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Application of microalgae in wastewater treatment with special reference to emerging contaminants: a step towards sustainability

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Emerging contaminants includes diverse types of synthetic or natural chemical compounds which are not detected, monitored, or controlled in the environment regularly and are released from anthropogenic activities. Substantial quantities of emerging contaminants can be found in the wastewater, originating from agro-industrial and industrial outlets, containing oil and grease, heavy metals, and harmful chemicals. Different species of microalgae can be applied in biological remediation of such contaminants in wastewater. This research emphasizes the multifaceted roles of microalgae in wastewater treatment in context of pollutants, especially the removal of emerging contaminants. A comprehensive overview of different emerging contaminant removal processes was conveyed through an in-depth examination and depiction of the uptake mechanisms employed by microalgae in wastewater treatment in this review. The final section of this review focuses on the articulation of difficulties and prospects for the future of microalgae-based wastewater treatment technology. It is subsequently established how the microalgal technologies for emerging contaminant remediation can be helpful to achieve Sustainable Development Goals (SDGs). This review establishes the connection between phytoremediation technologies with Sustainable Development, and shows how successful implementation of such technologies can lead to the remediation of emerging contaminants and effective management of wastewater.

KEYWORDS

microalgae, emerging contaminants, phycoremediation, wastewater treatment, biodegradation, sustainable development

1 Introduction

Chemicals of emerging concern and are of anthropogenic origin, found in different water bodies because of commercial, agricultural, and domestic discharges with concentrations ranging from microgram to milligram per litre are generally referred to as emerging pollutants (EPs) (Wanda et al., 2017). These pollutants can be organic or inorganic in nature. Organic pollutants include pharmaceutical ingredients, personal care products, endocrine disruptors, hormones, etc.,; heavy metals are examples of inorganic pollutants. These contaminants ultimately cause ecosystem imbalances due to their exceptionally high biological and chemical oxygen demand (BOD and COD). Excess nutrients, such as nitrogen (N) and phosphorus (P), will lead to eutrophication of waterbodies, disrupting the health of water systems. COD, nitrogen, and phosphorus concentrations in various wastewaters were investigated (Amenorfenyo et al., 2019; Chai et al., 2021; Noorani et al., 2024). This phenomenon causes environmental concerns such as the generation of solid waste and byproducts, the emission of undesirable products into the atmosphere, the excessive growth of undesirable microbes that threaten aquatic life forms, and the deterioration of water quality, which leads to widespread health-related problems in areas close to the discharge range. The global issue of emerging pollutants (EPs) accumulated in wastewater has garnered attention. Recently, policymakers and researchers have shown interest in addressing emerging pollutants in wastewater due to their potential hazards to human health and the ecosystem. The treatment of emerging pollutants (EPs) is receiving significant attention due to the potential risks to human health and adverse effects on the environment. (Wanda et al., 2017).

The treatment of wastewater is conducted through primary, secondary, or tertiary levels, employing physical, biological, or chemical methods. Primary treatment targets the removal of easily settled materials, which could lead to operational challenges in subsequent treatment stages. On the contrary, secondary treatment involves physical or biological processes that break down the organic content in wastewater by utilizing dissolved organic matter and oxidizing essential nutrients into nitrate and orthophosphate. Consequently, secondary effluent contains elevated levels of inorganic nitrogen and phosphorus, contributing to eutrophication and posing severe threats to aquatic habitats and human health due to the release of unmanageable amount of organic compounds and heavy metals. (Gondi et al., 2022; Rathod, 2014; Shitu et al., 2024). However, tertiary treatment, which is a progressive treatment method that reduces nitrates, phosphates, and organic matter, is required to produce clean and harmless effluent that will be released into water bodies (Molazadeh et al., 2019). In tertiary treatment, denitrification involves the reduction of nitrate to nitrite, followed by the further reduction of nitrite to nitrogen gas, which is then released into the atmosphere. The inadequate performance of wastewater treatment facilities in certain countries can be attributed to design deficiencies in the water treatment process, a shortage of expertise, and insufficient financial resources. Consequently, the need for well-designed wastewater treatment methods and feasible economic approaches is becoming progressively crucial. (Farazaki and Gikas, 2019).

Conventional wastewater treatment systems focus primarily on eliminating solid suspension and reducing BOD through activated sludge. Consequently, the efficacy of traditional water treatment methods in removing micropollutants and inorganic nutrients remains suboptimal. In situations where water contains substantial quantities of additional components like heavy metals, xenobiotics, and nutrient loads, the biodegradation process, limited by the capabilities of traditional wastewater treatment methods to break down both organic and inorganic constituents, is likely to be ineffective. (Gondi et al., 2022; Wollmann et al., 2019). This phenomenon will result in a lethal environmental issue affecting the ecosystem, namely, oxygen depletion and a higher level of effluent toxicity to aquatic life (Umamaheswari and Shanthakumar, 2016). Furthermore, untreated nutrients in wastewater effluent will reduce the functionality of the disinfection stage, resulting in an increase in chlorine demand, which is harmful to the aquatic ecosystem and human health. As a result, there is a higher demand for treatment processes that can eradicate these nutrients prior to discharge (Chai et al., 2021).

According to the United Nations' Report (United Nations, 2019), only 70% of domestic and industrial wastewater undergoes treatment in high-income countries. In contrast, the situation is significantly worse in middle- and low-income countries, where only 28%–38% and 8% of wastewater, respectively, is treated. This means, globally more than 80% of all wastewater is discharged into the environment without proper treatment. Traditional wastewater treatment plants (WWTPs), however, are only capable of removing approximately 50% of pharmaceutical contaminants typically present in wastewater (World Health Organization, 2024). These facilities are, in fact, a major source of pollutant discharge into natural water bodies, as illustrated by Zhang, et al. (2017).

For example, Castiglioni et al. (2018) reported that three WWTPs in Milan managed to treat only 13% of personal care products (PCPs) present in their influent. The occurrence of various classes of emerging contaminants (ECs) in wastewater has been studied globally, revealing significant variations in their concentrations depending on geographical location (Tran, et al., 2018). Ciprofloxacin, a commonly used antibiotic, has been detected at concentrations ranging from below detection limits to 6.4 μg L^{-1} in Asia, and from <LDL to 246.1 μg L^{-1} in North America. Similarly, ibuprofen concentrations in wastewater have ranged from 34.8 to 55,975 ng L^{-1} in Asia and from 2,500 to 45,000 ng L^{-1} in North America. Table 1 summarizes concentrations of widely used antibiotics in WWTP influent and effluent across Asia, Europe, and North America.

Pharmaceuticals in drinking water can pose significant risks to the environment and wildlife. For instance, natural and synthetic hormones like progesterone have been detected in wastewater (Houtman, et al., 2018). When animals ingest such compounds, their endocrine systems may be disrupted, potentially leading to fertility issues, delayed development of reproductive organs, and damage to the kidney or liver (Fang, et al., 2021). Observed that chronic or sub-chronic exposure to 17-β-estradiol in mosquitofish altered hormonal balances and vitellogenin protein levels. The growing production of pharmaceuticals further exacerbates the issue, increasing the concentrations of these ECs in domestic wastewater. For example, India's pharmaceutical market is expanding at a rate of 10% annually, making it one of the fastest-growing globally (IQVIA, 2018). This raises concerns about the emergence of antibiotic resistance genes, which could undermine the efficacy of antibiotics. Additionally, microplastics have recently been classified as emerging contaminants.

Finally, it is important to emphasize that the "emerging" nature of these contaminants reflects the fact that many of their impacts remain insufficiently studied or understood, leaving significant gaps in our knowledge of their long-term effects.

Table 1 shows the concentration ranges of various emerging contaminants (ECs) in raw influent and treated effluent from full-scale wastewater treatment plants (WWTPs), adapted from Tran et al., 2018. Wastewater treatment technologies based on microalgae present an attractive solution due to their efficient fixation of inorganic compounds like carbon dioxide and heavy metals, and to deal with emerging contaminants (Inuwa et al., 2023). Microalgae

10.3389/frans.2024.1513153

TABLE 1 Typical concentration ranges of various emerging contaminants (ECs) in raw influent and treated effluent from full-scale wastewater treatment plants (WWTPs). Adapted from (Tran, et al., 2018).

