119]. Hence promoting the growth of each other synergistically, as depicted in Figure 2. Also, these bacterial members have been reported to produce valuable metabolites like indole-3-acetic acid, Vit B_{12}, etc., that could enhance microalgae growth in the wastewater, resulting in greater biomass production. Bacterial members of this consortium can also increase the availability of several organic and inorganic compounds like iron, sodium acetate, D-glucose, etc. which usually remain unavailable for the microalgae in their native environment [120] and some proteins and polysaccharides released by the bacterial member can also promote the self-flocculation for the microalgal biomass [121].

Although, several interactions can occur in systems where bacteria and microalgae coexist, including mutualistic, synergistic, competitive, or inhibitory relationships. While there are instances where bacteria can enhance microalgal growth and vice versa, as discussed above, the competition for resources, such as nutrients and light, can also arise between them [122]. These competitive interactions can impact the overall performance and productivity of the system, making it challenging to secure consistent and predictable gains. By recognizing the potential competition and complexity of algal/bacterial interactions, it is crucial to adopt a balanced perspective when discussing the potential benefits of synergy [123]. Emphasizing these relationships' intricate nature can help set realistic expectations and provide a more comprehensive understanding of the challenges and opportunities associated with such systems.

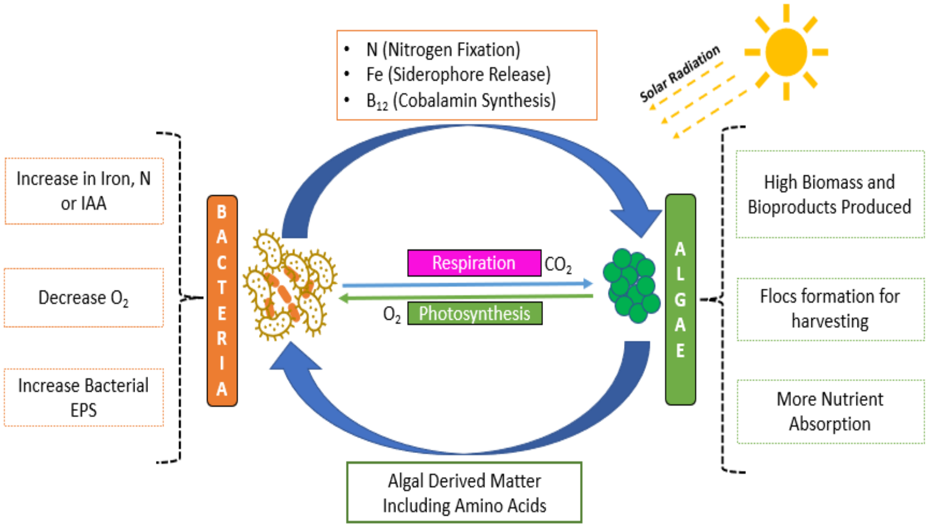

Figure 2. Schematic diagram representing mutualistic algal bacterial interaction.

In one of the recent studies conducted by [124] on the algal bacterial consortium for CI RB 40 reactive azo dye degradation, they demonstrated that the consortium of *Pseudomonas putida*, *Chlorella* and *Lactobacillus plantarum* under the optimized conditions was able to decolorize CI RB 40 dye up to 99% along with COD removal of 89% at 1000 ppm of dye concentration. In another study, Ref. [76] compared the conventional activated sludge system (CAS) and algal bacterial symbiosis (ABS) for treating printing and dyeing wastewater under natural light conditions. This study determined that ABS was more efficient than CAS and demonstrated 80% more color removal through ABS with a hydraulic retention time (HRT) of 16 h. Ref. [125] evaluated the decolorization and heavy metal removal potential of *Chlorella* and *Enterobacter* sp. MN17 at different dilutions of real textile wastewater. This study demonstrated that with a 5% dilution, their algal bacterial synergism decreased the COD up to 74% and decolorized the real textile effluent by 70%. Along with this, a considerable amount of heavy metal removal was also observed in the study. In a study by Rawat et al. [126], the role of bacterial partners in increasing the bioavailability of micronutrients to the algal partner was demonstrated and found to enhance the dye degradation phenomenon. They revealed that synergism between the algae *Chlorella sorokiniana* and siderophores producing bacteria *Ralstonia pickettii* helped the algal member in the uptake of iron, an essential micronutrient that generally is a vital micronutrient largely remains unavailable to the algal member from the environment and in return, the algal member provides dissolved organic matter to sustain this mutualistic interaction. In this study, they showed that this interaction increased the degradation potential of Acid Black 1 dye by the *C. sorokiniana* through the enhancement of azoreductase activity by increasing the bioavailable iron that regulates this oxidoreductase pathway.