Emerging contaminants	Concentration (ngL^{-1})					
	Asia		Europe		North America	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Antibiotics						
Amoxicillin	<LDL–6516	<LDL–1670	<LDL	<LDL–190	Nr	<LDL
Azithromycin	1537–303,500	60–980	77–1139	38–784	61–2500	57–1300
Ceftazidime	<LDL	<LDL	–	–	–	–
Chloramphenicol	<LDL–2430	<LDL–1050	<LDL–319	<LDL	–	–
Chlortetracycline	2333–15,911	<LDL–1986	Nr	<LDL	<LDL–310	<LDL–420
Ciprofloxacin	15.5–6453	<LDL–524.1	<LDL–13,625	<LDL–5692	<LDL–246,100	<LDL–620
Clarithromycin	26–1854	4.79–637.1	0.4–647	25–359	<LDL–8000	130–7000
Clindamycin	23.8–26.6	2.94–4.2	<LDL–101	10–180	–	–
Enrofloxacin	<LDL	<LDL	<LDL–18	<LDL–636	5.9–250	3.5–270
Erythromycin	111.4–403.3	70–186.6	<LDL–2130	<LDL–290	–	–
Erythromycin-H_2O	226–20,600	194.5–14,400	24–6755	15–2841	<LDL–3900	<LDL–838
Lincomycin	<LDL–19,401	3.92–21,278	<LDL–281	<LDL	<LDL–360	4.9–510
Meropenem	264.8–433.6	27–67.9	–	–	–	–
Minocycline	730.9–3808	<LDL	–	–	<LDL	<LDL
Ofloxacin	54.8–1274	13.3–7870	Nr	71–8637	470–1000	<LDL–506
Oxytetracycline	<LDL–30,049	<LDL–2014	<LDL–7	<LDL–5	<LDL–47,000	<LDL–4200
Sulfamethazine	<LDL–1814	<LDL–260.8	<LDL–680	<LDL	<LDL–300	<LDL–363
Sulfamethoxazole	3.0–1389	<LDL–562	<LDL–11,555	<LDL–544	<LDL–4200	<LDL–1800
Tetracycline	<LDL–12,340	<LDL–1536	<LDL–790	<LDL–850	<LDL–48,000	<LDL–3600
Trimethoprim	19.5–570	3.7–772	<LDL–4342	<LDL–3052	<LDL–6796	<LDL–37,000
Tylosin	<LDL	<LDL	<LDL	<LDL–173	<LDL–1500	21–720
Vancomycin	962–43,740	<LDL	Nr	<LDL–8514	–	–
Anticonvulsants						
Carbamazepine	<LDL–18,500	<LDL–900	<LDL–3110	<LDL–4596	<LDL–440	28–551
Gabapentin	4825.5–15,359	213–8855	6442–25,079	7651–56,810	Nr	1000 ± 900
Sulpiride	64.9–15,358.8	70.7–322.4	113–1100	110–294	Nr	33–137
Anti-itching						
Crotamiton	<LDL–1500	<LDL–1000	<LDL–140	<LDL–100	–	–
Antimicrobials						
Miconazole	<LDL–597	<LDL	<LDL–337.9	<LDL–35.7	5.2–43	1.6–27
Thiabendazole	<LDL–1.3	<LDL	–	–	6.8–220	6.2–140
Triclocarban	341.1–8880	8.4–5860	97–140	Nr	340–4644	64–617
Triclosan	1.3–2500	49.1–263.9	<LDL–5260	<LDL–430	14–6817	3.1–360
Artificial sweeteners						
Acesulfame	560–13400	5840–9147	12,000–43,000	15,000–46,000	90–2270	600–4330

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TABLE 1 (*Continued*) Typical concentration ranges of various emerging contaminants (ECs) in raw influent and treated effluent from full-scale wastewater treatment plants (WWTPs). Adapted from (Tran, et al., 2018).

Emerging contaminants	Concentration (ngL^{-1})					
	Asia		Europe		North America	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Cyclamate	<LDL–66,400	<LDL–160	10,000–65,000	<LDL–450	–	–
Saccharin	9310–389,000	<LDL–2370	7100–18,000	<LDL–1800	1860–25,100	220–700
Sucralose	1100–6520	1300–5490	2000–9100	2000–8800	17,500–46,100	18,700–48,900
β-blockers						
Atenolol	<LDL–294,700	<LDL–518.6	<LDL–33,106	<LDL–7602	500–2642	<LDL–14,200
Metoprolol	<LDL–79,500	<LDL–268	<LDL–4148	<LDL–5762	16–154	15–212
Propranolol	<LDL–9.56	<LDL–8.3	<LDL–1962	<LDL–615	–	–
Insect repellent						
N,N-diethyl-meta-toluamide (DEET)	124–2341.9	21.6–324.8	<LDL–6900	Nr	200–42,334	13–1663
Hormones						
Estrone	<LDL–132.5	<LDL–51.2	2.4–670	<LDL–95	8–52	<LDL–56
Estriol	<LDL–802	<LDL–30.2	<LDL–660	<LDL–275	<LDL–217	<LDL
17 α- ethinylestradiol	<LDL–26.1	<LDL–13.1	0.4–70	0.5–106	<LDL–242	<LDL
Lipid regulators						
Bezafibrate	16.8–159	<LDL–51.4	100–7600	<LDL–4800	–	65–359
Clofibric acid	<LDL–65	<LDL–44.9	<LDL–265.9	<LDL–91	<LDL	<LDL–44
Gemfibrozil	<LDL–453.4	<LDL–535.2	<LDL–17,055	<LDL–5233	<LDL–36,530	<LDL–1493
Nonsteroidal anti-inflammatory drugs						
Acetaminophen	67–147,700	<LDL–2568	<LDL–482,687	<LDL–24,525	21,000–500,000	<LDL–62,000
Codeine	<LDL–242	<LDL–208	150–32,295	9.7–15,593	77–5700	80–3300
Diclofenac	13–445	<LDL–69.2	<LDL–4869	<LDL–5164	140–2450	<LDL–359
Fenoprofen	<LDL–2260	<LDL–23.4	Nr	<LDL–280	<LDL	<LDL–405
Ibuprofen	34.8–55,975	<LDL–1890	<LDL–83,500	<LDL–24,600	2500–45,000	16–14,600
Indomethacin	<LDL–449.4	<LDL–61.4	<LDL–297	<LDL	<LDL–640	<LDL–507
Ketoprofen	<LDL–286	<LDL–183	<LDL–5700	<LDL–1620	60–150	40–90
Naproxen	<LDL–7762	<LDL–159	<LDL–611,000	<LDL–33,900	1700–25,000	<LDL–3500
Salicylic acid	167–16,900	<LDL–1426	<LDL–164,400	<LDL–10,100	2820–27,800	<LDL–320
Plasticizer						
Bisphenol A	55.6–5850	<LDL–123	<LDL–2376	16–1840	595–2469	2–450
Stimulant						
Caffeine	759–60,500	13–51,700	102–113,200	30–13,900	5809–82,882	<LDL–37,200
UV filters						
Octocrylene	<LDL	<LDL–153	100–1200	<LDL–300	–	–
Oxybenzone	<LDL–2616.8	<LDL–772	<LDL–7800	<LDL–700	–	–

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TABLE 1 (*Continued*) Typical concentration ranges of various emerging contaminants (ECs) in raw influent and treated effluent from full-scale wastewater treatment plants (WWTPs). Adapted from (Tran, et al., 2018).

Emerging contaminants	Concentration (ngL^{-1})					
	Asia		Europe		North America	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
X-ray contrast media						
Iohexol	63.8–124,966	2100–8700	18,000 ± 2000	1200 ± 100	Nr	8623–9237
Iopromide	47.7–12,200	<LDL–7140	<LDL–7500	<LDL–9300	–	–
Iopamidol	82.8–45,611	<LDL–6520	4300 ± 900	4700 ± 1000	–	–

exhibit a notable capacity for the uptake of inorganic nutrients, requiring nitrogen and phosphorus for protein synthesis and utilizing heavy metals as micronutrients for their development. Consequently, employing microalgae as agents for bioremediation in wastewater proves effective in extracting nitrogen and phosphorus from the wastewater, maintaining dissolved oxygen levels, and contributing to the reduction of pathogens and faecal bacteria present in the wastewater. The study's findings indicate that the interaction between wastewater and microalgae resulted in a significant decrease in levels of several contaminants, especially the emerging contaminants in wastewater (Das et al., 2019; Rathod, 2014). Microalgae treatment is also a more efficient method of wastewater treatment because it can treat wastewater in a single step, as opposed to traditional wastewater treatment, which requires a number of steps to fix the carbon, nitrogen, and phosphorus ratios (C:N:P). It is also an environmentally sustainable option because it can convert carbon dioxide into chemical substances and fuel products without resulting in pollution, thereby aiding in the reduction of greenhouse gas emissions (Klinthong et al., 2015). Microalgal biomass harvested from wastewater treatment can be converted into valuable bio-based products such as health supplements, biohydrogen, bio-alcohols, and bio-hydrocarbons to offset its production costs (Koyande et al., 2019; Perez-Garcia and Bashan, 2015). Microalgae have found widespread application in wastewater treatment, with eukaryotic and prokaryotic blue-green algae being the most commonly employed species in experimental setups. The concentrations of non-renewable resource phosphorus and another essential nutrient, nitrogen, found in wastewater, are sufficient to support the cultivation of microalgae for cell growth substrates, biomass yields, and carbon neutrality. Consequently, there is a reduced reliance on freshwater and industrial nutrients typically needed for conventional biological purification, leading to a significant reduction in overall operational costs and the environmental impact of the treatment process. (Delrue et al., 2016).

This review aims to demonstrate the potential of microalgae in removal of emerging contaminants from wastewater through different treatment processes. Different sections discuss phycoremediation of wastewater in removal of several chemicals of emerging concern (ex. dyes, heavy metals, xenobiotic compounds, pesticides, pharmaceuticals, inorganic nutrients, and different microorganisms, especially the pathogens). Different mechanisms employed by microorganisms to remove the emerging contaminants (ex. biosorption, bioaccumulation, biodegradation, etc.) are explained. Also, the influences of several environmental factors (pH, temperature, light, etc.) on the actions of microalgae for wastewater treatment are discussed in this article. Finally, the advantages, limitations, and future perspectives of the microalgae-based treatment method are explained, and it is established that how these eco-friendly technologies can ensure sustainability.

2 Phycoremediation of wastewater

Microalgae, minute organisms consisting of eukaryotic cells, employ the photosynthetic process akin to that found in higher plants. The cellular structure of microalgae encompasses essential components such as cell walls, plasma membranes, cytoplasm, nuclei, and organelles. Notably, microalgae cells contain plastids housing chlorophyll, a pigment crucial for synthesizing food through photosynthesis. A distinguishing feature of microalgae is the absence of a vascular system for nutrient transport, a contrast to higher plants. This lack is compensated by the photoautotrophic nature of each microalgal cell, enabling direct absorption of nutrients without the need for an elaborate vascular network. This unique characteristic simplifies nutrient uptake processes in microalgae, setting them apart from higher plants in terms of nutrient transport strategies. (Emparan et al., 2019). Through their uptake mechanism, microalgae-based wastewater treatment is effective in removing inorganic compounds such as nitrate, phosphate, heavy metals, inorganic carbon, toxic substances (organic and inorganic), BOD, COD, and other impurities dissolved in wastewater (Borowitzka, 1998). Microalgae use photons as energy in their chloroplast cells and extract CO_2 from exhaust gases generated by combustion or bacterial respiration, as well as nutrients from wastewater, to synthesise biomass while producing oxygen. As a result, the microalgae biomass is obtained and O_2 is released into the atmosphere. The conversion of CO_2 and water into organic compounds does not require any additional energy, thereby avoiding secondary pollution. The oxygen released by microalgae is sufficient to meet bacteria's aerobic requirements for metabolising residual organic substances in treated wastewater (Chai et al., 2021).