These recent studies showed that this synergism of algal bacterial interaction could have broad applicability for efficiently bioremediating dye-laden wastewater. These interkingdom interactions are mutualistic and self-sustaining, significantly promoting each other's growth and metabolic activity. So, these mutualistic interactions need to be exploited through in-depth study. Their textile dye bioremediating potential must be explored for an efficient and comprehensive biological treatment of the wide variety of dyes in textile wastewater.

6. Opportunity and Challenges of Phycoremediation

Conventional biological treatment methods usually result in the generation of a large amount of sludge which creates the problem of its disposal [127]. Further, this treatment method also releases a significant amount of CO_2 into the atmosphere [128]. Phycoremediation can overcome these limitations as it can be used for wastewater treatment, biomass generation, and CO_2 sequestration. The phycoremediation approach has already been applied to the tertiary treatment [129] as well as in secondary treatment [130] of wastewater as they tend to withstand stress due to a polluted environment and can grow in them [24]. Also, they can be used in the primary treatment process as a biosorbent. Integrating pollutant and dye removal using algal biomass may establish an effective biological textile wastewater treatment and generate valuable algal biomass. This generated biomass can be used to produce value-added products like lipids, pigments, fertilizers, etc., offsetting the cost of the overall treatment process. Hence, algae can be explored as an eco-friendly approach for textile dye and effluent treatment [131,132].

Though with such a great potential of phycoremediation to mitigate the contaminant from the environment. There are still some constraints regarding its applicability in real-world scenarios as most studies are lab-based, working on simulated textile wastewater with few dyes. Their applicability in natural conditions remains unpredictable. Though several pollutants of the real textile effluent remain constant, the exact composition of these effluents is hard to mimic because they are based on several other biotic and abiotic factors. When such studies are conducted in real textile effluent, their color removal efficiency is reduced significantly. Hence, field studies are needed to prove reliability to demonstrate their efficiency with respect to variable pH, temperature, and changing characteristics of real textile effluent. Also, in large-scale applications of the phycoremediation process, sunlight is one of the most critical aspects for the biodegradation of pollutants. Microalgae use photosynthesis to convert light into chemical energy, fueling their metabolic activities. Therefore, an adequate and consistent supply of light is essential to support microalgae growth and optimize their remediation capabilities [133,134]. Microalgae cultivation typically involves constructing open ponds or closed bioreactors, which must be exposed to sunlight for extended periods. The land area required can be significant, especially when aiming to achieve high biomass productivity and efficient pollutant removal. The land area requirement for light capture depends on various factors, including the specific microalgae species used, local climatic conditions, cultivation system design, and the target pollutant concentration [135]. The availability of suitable land and associated costs can challenge the widespread implementation of large-scale bioremediation with microalgae. Researchers and industry practitioners have explored alternative approaches to optimize light utilization and minimize land requirements to mitigate this drawback. Some strategies include using high-efficiency photobioreactors that maximize light exposure and capture and implement floating systems to utilize water bodies effectively should be explored [136,137]. Other significant challenges faced during the phycoremediation involve the identification of robust algal species [138], scaling up of the developed algal treatment [128], and designing a cost-effective treatment system [108]. These are additional problems that need to be addressed while planning a phycoremediation based technology for treating textile wastewaters.

7. Scope for Algal Biomass as a Resource for Bio-Based Pigments

As discussed in the earlier sections, the existing technologies for textile dye removal were majorly concerned with phycoremediation rather than its valorization of generated biomass through this process. However, some studies have focused on converting algal biomass into biofuels productions or generating bioelectricity during phycoremediation [121]. Excluding these, using generated algal biomass for natural pigment production could be encouraged to potentially replace the synthetic dyes used in the textile application since several studies reported on natural dye production from algal pigments.