2.1 Nutrient removal

The uptake and consumption of nitrates and phosphates by microalgae cells for growth can significantly reduce the nitrogen and phosphorus content of wastewater and improve the quality of the wastewater discharge. The ability of different microalgae strains to remove nitrogen and phosphate was investigated (*Chlamydomonas sp., Chlorella sp., and Oocystis sp.*) by assessing NO_3^--N and PO_4^{3-}- P loss. Algae require nitrogen and phosphorus to grow (Rasoul-Amini et al., 2014). Phosphorus is required for the synthesis of nucleic acids, phospholipids, and phosphate esters in the cells, whereas nitrogen binds to proteins in the algal cell, which account for 45%–60% of the dry weight. They use nitrogen and phosphorus-containing organic compounds derived from their carbon sources. The use of those compounds by algae results in the removal of nutrients from the wastewater, a process that can last from a few hours to a few days (Kaloudas et al., 2021).

2.1.1 Phosphorus removal

Inorganic phosphorus, which can be found naturally in lipids, nucleic acids, and proteins in wastewater, is important for microalgae energy metabolism and growth. Inorganic phosphates are transported across the plasma membrane of microalgae cells. Through phosphorylation, inorganic phosphorus in the forms of mono- and dihydrogen phosphate (HPO_4^{2-} and H_2PO_4) is integrated into organic compounds such as adenosine diphosphate (ADP) in the case of algae. To produce its final product, ATP, the phosphorylation process requires energy. Energy can be obtained through the oxidation of respiratory substrates, the electron transport system of mitochondria found in eukaryotic microalgae, and light used in photosynthesis (Chai et al., 2021; Emparan et al., 2019).

2.1.2 Nitrogen removal

Organic nitrogen can enter wastewater from land where animal manure is stored or applied via sewage effluent. Organic nitrogen is a critical component of biological substances such as enzymes, peptides, proteins, chlorophylls, and energy transfer molecules like ADP and ATP. Organic nitrogen is derived from inorganic sources encompassing nitrite (NO_2^-), nitrate (NO_3^-), nitric acid (HNO_3), ammonia (NH_3), ammonium (NH_4^+), and nitrogen gas (N_2). The presence of nitrogen in wastewater is usually in the form of NH_4^+, NO_2^- and NO_3^-. Assimilation can be used by eukaryotic microalgae to convert inorganic nitrogen into organic forms. transformation mechanism that takes place across the microalgae plasma membrane is the reduction of nitrate (NO_3^-) to nitrite (NO_2^-) and to ammonium (NH_4^+) subsequently, which is then integrated into amino acids (the organic form of nitrogen). The first step in nitrate assimilation involves nitrate reductase (NR), which is the reduced form of nicotinamide adenine dinucleotide (NADH), $C_{21}H_{27}N_7O_{14}P_2$, which is found in microalgae and transfers two electrons in the reaction of converting nitrate to nitrite. Following that, ferrodoxin (Fd) from microalgae and nitrite reductase (NADPH, $C_{21}H_{29}N_7O_{17}P_3$) produced from the photosynthesis reaction involving ADP, phosphate, and NADP transfer six electrons in the reaction of reducing NO2 to NH_4+. All inorganic forms of nitrogen will be reduced to NH4+ as a result of this action within the intracellular fluid of microalgae. Finally, glutamic acids (Glu), $C_5H_9NO_4$, neuroactive amino acids found in microalgae, and adenosine triphosphate (ATP) released from phosphorylation (the process of assimilation of phosphates into organic compounds) incorporate ammonium into amino acids (glutamine) within microalgae intracellular fluid (Chai et al., 2021; Emparan et al., 2019; Kaloudas et al., 2021).

In one of the recent studies, two microalgal species (*Chlorella* sorokiniana and Selenastrum sp.) were applied for fish processing wastewater (FPWW) after fat and oil removal, with an objective of facilitating the reuse of wastewater and recovery of several nutrients. The results showed that Chlorella sorokiniana cultivated in the unfiltered FPWW displayed the highest growth and nutrient removal (Khalatbari et al., 2024).

2.2 Xenobiotic compounds removal

Microalgae play an important role in the dispersion, chemical transformation, and bioaccumulation of many toxic xenobiotic compounds. Incomplete combustion of organic materials produces polycyclic aromatic hydrocarbons (PAHs). Because they are generally persistent and highly toxic, with carcinogenic and/or teratogenic properties, they are the subject of strict control and monitoring (Torres et al., 2008). Some microalgae species have a metabolic profile that allows them to survive in PAH-contaminated environments and even assimilate and degrade these contaminants under certain conditions. These organisms can bio-transform low-molecular-weight PAHs; naphthalene can be hydroxylated to form two-ringed PAHs, while phenanthrene (tricyclic PAH) can be bio-transformed to its hydroxylated intermediates (Olmos-Espejel et al., 2012; Lei et al., 2007) tested the possibility of removing fluoranthene (1.0 mg/L), pyrene (1.0 mg/L) and a mixture of fluoranthene (0.5 mg/L) and pyrene (0.5 mg/L) using four microalgae species (*C. vulgaris, S. platydiscus, S. quadricauda, and Selenastrum capricornutum*) incubated for 7 days. *S. capricornutum* performed best, with removal efficiencies ranging from 88% to 98% for various pollutant concentrations.

Monoaromatic hydrocarbons are also known to be mutagenic and carcinogenic. The production, transportation, and storage of oil and oil products are the primary sources of contamination by these compounds. They are highly soluble in water and are strongly absorbed by the soil. When macro- and micronutrients are available at ideal environmental conditions for microalgae growth, these pollutants serve as carbon sources (Semple et al., 1999; Paixão et al., 2007) performed controlled experiments in which they exposed *T. chuii* cultures to 14 different types of gasoline at varying concentrations (0%, 4.6%, 10.0%, 22.0%, 46.0%, and 100%) for 96 and 24 h. Growth inhibition and abnormalities occurred only at concentrations greater than 50% gasoline, demonstrating significant tolerance to such monoaromatic hydrocarbon mixtures. Chlorophenols are another type of highly toxic and persistent xenobiotic with carcinogenic properties. These compounds are widely used in the manufacture of pesticides and wood preservatives (Petroutsos et al., 2008). investigated the potential of 2,4-dichlorophenol (2,4-DCP) removal using the microalgae *Tetraselmis marina* and found that the microalga could metabolise more than 1 mmol L1 2,4-DCP in a 2 L photobioreactor after 6 days of exposure to the contaminant. *Anabaena* and *Aulosira fertilissima* demonstrated remarkable abilities to bioconcentrate and degrade DDT into its two main metabolites; dichlorodiphenyldichloroethylene (DDD) and dichlorodiphenyldichloroethane (DDE) (Lal et al., 1987).

2.3 Dyes removal

Because of their high surface area and binding affinity, microalgae have been used to remove colour and vinyl sulfone dye from textile wastewater. The cell wall of microalgae is involved in dye removal mechanisms such as biosorption, electrostatic attraction, complexation, and bioconversion (Andrade et al., 2018). Dye ions adhere and accumulate on the surface of algal biopolymers, then diffuse onto the biopolymer's solid phase. Extracellular polymers with functional groups can aid in the biosorption of dye molecules onto polymer surfaces (Saha et al., 2023). *Spirogyra* biomass, a microalga species, has been demonstrated to be an effective biosorbent for reactive dye removal. *Caulerpa lentillifera* and *Caulerpa scalpelliformis* biomass can remove basic dyes via biosorption. Furthermore, *C. vulgaris* has been widely used as a biosorbent for the removal of reactive dyes like Remazol Black B (Aksu and Tezer, 2005). Microalgae disintegrate dyes into simpler compounds for bioconversion. *Chlorella vulgaris* can remove (63–69) % of the colour from mono-azo dye by converting it to aniline, as demonstrated by adding them to different concentrations of textile wastewater (Supranol Red 3BW) for a 10-day culture period. Furthermore, five microalgal strains, *A. flos aquae*, *N. elepsosporum*, *N. linkia*, *A. variabilis*, and *C. vulgaris*, were evaluated for their ability to remove red coloration from textile industrial effluent. The experiment revealed that all microalgae strains tested could remove the red dye from the treated textile wastewater effluent with varying reduction percentages. The dye was completely removed by *N. elepsosporum*, followed by *C. vulgaris* (96.16%), *A. variabilis* (88.71%), *N. linkia* (79.03%), and *A. flos aquae* (50.81%). The complexity of the textile wastewater, which contains entangled compositions of other chemicals such as heavy metals, does not appear to affect the efficacy of colour removal by microalgae (Ghazal et al., 2018; Kumar et al., 2014).

2.4 Heavy metals (HM) removal

Heavy metals are metals with atomic densities greater than 4000 kg/m^3 (Vardhan et al., 2019). HMs pollution is a major issue worldwide due to their non-biodegradable properties, abundant sources, toxicity, and accumulative behaviour. Even at low concentrations, HMs are naturally toxic and cause serious diseases in humans and animals (Edelstein and Ben-Hur, 2018). HMs are classified as radionuclides (U, Ra, Am, and Th), precious metals (Au, Pd, Pt, and Ru), and toxic metals (Cu, Cr, As, Zn, Ni, Ag, Sn, Co, and Pb). HMs enter aquatic systems through industrial discharges and agricultural runoff, in addition to naturally occurring sources (Pavithra et al., 2020). Various treatment approaches are available, with varying degrees of success, to remove HMs from the aquatic environment. In any case, these traditional treatment methods generate secondary waste while incurring high operating and maintenance costs. As a result, developing effective, environmentally friendly, and economically viable treatments is critical. Metal bioaccumulation by microalgae may be a viable method of wastewater remediation (Vardhan et al., 2019). Most metal removal techniques use algae, both dry biomass and dead forms, with adsorption as the primary removal mechanism. Microalgae can accumulate toxic heavy metal ions from aqueous solutions at concentrations on the order of 15 mg/g biomass, demonstrating that the process is competitive with other treatment methods (Abdel-Raouf et al., 2012).