For instance, *Kappaphycus alvarezii* (red seaweed) has been utilized as natural colorants such as greenish-yellow and brown shades of chlorophyll and carotenoids for dyeing silk and bamboo fabrics [139]. Similarly, *Galaxaura subverticillata*, red algae with fucoxanthin and carotenoid pigments, have been used to produce dark red and brown color dyes [44]. Also, brown algae like *Sargassum muticum* and *Colpomenia sinuosa* can produce brown and creamy white dyes for cotton fabrics [140]. The dye production from diverse algal species is mainly due to different classes of pigments such as chlorophyll, phycobiliprotein, carotenoids, and fucoxanthin.

7.1. Algal Pigments and Their Applications

7.1.1. Chlorophyll

Chlorophyll is an abundant green pigment in chloroplast and photosynthetic lamellae of microalgae and blue-green algae, respectively. There are different types of pigments, such as chlorophyll-a, b, c, d, and f (Figure 3). Based on its distribution, chlorophyll a is commonly distributed among all algal species, whereas chlorophyll b, c, d, and f were present mainly in classes like Chlorophyceae, Phaeophyceae, Rhodophyceae, and blue-green algae, respectively [141].

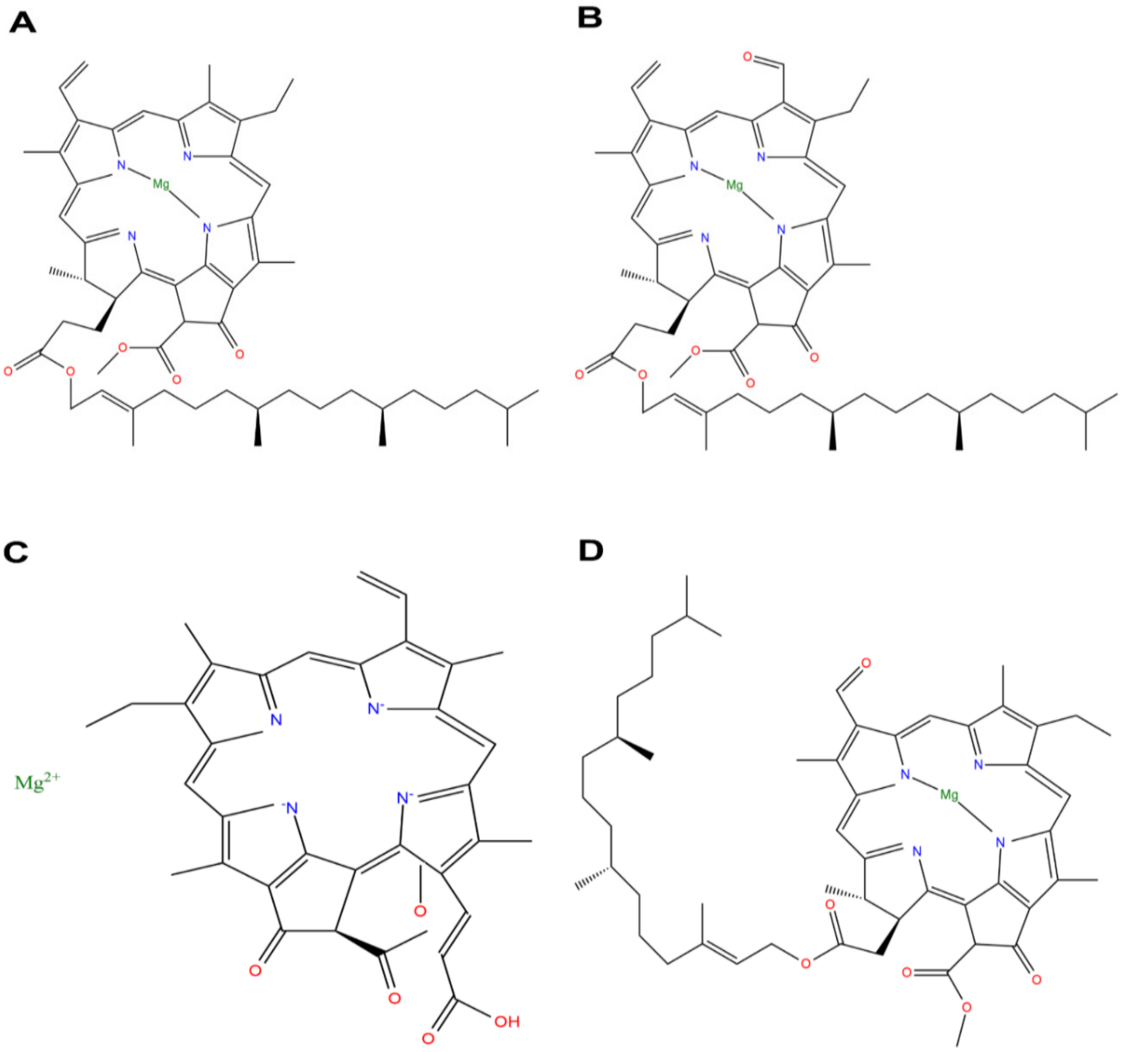

Figure 3. Structural diagram of Chlorophyll pigment: (**A**) Chlorophyll a; (**B**) Chlorophyll b; (**C**) Chlorophyll c; (**D**) Chlorophyll d.

Several methods have been proposed to extract this chlorophyll which does not follow a common protocol due to the diverse nature of algal species [142]. The efficiency of extraction depends on its duration, the resistance of the cell wall towards solvent, the properties of the solvent, and the cell disruption method used [143]. Generally, organic solvents such as