Several microalgae species, including *C. vulgaris*, *Scenedesmus sp.*, *Chlorococcum sp.*, *Lyngbya spiralis*, *Tolypothirx tenuis*, *Stigonema sp.*, *Phormidium molle*, *Aphanothece halophytica*, and *Chroococcus paris*, can remove Hg (II), Cd (II), and Pb (II) (Tüzün et al., 2005). Metal absorption by microalgae occurs in two stages: first, the surface of algal cells interacts with metals via physical adsorption or ion exchange in a fast process. The following step, known as chemisorption, is slower and takes place intracellularly, and it is related to metabolic processes involving active binding groups. A cellular distribution analysis revealed that large amounts of metal ions bind to the cell wall, while an insoluble fraction accumulates intracellularly (Omar, 2002).

In a detoxification assay using *C. vulgaris* (Shen et al., 2013), investigated the mechanism of bioconversion of Cr (VI) into its less toxic form of Cr (III). Secondary alcohols were found to be primarily responsible for the reduction of Cr (VI) to Cr (III), with -NH2 and -COOH being the main functional groups associated with the biosorption and bio-fixation of these elements. Magro et al. report a chromium hexavalent (Cr VI) removal value of 60.92% when cultivating Spirulina platensis strain in a mixture of artificial medium and wastewater under controlled air, temperature, and lighting conditions.

(Chong et al., 2000) investigated the treatment of synthetic wastewater containing nickel (Ni) and zinc (Zn) using 11 microalga species with the same cell density. The *S. quadricauda* species was singled out for its ability to reduce an initial concentration of nickel (Ni) and zinc (Zn) of 30 mg/L to 0.9 mg/L. The removal of these metals reached 97% within the first 5 min, then dropped to 0.4 mg/L within the next 90 min. This efficiency can be attributed to the fact that it has a larger surface area than the other microalgae studied.

Arsenic (As) is a toxic element that can be found in nearly all terrestrial environments. The organic forms are less toxic than the inorganic forms [arsenite, As (III) and arsenate, As (V)]. Arsenic exposure through drinking water is linked to a variety of skin diseases, respiratory, neurological, cardiovascular, gastrointestinal, and urinary disorders, as well as an increased risk of high blood pressure and diabetes (Mestrot et al., 2013; Zhang et al., 2013) demonstrated that the marine microalga *Ostreococcus tauri* can convert inorganic arsenic into a less toxic organic form that can be easily incorporated into biogeochemical cycles and can promote As volatilization via the biomethylation metabolic mechanism.

2.5 Pathogens removal

Pathogen removal mechanisms of microalgae in wastewater include nutrient competition, pH and dissolved oxygen level elevation, pathogen adhesion and sedimentation, and algal toxins (Dar et al., 2019). The CO_2 assimilation in photosynthesis causes the pH value to rise during microalgae cultivation. Nitrogen absorption by microalgae raises the pH of the medium because every nitrate ion converted to ammonia produces one OH^- ion. This phenomenon will result in pathogen eradication. Because of the limited transfer of

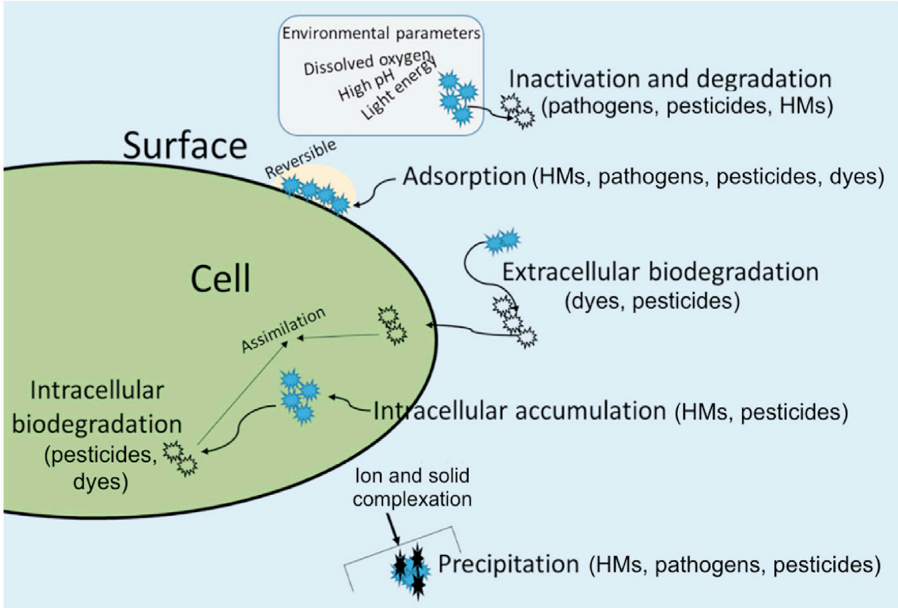

FIGURE 1
Removal mechanisms of pathogens, pesticides, dyes and heavy metals by microalgae. Reprinted with permission from Elsevier (Chai et al., 2021), licence number 5705400764493.

carbon dioxide from the atmosphere and the process of microbial oxygenation, microalgae will also raise pH levels, potentially causing pathogens to die off. Fluctuations in pH are also known to have an adverse effect on *E. coli* survival, resulting in a remarkable elimination of faecal coliforms such as *Escherichia coli*, *Enterococci*, and *Clostridium perfringens* in waterbodies (Ansa et al., 2011). Oxygenation caused by bacterial respiration in treatment ponds that contributes to algal growth has been linked to faecal bacteria annihilation due to the presence of toxic oxygen formations. Microalgae photosynthesis activity is also sufficient to raise oxygen concentrations in waterbodies to levels that are harmful to faecal bacteria. Oxygen concentrations greater than 0.5 mg/L have been linked to faecal bacteria removal (Ansa et al., 2011). The adhesion of faecal bacteria to microalgae in wastewater is critical because it ensures that bacterial cells are in close proximity when microalgae elevate pH and dissolved oxygen. Pathogens will first attach to the solid matter that will sink as sediment and deposit on the surface of microalgal cells for adhesion to occur. Following that, the polysaccharides that are available for expression by bacterial cells will form positively charged amino groups. The positively charged polymers will then neutralise the negatively charged microalgal surface, resulting in the formation of a bridge between the particles and bacterial cell adhesion to microalgae (Dar et al., 2019). Furthermore, a toxin called microcystin-LR produced by an algal strain called *Synechocystis sp*. and toxins of long-chain fatty acids produced by *C. vulgaris* under high pH conditions have been found to be toxic to pathogens and faecal bacteria (Mohamed, 2008). In another experiment, *Salmonella enterica* was found to be eliminated by a microalgae species, *Scenedesmus sp.* (Mezzari et al., 2017). The effect of elevated microalgae pH and dissolved oxygen (DO) levels on the removal and inactivation of *E. coli*, *Enterococci*, and *C. perfringens* was studied (Liu et al., 2020).

2.6 Pesticides removal

Through biosorption and biodegradation, microalgae can assimilate a wide range of organic pollutants, including pesticides, as an energy source for their growth in wastewater. Biosorption includes mechanisms of absorption, adsorption, surface complexation, ion exchange, and precipitation that occur in both living and dead cell walls. Biodegradation occurs when microalgae produce enzymes that break down the bonds in pesticide molecules. *Chlorella vulgaris* was exposed to four common fungicides, propamocarb, mandipropamid, cyprodinil, and metalaxyl, in two experiments: short-term involving biosorption (60 min) and long-term involving biodegradation (4 days) in a study conducted by (Chai et al., 2021). Another set of short and long-term experiments was carried out to determine the percentage of pesticides removed by microalgae. Chlorella vulgaris was used in the experiment, and the pesticides used were molinate, simazine, isoproturon, atrazine, propanil, carbofuran, dimethoate, pendimethalin, metoalcholar, and pyproxin. The results showed that microalgae removed more pesticides in the long-term experiment than in the short-term experiment (Hussein et al., 2016).

Removal of pathogens, pesticides, dyes and heavy metals by microalgae with associated mechanisms are shown in Figure 1.

2.7 Pharmaceuticals removal

Pharmaceutical compounds (PCs) are a broad class of chemical substances that are widely used around the world. PC residues pollute aquatic environments from agricultural operations, hospital effluents, industrial pollution, and household trash. The removal of emerging pharmaceuticals in conventional wastewater treatment plants ranges from 10% to 100%, depending on the method and the emerging

TABLE 2 Quantitative comparison between the steps of phycoremediation.

	Biosorption	Bioaccumulation, or bio-uptake	Biodegradation	Photodegradation	Hydrolysis	References
Definition	The attachment of pollutants on the surface of the microorganisms is referred to as biosorption	The accumulation of pollutants from an external environment inside the cell's cytoplasm	Biodegradation is the metabolic breakdown or degradation of pollutants	The degradation of a material due to photon exposure	The chemical breakdown of a compound due to reaction with water	Gondi et al. (2022)
pH	pH of solution strongly affects sorption capacity of heavy metals though the process can take place over wide range of pH	Significant pH can seriously affect living cells	Initial pH does influence bioremediation	The initial pH is one of the most effective parameters in photodegradation processes	Hydrolysis reaction is pH dependent at some level	Chai et al. (2021)
Cost	Usually, low. Biomass can be got from wastes	Usually high since process involves living cells that need to be supported (in case of bio-uptake)	Cost effective step	Usually, low cost. Requires high cost where artificial light is needed	In most of the cases, enzymatic hydrolysis is considered to be the most expensive operational process	Kaloudas et al. (2021)
Rate of uptake	Generally fast, few seconds for outer cell wall accumulation	Slower compared to biosorption. Intercellular uptake takes a long time	Initially slow. Later goes comparatively fast as growth of microalgae takes place simultaneously	Too much lengthy process	Begins slowly but becomes fast after sometime	Gondi et al. (2022)
Energy demand	Low	Energy is required for cell growth	Highly dependent on energy involved in breaking down contaminants	Caused by photon energy in light	Still uncleared though timed additions of fixed amounts of substrate may help in minimizing the energy required	Olawale (2021)
Regeneration and reuse	High possibility of biosorbent regeneration and reuse	Reuse is limited due to intercellular accumulation	Reuse is not possible	In most of the cases, it can be easily recovered	It is possible to reuse the free enzymes	Olawale (2021)
Temperature	Within a modest range	Inhibited by low temperature	The temperature will vary with micro-algae species. The optimal temperature range for microalgae cultures is 20°C–30°C	Within a modest range	Mostly higher temperature	Gondi et al., 2022

pollutant (Kruglova et al., 2016). Pharmaceutical compounds have measured concentrations ranging from 0.008 to 55.78 g/L, while pesticides have measured concentrations ranging from 0.01 to 8845 g/L. Some of the negative effects on aquatic organisms include behavioural changes, the accumulation of pharmaceutical and cosmetic products, reproductive damage, and the inhibition of cell proliferation (Mascolo et al., 2010). Microalgae extracellular enzymes convert certain antibiotics into less toxic or even non-toxic intermediates. Enzymes in cells then bioaccumulate and degrade these intermediates. Furthermore, the degree of biodegradability is determined by the complexity of the structures (Naghdi et al., 2018). Both ketoprofen and ibuprofen, which are both nonsteroidal anti-inflammatory drugs, are eliminated from wastewater in different ways. Ibuprofen was eliminated more efficiently than ketoprofen using vascular plants and microalgae-mediated treatment. *Chlorella sorokiniana* completely destroyed paracetamol and ibuprofen (Bai and Acharya, 2017). Adsorption, accumulation, and eventually biodegradation of various substances is facilitated by the EPS matrix. Because of the presence of carboxyl, hydroxyl, and phosphoryl functional groups, microalgae are predominantly negatively charged, which is advantageous for capturing positively charged PC molecules (Hom-Diaz et al., 2015). Many recent studies have demonstrated the rapid uptake of PCs onto the cell wall using EPS. In general, the studies suggest that PCs are eliminated through a variety of mechanisms, with bio-adsorption being the most common. Bio-adsorption contributes differently depending on the microalgae used and the micropollutant absorbed (Bai and Acharya, 2017). Study has demonstrated that *Scenedesmus dimorphus* can biodegrade about 85% of 17 a-estradiol within 7 days (Zhang et al., 2014).

2.8 Carbon dioxide fixation

Industrial effluents contain about 10%–15% CO_2, making them an excellent source of CO_2 for microalgae cultivation and a potentially more efficient route for bio-fixation (Ji et al., 2013). Microalgae have received a lot of attention among biological CO_2 fixation technologies because they can convert CO_2 (and complementary nutrients) into biomass at much higher rates than conventional crops (Farhadian et al., 2008). Furthermore, they are a sustainable ecological alternative to CO_2 mitigation in the atmosphere. Microalgae contain approximately 50% carbon in their composition, and to produce 1 tonne of microalgae requires approximately 1.83 tonnes of CO_2. Direct use of combustion gases from chimneys in microalgae cultures reduces pre-treatment costs but requires tolerance to extreme conditions such as high CO_2 concentrations and the presence of inhibitory compounds such as NOx and SOx (Kumar et al., 2010; Cheng et al., 2006) tested different concentrations of CO_2 as the input gas when controlling CO_2 levels in a culture of *C. vulgaris* in membrane photobioreactors with a closed environment and achieved the best results for CO_2 removal at a concentration of 1.0% (Chiu et al., 2011). Investigated the growth and potential for on-site bioremediation of Chlorella sp. MTF-7, a thermotolerant and CO_2-tolerant strain. This microalga was grown in a tubular photobioreactor with an artificial directly aerated medium and an intermittent flow of steel industry combustion gas. In this cultivation, average CO_2, SO_2, and NO removal efficiencies of 60, 70, and 50%, respectively, were obtained.

2.9 Biological oxygen demand (BOD) reduction

High levels of biochemical oxygen demand can deplete the oxygen in the water, causing the fish to suffocate and creating conditions for anaerobiosis in the water. When it comes to wastewater treatment, removing biochemical oxygen demand is a primary goal. Because microalgae produce oxygen through photosynthesis, they can reduce biological oxygen demand in wastewater. The removal of phenolic compounds reduces the waterbody's biochemical oxygen demand (Kaloudas et al., 2021). Microalgae such as *Chlorella pyrenoidosa*, *Chlorella kessleri*, and *Spirulina sp*. have been shown in experimental procedures to have the ability to remove phenolic compounds from water and can be prominent species for phenol removal (Zhang C. et al., 2020). Although the removal of phenolic compounds by algae in wastewater treatment may be difficult because microalgae can only biodegrade phenol under limited carbon source conditions in which they use phenol as an alternative carbon source, wastewaters are typically rich in carbon sources for the algae to utilise, reducing the potential use of phenol compounds as an alternative energy source (Kaloudas et al., 2021).

3 Microalgal mechanisms for the removal of emerging pollutants

Pollutant removal via a microalgal-based treatment system involves a variety of reaction mechanisms. The bioremediation mechanisms of the microalgae-based treatment method for removing emerging pollutants are depicted in Figure 1. The mechanisms underlying microalgal-based EP bioremediation are described as follows, (a) During bio uptake, pollutants pass through the algal cell wall and attach to intracellular proteins in living cells and (b) in the non-living cell during bioaccumulation (c) during biosorption, pollutants are adsorbed into the algal cell wall or Extra Polymeric substances (EPS) (d) During biodegradation, complex pollutants are broken down into simpler, less toxic compounds (e) During photodegradation, they undergo exposure to direct or UV light (Gondi et al., 2022). Table 2 shows the quantitative comparison between the steps of phyco-remediation.

3.1 Biosorption

Biosorption refers to the adherence of pollutants to the surface of microorganisms. Algae has the potential to be used as a bio-sorbent. On the algal cell surface, different functional groups such as polysaccharides, lipids, and proteins serve as adsorption sites (El-Naggar et al., 2019). There are two types of biosorption; physisorption (physical biosorption) and chemisorption (chemical biosorption). Solute molecules interact with the binding sites on the sorbent surface during physical adsorption, whereas chemical bonds are formed during chemisorption. The advantages of this method include lower costs, simple processes, no sludge production, and the ability to remediate large amounts of wastewater with low pollutant concentrations (Lo et al., 2014; Olawale, 2021). Microalgae, which can produce Exopolysaccharides (EPSs), are used as surface-active agents for eliminating pollutants (primarily heavy metals). Algal biosorption is influenced by a variety of factors, including cell wall composition, which is essential for electrostatic attraction and chelation or complexation. Algal bioremediation is facilitated by functional groups on the algal cell surface, especially the carboxyl group. The interaction of positively charged pollutants and negatively charged microalgae cellular walls is involved in the biosorption mechanism. The rate of biosorption is influenced by dissolved oxygen, pollutants concentration, initial pH level, and hydraulic retention time (Gusain et al., 2020; Ma et al., 2020).

3.2 Bioaccumulation and bio-uptake

Bioaccumulation is defined as the accumulation of contaminants from the external environment within the cytoplasm of a cell. *Spirogyra*, for example, can efficiently absorb and collect contaminants inside their cells and use them to grow. *Nannochloris sp*. absorbed only 11% of sulfamethoxazole, 11% of trimethoprim, 27% of triclosan, and 13% of carbamazepine (Rezania et al., 2016). Pollutant bio-adsorption and bioaccumulation mechanisms are completely distinct. The estimation of bioaccumulation and bio-adsorption of pollutants is difficult because both processes occur in most cases in parallel. The first stage of the bioaccumulation process is bio-adsorption. Molecules must be adsorbed within the microalgal cell in order to bioaccumulate there. Pharmaceuticals (triclosan and sulfamethoxazole) have been found to bioaccumulate in microalgae, resulting in an excess of reactive oxygen species and, eventually, cell death (Bai and Acharya, 2017).

In bioaccumulation and bio-uptake, contaminants can enter algal cells through the cell wall and bind to intracellular proteins.

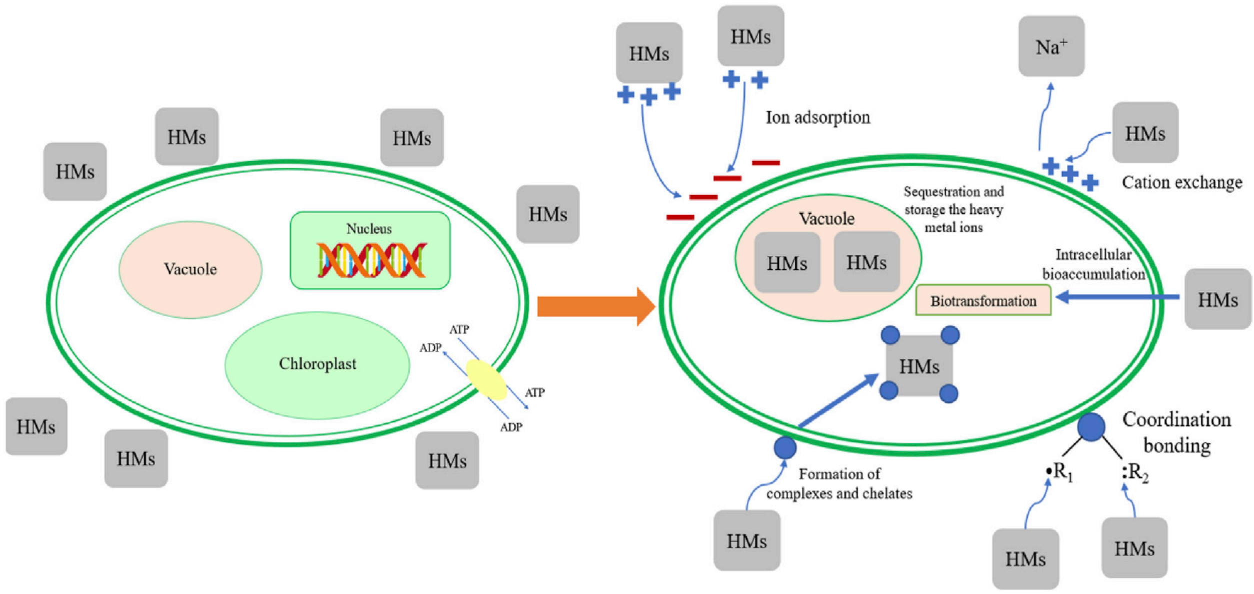

FIGURE 2
Biosorption, biodegradation and detoxification of heavy metals by microalgae. Reprinted with permission from Elsevier (Yan et al., 2022), licence number 5705480505642.