acetone, ethanol, methanol, and dimethylformamide were used for the extraction of intracellular chlorophyll after the pre-treatment of algal biomass through homogenization, microwave, and sonication methods for disruption of the cell wall [144]. The extracted pigment is quantified using a spectrophotometric equation [145].

For textile application, the chlorophyll pigment extracted from green algae such as *Cladophora glomerata* and *Spirogyra* sp. has been shown to impart green color onto cotton and wool fabrics, respectively [42,43]. Also, other green algae, such as *Ulva reticulata*, rich in chlorophyll c and phycocyanin pigments, have been shown to produce green dye [44]. Surprisingly, they act as strong radical scavengers and exhibit beneficial biological activities such as anti-obesity and antimutagenic [146].

7.1.2. Phycobiliproteins (PBPs)

PBPs are water-soluble, autofluorescent, and multi-colored accessory pigments in the thylakoid membrane (Figure 4). On a dry weight basis, it accounts for about 20–30% of the algal cells, which could be enhanced through optimization of light intensity [147]. According to Kannaujiya et al. [148], based on absorbance spectra of chromophore present in PBPs structure, it is classified into three subunits such as phycoerythrin (560–570 nm), phycocyanin (610–620 nm) and allophycocyanin (650–660 nm). The effective methods for isolating PBPs were sonication, organic solvent extraction, freeze, and thaw method, microwave-assisted extraction, homogenization, etc. [149]. The most challenging parameter for its extraction is the presence of multilayered and rigid cell walls, which could be pretreated with hydrolyzing enzymes (especially polysaccharides) to release PBPs from the algal cells [150].