The primary distinction among bioaccumulation and bio-uptake is that bio-uptake of contaminants can only occur in living microalgae cells. The transfer of hazardous substances or pollutants from the surrounding environment into the cells is known as biological or bio-uptake. Microalgae can absorb nutrients and can be mass cultivated (Mulla et al., 2019).

3.3 Biodegradation

Enzymes catalyse the metabolic breakdown or degradation of contaminants during biodegradation. In general, microalgae degrade complex parent compounds into simpler ones. Several enzymatic processes, such as hydroxylation, glycosylation dehydrogenation, hydrogenation, and hydrolysis, may be involved (Varjani, 2017). Pollutant biodegradation by algal-bioremediation occurs in three stages, with several enzymes involved in the catalysis. The first phase of cytochrome P450 detoxification involves hydrolysis, oxidation, or reduction activities. During this phase, the addition of the hydroxyl group transforms the lipophilic molecules to hydrophilic molecules. In the second phase, compounds with electrophilic groups develop a conjugate bond with glutathione in the second phase that shields the cell from oxidative damage. A variety of enzymes (such as carboxylase, dehydrogenase, laccases, and decarboxylase) are used in the third phase. The biodegradability of compounds is determined by the complexity of their structures (Xiong et al., 2016). Compounds with a linear and unsaturated structure, as well as electron-donating groups, biodegrade faster than complex compounds with a cyclic structure, as demonstrated by *Navicula* sp., *C. pyrenoidosa, and S. obliquus,* which showed 95% biodegradation. Other examples include the biodegradation of levofloxacin by *C. vulgaris*. Due to the presence of few extracellular enzymes, EPS is hygroscopic, forming a matrix around the cells that aids in adsorption, accumulation, and biodegradation (Xiong et al., 2016; Posadas et al., 2014) proposed that contaminants biodegradability is affected by the C:N:P ratio of wastewater, and that the ideal C:N:P for optimum biodegradability is 100:18:2. Biodegradation, as opposed to bioaccumulation or biosorption, can reduce contaminants toxicity in algae cells, and algal biomass could be used to produce biofuels and value-added bioproducts. Biodegradation can occur in two ways; co-metabolism and metabolic biodegradation. The co-metabolism biodegradation process includes the breakdown of contaminants catalysed by enzymes, with contaminants serving as a carbon source for algae throughout metabolic biodegradation (Norvill et al., 2016).

Biosorption, biodegradation and detoxification of heavy metals by microalgae is shown in Figure 2 with possible mechanisms.

3.4 Photodegradation

Even if a pollutant cannot be bioremediated using the techniques described above, microalgae can still play an essential part in effective bioremediation via photodegradation. There are two types of photodegradation: photooxidative degradation and photolysis (Abo et al., 2016). When a pollutant interacts with oxidants like hydroxyl radicals formed as a result of photooxidation, photooxidative degradation occurs. Photolysis occurs when a pollutant absorbs light, causing a change in the pollutant's conformation and, as a result, its degradation. The photodegradation process is controlled by the physicochemical characteristics of the pollutant and wastewater, as well as the intensity and wavelength of light. The introduction of Dissolved Organic Molecules (DOM) is another method for increasing the rate of photodegradation. DOM is a class of compounds that include fulvic acids, humic acids, and hemicellulose and play an active part in enhancing photodegradation through mechanisms such as hydroxyl radical production or redox cycling. Pollutants that absorb less light become photosensitized and transformed as a result of interactions with EOMs (Extracellular Organic Matter) and DOMs (Gondi et al., 2022). There are two types of photo-degradation; direct and indirect photo-degradation. Algal systems use algal scrubbers and turbulent mixing in both photobioreactors to increase light exposure. This process, however, is highly selective, as not all pollutants can be photodegraded (Reymann et al., 2020).

3.5 Hydrolysis

In conventional treatment processes, hydrolysis can be used to deactivate some emerging pollutants. This process is primarily determined by the pollutant structure. The disadvantage of the method is the fact that numerous emerging pollutants, particularly pharmaceuticals, can withstand hydrolysis. Hydrolysis, for example, can only be used to break down a few pharmaceuticals, such as lactam antibiotics. This process is resistant to pharmaceuticals that include sulphonamide and fluoroquinolone (Banu et al., 2020). Chemical structure, pollutant concentration, temperature, and pH are all factors that influence hydrolysis. Although information on antibiotic hydrolysis in micro-algal bioremediation is limited, the chemical reactions involved are pollutant-specific. The rate of hydrolysis in an algal pond can increase as the temperature rises (Zhang S. et al., 2020). Furthermore, because the pH of algal ponds can vary greatly, new contaminants that hydrolyse at high pH levels can breakdown significantly during the day. Emerging pollutants that were hydrolysed at neutral pH, on the other hand, may still degrade at night while the pH values return to neutral bandwidth (Gondi et al., 2022).

4 Factors affecting wastewater treatment by microalgae

The efficiency of microalgal-bioremediation processes is affected by various physicochemical factors. These factors include pH levels, redox potential, temperature, the duration and intensity of light exposure, hydraulic retention time, and the size of the adsorbent. These elements collectively play a crucial role in shaping the rate and effectiveness of microalgae-mediated bioremediation mechanisms. The pH of the environment, the redox state, and the prevailing temperature can significantly impact the metabolic activity and growth of microalgae, influencing their capacity to remediate contaminants. The duration and intensity of light exposure are essential considerations, as they directly affect photosynthesis, a key process in microalgal remediation. Hydraulic retention time, representing the duration of water within the system, and the size of the adsorbent particles also contribute to the overall efficiency of microalgal-bioremediation processes by influencing contact time and surface area availability for remediation processes.

4.1 pH

pH is a critical parameter that can influence the mechanism of microalgal bioremediation. pH also influences the ionisation states of various functional groups on the adsorbent's surface (Ummalyma et al., 2016). Any change in the optimal pH of any biological process may slow down the rate of the reaction. Because at lower pH, the algal surface becomes positively charged, reducing molecule adsorption (Chen et al., 2016). When the pH rises above the isoelectric point, the algal surface becomes negatively charged, causing absorption to increase. A pH greater than 9 has a negative impact on algal growth because the capacity for carbon dioxide absorption is significantly reduced and RuBisCO activity cannot be maintained (Sutherland et al., 2015).

4.2 Temperature

Industrial wastewater effluents, when discharged, often carry elevated temperatures, posing a risk of thermal pollution in aquatic ecosystems. Microalgae, despite having strain-specific optimal temperatures, exhibit a versatile ability to thrive across a broad temperature spectrum. This adaptability allows them to withstand and potentially mitigate the thermal impacts associated with the immediate disposal of heated industrial wastewater into aquatic habitats. In essence, while microalgae have temperature preferences, their capacity to flourish within a wide range makes them valuable in scenarios where temperature fluctuations in wastewater discharges are a concern. The optimal temperature range for commonly cultivated microalgal strains is 15°C–35°C. Once the optimal temperature is reached, biomass productivity decreases dramatically with increasing temperature (Chen et al., 2020). Temperature fluctuations are a major source of concern in microalgae cultivation facilities. Microalgal species such as *Spirulina plantesis* thrive at 35C, while *Scenedesmus* sp. thrives at varying temperatures. As a result, microalgae that can grow in wastewater at high temperatures (30°C–40°C) are critical microorganisms for algal-bioremediation of emerging pollutants (Cheah et al., 2015).

4.3 Light intensity

Algae, being phototrophic organisms, harness light energy to synthesize the essential chemical compounds necessary for their growth. The photosynthetic process, facilitated by the presence of inorganic carbon, adequate light, and suitable temperatures, enables algae to absorb nutrients vital for their development. The growth of algae is intricately linked to the availability and intensity of light, a factor that plays a pivotal role in shaping the nutrient utilization efficiency within the waterbody. The interplay of these factors underscores the complex relationship between light, photosynthesis, and nutrient dynamics, influencing the overall ecological balance of the aquatic environment. (Whitton et al., 2015). Microalgae photosynthetic systems are more productive in the blue and red regions of the spectrum, 400 and 600–700 nm, respectively, resulting in better utilisation of nitrogen and phosphorus from wastewater, with red light stimulating algal growth. Although the use of artificial light increases the cost of wastewater treatment, the technology of the light-emitting diode, which provides a longer lightbulb lifespan in combination with lower electricity consumption, makes the use of artificial light sources to enhance the photosynthetic activity of the algae and thus enhancing nutrient uptake from the waterbody more prominent (Ibrahim et al., 2014). The best light source for algae cultivation is thought to be developed light-emitting diode technology with narrowband wavelengths. A study using *Spirulina platensis* found that red light increased the growth rate of the microalgae by 38%. Green light was used to achieve maximum productivity with *C. vulgaris* (Wang et al., 2007).