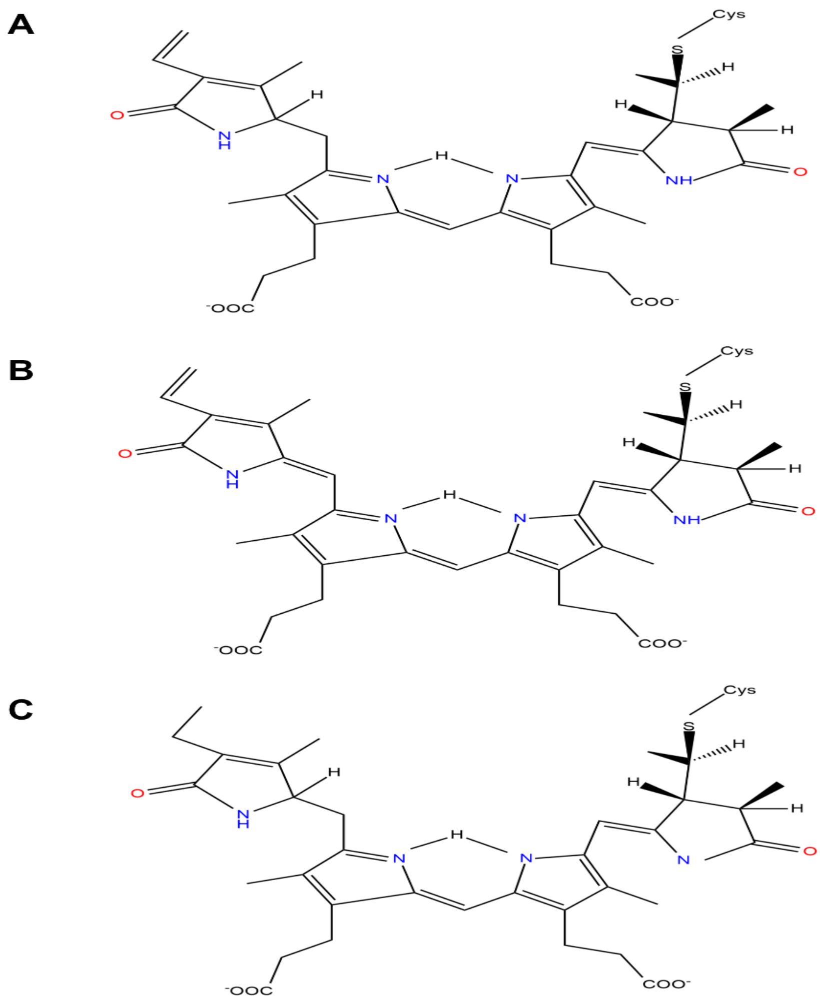

Figure 4. Structural diagram of phycobiliprotein pigment: (**A**) Phycoerythrin; (**B**) Phycocyanin; (**C**) Allo-phycocyanin.

From a textile application perspective, the phycocyanin pigment from microalgae is used as a natural dye for cotton fabrics [151]. Besides utilising PBPs to produce eco-friendly dyes, it has several other diverse applications in the food, cosmetics, and nutraceutical industry. For instance, PBPs are used as the natural colorant for food processing, such as jellies, cake decorations, lollipops, soft drinks, and fermented milk products, due to their non-toxic nature over synthetic colorants [146]. Besides, PBPs obtained from microalgae exhibit spectroscopic properties such as high fluorescence and absorption in the visible light range. Hence, it has been widely applied in molecular science as a marker for chromatography, electrophoresis, flow cytometry, histochemistry, and fluorescence-activated cell sorting [152]. Also, PBPs act as pharmaceutical agents due to their biological activities, such as antioxidants, anti-inflammatory, and anticancer [146,152]. In the commercialization aspect, few companies employ microalgae as a source for PBPs extraction to produce eco-friendly dye like Linablue® spirulina extract, which is popular for producing blue colorant with wide application in food products. Moreover, other companies promote natural dyes for cosmetic applications from PBPs subclasses, such as phycoerythrin and phycocyanin produced from *Porphyridium* sp. and *Spirulina* sp., respectively [146].

7.1.3. Carotenoids

Carotenoids are yellow to red-coloured compounds which two subgroups, such as carotenes and xanthophylls, based on their structural difference [153]. Carotenes comprise α-carotene and β-carotene, whereas xanthophylls comprise lutein, violaxanthin, and canthaxanthin (Figure 5) [154]. Some of the carotenoids are specifically identified among diverse algal species. For instance, blue-green algae: β-carotene and zeaxanthin; red algae: α-carotene, β-carotene, lutein, zeaxanthin, and antheraxanthin; brown algae: fucoxanthin; green algae: lutein, β-carotene, and siphonaxanthin pigments [155–157]. The extraction of carotenoid pigments is efficiently achieved by addressing several obstacles such as polarity, prone to degradation, and oxidation of carotenoids. Considering these limitations, effective protocols were developed based on short extraction time, control over temperature, and light exposure. In this context, organic solvents with a range of wide polarities, such as possible combinations of hexane, ethanol, acetone, and other solvents, were used for the extraction of carotene and xanthophyll, which are non-polar and polar, respectively [158].