4.4 Hydraulic retention time

The efficiency of microalgae in taking up pollutants can be influenced by the hydraulic retention time. A shorter hydraulic retention time may lead to incomplete or partial removal of pollutants in certain instances. The interplay between microalgal biomass and hydraulic retention time is a critical factor influencing pollutant removal. There is an observable trend where, up to a certain threshold, the removal rate increases with higher concentrations of microalgae and longer hydraulic retention times. However, once the hydraulic retention time surpasses a certain limit, or if it is prolonged excessively, the removal efficiencies may experience a notable decrease. This highlights the importance of optimizing hydraulic retention time in conjunction with microalgal biomass for effective pollutant removal in wastewater treatment processes. (De-Bashan and Bashan, 2010).

4.5 Dose of adsorbent and particle size

The greater the permeability of the pollutant particle, the greater the absorption into the cell wall. This interaction is also affected by the pollutant's toxicity. It is due to the availability of more surface area, which increases the availability of binding sites. Nano compounds are more readily absorbed. Surface area, electrostatic capacity, and the functional groups involved in the interaction are all factors that influence algal bioremediation via adsorption (Hlongwane et al., 2019). The absorption was found to increase as the hydraulic retention time between the pollutants and the adsorbent increased (Sarkar and Dey, 2021).

5 Transformation and fate of contaminants inside the microalgal cells

Despite the benefits of the bioaccumulation process, many studies fail to consider the fate of emerging contaminants within the algal cell. There is still much debate about how to safely dispose of hazardous algal biomass after bioaccumulation (Gojkovic et al., 2019). The conversion and breakdown of complex compounds into simpler molecules is known as biodegradation or biotransformation. Compound breakdown can take place both intracellularly and extracellularly. Biodegradation has the capability to minimise the toxic effects of contaminants within algal cells and in bulk medium when compared to bio-adsorption or bioaccumulation processes. Microalgae biomass can be converted into additional value-added products. Biodegradation can take place through two main mechanisms: metabolic degradation and co-metabolism. Contaminants provides carbon to microalga throughout metabolic degradation. The degradation of contaminants in the co-metabolism process is mediated by enzymes that catalyse the substrates in the bulk medium (Tiwari et al., 2017).

Considerable research efforts have been dedicated to exploring the effectiveness of microalgal biodegradation in removing pharmaceuticals and personal care products from wastewater. This ongoing research aims to understand and optimize the capabilities of microalgae in breaking down and eliminating these contaminants, offering a potential environmentally friendly solution for wastewater treatment. The investigation focuses on the mechanisms and efficiency of microalgal biodegradation, with the goal of developing sustainable and effective methods to address the presence of pharmaceuticals and personal care products in wastewater. (Nguyen et al., 2021). Microalgal biodegradation was found to be the most effective method of removing estrogenic hormones. It was discovered that enzymes oversee biodegradation, and enzyme activation can be measured by the concentration of EC in the bulk medium. Thus, the EC threshold concentration is critical for triggering enzyme activity and microalgal biodegradation (Xiong et al., 2018). Microalgae biotransformation of these constant and robust ECs is complex. There is still substantial disagreement about the role of enzymes in the biodegradation process (Sutherland and Ralph, 2019). Further investigation into the function of enzymes and their degradation procedure in wastewater medium is required.

It is also worth noting that not all the contaminants are readily biodegradable, and some can be toxic to microalgal cells (Villar-Navarro et al., 2018). Some non-biodegradable pharmaceutical contaminants (e.g., carbamazepine) were found to be resistant to photolysis in high-rate algal ponds. It is proposed that microalgal strains can be pre-acclimated to target EC concentrations that are not toxic. This is a critical first step towards effective toxic substance remediation. Studies have shown that when microalgae are exposed to contaminants, their metabolisms and cellular processes improve. Microalgae tolerance to ECs appeared to increase in response to chronic exposure to target EC. This is because enzymatic pathways are activated to combat the toxic effects of ECs (Norvill et al., 2016; Chen et al., 2015) reported that when *C. pyrenoidosa* was pre-exposed to the antibiotic cefradine, its removal efficiency increased.

Microalgae may indirectly improve the biodegradation process through symbiotic interaction with bacteria. The synthesis of reactive oxygen species during photosynthesis was thought to be aided by photosynthetically mediated pH changes and high oxygen production. Because algal biomass is less toxic after biodegradation, it can be used for a variety of purposes, including biofuel. However, there is a chance that accumulation and sorption will leave some ECs after bioremediation (Agüera et al., 2020).

6 Advantages of microalgal-bioremediation systems for removal of emerging pollutants

Flocculation, chemical precipitation, activated charcoal, reverse osmosis, ultraviolet disinfection (UV disinfection), ultrafiltration, electro-coagulation, and ion exchange are the most common wastewater treatment methods. These approaches are not cost-effective because they necessitate a significant amount of energy and labour (Sankaran et al., 2020). Microalgal-bioremediation systems have been shown to be an effective method of wastewater treatment. Microalgae are abundant in most environments, do not generate toxic substances, grow quickly, and have a large surface area.

- Cultivating microalgae recovers essential nutrients from wastewater and prevents eutrophication of freshwater, whereas in conventional treatments, nitrogen is removed as atmospheric nitrogen, carbon is oxidised to carbon dioxide, while phosphorus is precipitated (Nagarajan et al., 2020).
- Microalgae can withstand a variety of emerging pollutants. *Scenedesmus*, *Chlamydomonas*, and *Chlorella Sp.* were discovered to be among the most reported microalgal strains in proof-of-concept studies and are extensively studied (Wang et al., 2016).
- Microalgae play a crucial role in mitigating global warming by capturing atmospheric carbon dioxide through photosynthesis. Utilizing this natural process, microalgae absorb carbon dioxide from the atmosphere and convert it into organic compounds, thereby serving as an effective carbon sink. This carbon sequestration by microalgae helps reduce the concentration of greenhouse gases in the atmosphere, ultimately contributing to the mitigation of climate change and alleviating the severity of global warming. (Kannah et al., 2021).
- Cultivating microalgae on barren land offers a valuable opportunity to alleviate pressure on traditional agricultural land. By utilizing barren or non-arable areas, microalgae cultivation provides an alternative and sustainable approach to food and biomass production. This method not only optimizes land use but also mitigates the competition for fertile soil resources with traditional crops. Additionally, microalgae cultivation on barren land has the potential to contribute to ecosystem restoration and enhance resource efficiency in areas where conventional agriculture may be impractical or unsustainable. (Farooq et al., 2015).
- Value-added products are bioproducts that have been modified or improved as a result of a process. Possibility of producing a variety of value-added bioproducts for various industries and applications (fish feed, lipids, biofuel, sugars, bio pigments, enzymes, biofertilizers, algal plastics, and biomaterials). Furthermore, determining the protein and oil content is critical for determining what types of bioproducts can be produced (Banu et al., 2020).
- Microalgae grow at a rate that is 10–50 times faster than that of other terrestrial plants. Numerous studies have shown that cultivating microalgae is effective. Several studies have reported successful cultivation of several microalgae species for wastewater treatment, including *Chlorella, Chlamydomonas, Botryococcus, Scenedesmus, Arthrospira, and Phormidium* (Pittman et al., 2011).

7 Limitations/challenges associated with microalgae-based wastewater treatment

Traditional wastewater treatment plants (WWTPs) primarily target organic matter and nutrients but are ineffective at fully removing emerging contaminants (ECs) such as pharmaceuticals, hormones, antibiotic resistance genes (ARGs), and microplastics, with removal rates for some contaminants as low as 50% (World Health Organization, 2024; Zhang et al., 2017). Advanced methods like ozonation, reverse osmosis, and advanced oxidation processes (AOPs) offer higher efficiency but are energy-intensive, costly, and often produce harmful byproducts, such as bromates. Emerging biological approaches, including microalgae-based treatments, show promise but face challenges such as scalability, large space requirements, and the need for controlled environmental conditions. These limitations are further compounded in low- and middle-income countries, where only a small fraction of wastewater is treated due to financial and operational barriers. Additionally, there are significant gaps in understanding the long-term environmental and health impacts of ECs, as well as variability in contaminant concentrations across regions, which complicates the standardization of treatment technologies. Residual sludge management and the lack of real-world validation for many pilot-scale innovations also remain critical challenges.

The limitations of microalgae-based wastewater treatment are as follows:

- While microalgae-based wastewater treatment is geared towards efficient nitrogen and phosphorus removal, not all emerging pollutants and heavy metals can be effectively eliminated. Before integrating microalgae with wastewater treatment, the inhibition factors from the environment and wastewater itself must be considered because they have a large impact on the growth and treatment efficiency of microalgae (Chai et al., 2021).
- Significant amounts of solids suspensions and high turbidity in industrial wastewater may affect light radiation through the wastewater, thereby affecting photosynthesis and interfering with microalgae growth. As a result, an additional wastewater method with high solids removal efficiency, such as sedimentation, adsorption, coagulation, and so on, can be used to ensure high photosynthesis efficiency (Amenorfenyo et al., 2019).
- Even though the cultivation of microalgae in wastewater is simple and effective, it is not an enticing alternative wastewater treatment method in terms of cost. According to (Umamaheswari and Shanthakumar, 2016) high downstream processing costs, a small scale of production, and only selected microalgae species and cultivation modes can yield high quality biomass that can be converted into useful bioproducts all contribute to this treatment method's less profitable property. Furthermore, enclosed photobioreactors that require an artificial light source and chemical agents for sterilisation raise the overall cost of production.
- It is critical to choose the right species of microalgae for wastewater treatment. The selected microalgae species should be able to cope with variations in environmental factors due to the different physical and chemical composition of wastewater from various sources. Furthermore, the species should be able to share metabolites in order to accommodate stress and survive any attack by unwanted species as well as nutrient