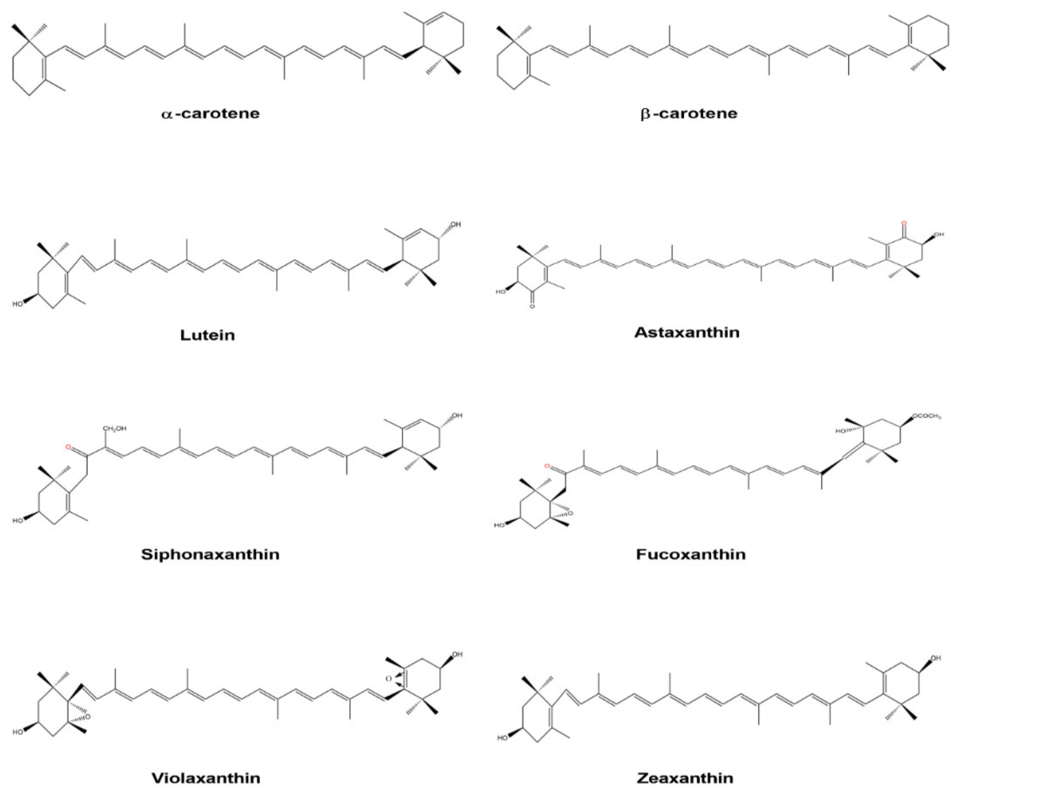

Figure 5. Structural diagram of some carotenoid pigments present in algal species.

Carotenoids have wide application in the cosmetic industry since it acts as an antioxidant and UV protectant that protect cells from the harmful effects of free radicals and protects skin cells against UV, respectively [159,160]. Specifically, some xanthophylls such as zeaxanthin, astaxanthin, and lutein exhibit several biological activities such as anti-inflammatory, anticancer, and anti-diabetic associated with chronic diseases [146,160,161]. In food applications, carotenoids were used as flavoring and coloring agents, such as soft drinks, juices, and confectionery [152]. Also, the β-carotene derived from the carotene is a provitamin that can be used as a vitamin supplement. Commercially, β-carotene from *Dunaliella* sp. is supplied as food supplements with a brand name called Solgar [146].

7.2. Potential Role of Microalgae in Textile Wastewater Treatment & Simultaneous Bio-Based Pigment Production

The phycoremediation research involves several potential algal species from the division of blue-green algae, microalgae, and macroalgae which tends to degrade the textile dye in the industry effluent, as discussed in earlier sections. Besides, these algal species have been effectively reported for their pigment extraction with several beneficial applications, including dye production. For example, genera of some microalgae such as *Chlorella*, *Spirulina*, *Scenedesmus*, *Haematococcus*, *Chlamydomonas*, and macroalgae like *Sargassum*, *Enteromorpha*, and *Codium*.

Briefly, microalgal strains like *Chlorella vulgaris*, *Scenedesmus obliquus*, and *Phormidium* sp. are enriched with carotenoids, phycobiliproteins, and chlorophylls which are efficiently extracted with ethanol as solvent [162]. This study reported total chlorophylls (a, b) and lutein with concentrations of 15.4 mg/g and 5.4 mg/g, respectively, from *Chlorella vulgaris* [162]. However, *Scenedesmus obliquus* contains 0.24% of total carotenoids and 0.71% of chlorophyll a, and 0.32% of chlorophyll b in biomass, respectively [163]. Similarly, *Phormidium* sp. has been reported to possess three important classes of pigments such as chlorophylls, carotenoids, and phycobiliprotein. The predominant pigments among these were carotenoids: β-carotene, lutein, and zeaxanthin; c-phycocyanin; chlorophyll a with concentration of 225.44, 117.56, 88.46, 2.05×10^5, and 2.700 µg/g, respectively [164]. These algal species predominated with specific pigments in their biomass are capable of simultaneously degrading the textile dyes such as Lanaset red 2GA, Congo red, and Acid red P-2BX [104,131,165].

Also, a few species of blue-green algae selectively contribute to this process, such as *Arthrospira platensis*, through the degradation of methylene blue [166]. At the same time, it can produce effective pigments by valorising their biomass like chlorophyll a, c-phycocyanin, and total carotenoids of 4.43, 10.8, and 251.2 mg/g, respectively [167]. Similarly, macroalgal species are recognized by their colored pigments, such as green algae (*Enteromorpha* sp. and *Codium* sp.) and brown algae (*Sargassum* sp.). The major pigment from *Enteromorpha* sp. was pheophorbide a pheophytin a, and chlorophyll a; *Sargassum* sp. and *Codium* sp. were pheophytin a and siphonaxanthin, respectively [168–171]. Concurrently, both *Enteromorpha* sp. and *Sargassum* sp. can degrade methylene blue, whereas *Codium* sp. degrades crystal violet [84,172]. Based on this evidence, algae are a rich reserve of different pigments that can be extracted from generated biomass after treating dye-laden wastewater. Also, the extracted pigment could be further explored for its applicability to produce dyes. Hence, this review highlighted the scope for utilizing the generated biomass from wastewater treatment for bio-based pigment production to form a closed-loop approach through the value addition of the entire phycoremediation process.

However, the extracted pigments were easily affected by physicochemical factors such as pH, temperature, and light during unit operations [173,174]. The major factor, pH plays a vital role in the spectral properties, aggregation, and dissociation of the pigments into their monomers, hexamers, and other oligomers in the dissolved solution. Among them, the predominant form is hexamer with optimal pH 6.0 to 7.0, which holds the most stable structure of the pigment and avoids denaturation, especially in the case of PBPs [173,175]. Additionally, an increase in the operational conditions, such as temperature and light, denature the pigment's structure by decreasing the alpha helix amount, resulting in stability loss. Hence, it needs an optimal range to resist the degradation of the pigment, such as temperature from 25 to 47 °C (PBPs) and 4 to 20 °C (Carotenoids and chlorophylls), whereas the light should be within 50 μmol m^{-2} s^{-1} to maintain its stability light [173,176,177]. Similar optimal conditions for the stability of the pigments were applied to improve the textile application's efficiency using natural dye. For instance, the dye Sandocryl Golden Yellow C-2G extracted from Caulerpa scalpelliformis (green macroalgae) resulted in increased uptake between the pH range 3.0 to 8.0 and temperature from 20 to 60 °C which influenced the surface properties of the adsorbent for the enhanced biosorption of the dye [178,179]. Also, another report involved phycocyanin from Spirulina platensis for the dyeing process where the step was performed at optimal temperatures (9–27 °C) as the pigment was sensitive to the higher temperature, which showed similar adherence and uptake of dye as control dyed fabric [180]. Nevertheless, future research on improving algal pigment stability might increase its applicability to the textile sector.

8. Future Prospects

- Algal biomass harvesting is a difficult task since it is costly, so its scale-up for the large production of value-added products is difficult. Innovative algal harvesting methods must be investigated to make algal treatment financially viable and ensure it is implemented on a large scale.
- In-depth studies are required to understand the microbial biochemical pathways that participate during the degradation of the dyes.
- Suitable and robust algal species are to be explored, which could be utilized for the dual role of dye abatement and bio-based pigment extraction.
- In most of the studies, techno-economical aspects and carbon footprint were missing, which is very important for analyzing the sustainability and cost-effectiveness of a treatment system.
- To treat high-strength textile effluents in a cost-effective and environmentally beneficial manner, hybrid solutions integrating with phycoremediation based systems should be emphasized.

9. Conclusions

In recent times algal-based bioremediation of contaminants is gaining popularity due to its multifaceted applications. It can potentially solve the dual problem of treating textile effluent and resource recovery in the form of value-added products obtained from its biomass, thus paving the way for sustainable wastewater management. The technologies discussed above highlight the trends in the phycoremediation of textile dye and effluent, along with successive usage of algal biomass for bio-based pigments extraction, as algae fulfil nearly most of the criteria to be an efficient dye mitigating tool. It can be well considered that phycoremediation can act as a potent technology for the abatement of dye-laden wastewater in the near future.

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