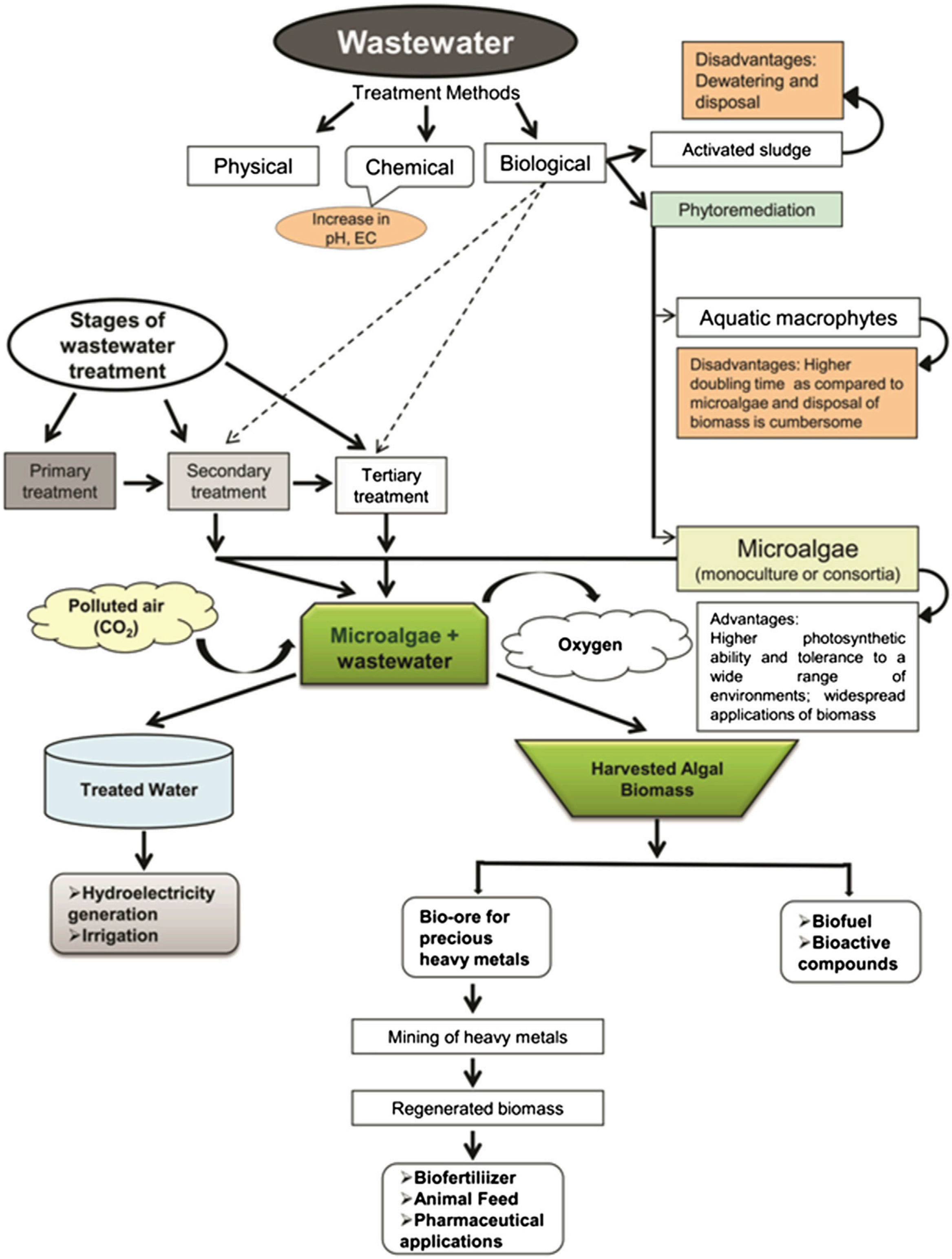

FIGURE 3
Different processes involving wastewater treatment by microalgae with their advantages and disadvantages. Reprinted with permission from Springer-Nature (Renuka et al., 2015), licence number 5705400031262.

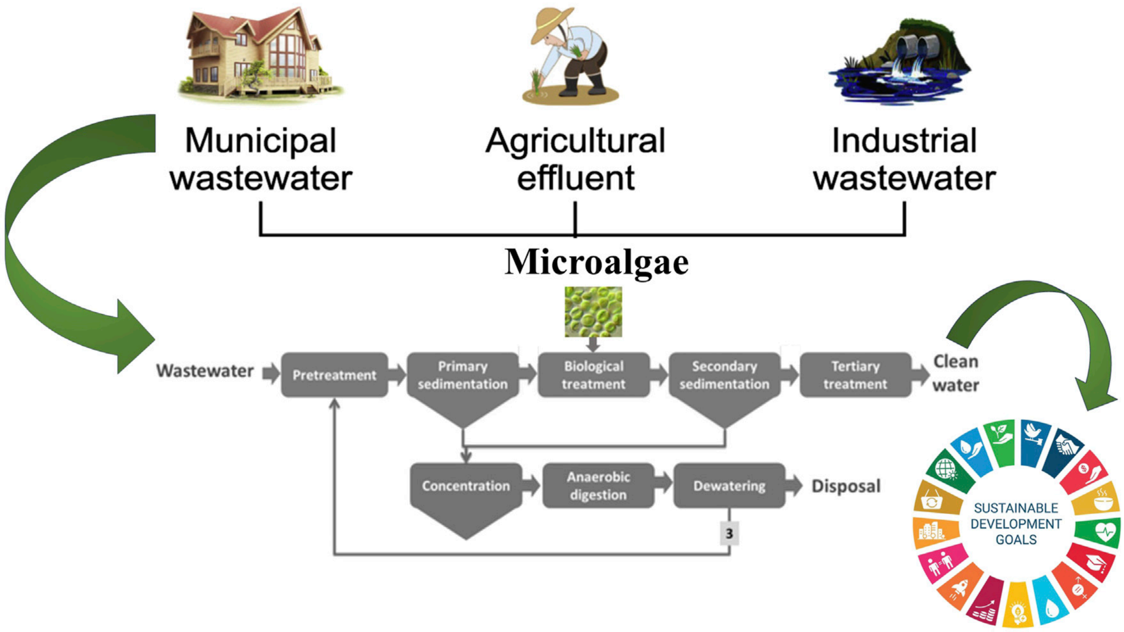

FIGURE 4
Different processes of microalgae-based wastewater system to achieve sustainable development goals.

limitations. Microalgae species that are facultative for utilising organic carbons as sole substrates and cut off any light source for cultivation are also limited for heterotrophic and mixotrophic microalgae (Amenorfenyo et al., 2019).

- Higher altitudes make it inconceivable to cultivate microalgae, which has a direct impact on algal biomass concentration. Selection and cultivation of extremophile varieties could be an option (Gondi et al., 2022). However, the effectiveness of such strains' microalgal bioremediation must also be considered.

Different processes involving wastewater treatment by microalgae with the advantages and disadvantages are summarized in Figure 3.

8 Applications of microalgae to achieve sustainable development goals (SGDs)

Goal 6 in UN Sustainable Development Goals (SDGs) aims to ensure availability and sustainable management of water and sanitation for all. Especially, target 6.a. under Goal 6 stated "By 2030, expand international cooperation and capacity-building support to developing countries in water-and sanitation-related activities and programmes, including water harvesting, desalination, water efficiency, wastewater treatment, recycling and reuse technologies" (United Nations, 2022). Target 6.3. stated "By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally." wastewater treatment using microalgae can be one of the sustainable solutions in this regard. Advanced application of different microalgal strains in wastewater remediation can play a direct role in advancing Sustainable Development Goal 6, which aims to ensure the availability and sustainable management of clean water. The removal of emerging contaminants from wastewater can thereby mitigate the potential health risks associated with the exposure of emerging contaminants and can foster overall wellbeing.

The approaches and findings discussed in this research can be applied to real-world wastewater treatment by integrating innovative and sustainable technologies into existing systems. Upgrading conventional wastewater treatment plants (WWTPs) with advanced processes like advanced oxidation processes (AOPs), membrane bioreactors (MBRs), or activated carbon adsorption can significantly enhance the removal of emerging contaminants (ECs), such as pharmaceuticals, hormones, and microplastics. This hybrid approach closes the efficiency gap in addressing these pollutants. Additionally, nature-based solutions, such as microalgae and constructed wetlands, offer sustainable, cost-effective methods for EC removal while reducing energy consumption and generating valuable byproducts like biofuels and fertilizers, promoting a circular economy (Dutta et al., 2023).

Real-time monitoring systems can further enhance treatment effectiveness by detecting and targeting high-priority contaminants. Scaling up pilot technologies, such as microalgae-based treatments, through collaboration between academia, industry, and government can validate their practicality in diverse environments. In low- and middle-income regions, decentralized and affordable solutions like algal ponds or modular bioreactors can address infrastructure limitations, offering scalable and cost-effective alternatives.

Policy support and public awareness are crucial to the success of these innovations. Stricter regulations on EC discharges and campaigns promoting responsible pharmaceutical disposal can reduce contaminant loads in wastewater systems. Additionally, incorporating technologies that target antibiotic residues and resistance genes can mitigate global health risks associated with antibiotic resistance. Resource recovery technologies that reclaim nutrients or water for reuse can further enhance the sustainability and economic viability of treatment systems, particularly in water-scarce areas. These strategies collectively provide practical, scalable, and eco-friendly solutions for improving wastewater treatment while safeguarding public health and ecosystems.

Large-scale algae production for wastewater treatment typically involves systems like open ponds, raceway ponds, or photobioreactors. Open or raceway ponds are cost-effective and simple to operate, while photobioreactors offer better control over environmental conditions (Qin et al., 2019), enhancing algae growth efficiency but with higher initial costs. The time required to achieve large-scale algal biomass depends on factors like species, nutrient availability, light, temperature, and system design (Pruvost et al., 2016). Sustainable approaches in developing large-scale remediation facilities can be effective in wastewater bio-treatment. In terms of cost-effectiveness, algae-based treatment can be competitive, especially when considering the co-benefits. Harvested algae can be converted into valuable byproducts like biofuels, bioplastics, animal feed, or fertilizers, generating additional revenue. The initial investment may be higher than conventional systems, but operational costs are often offset by reduced chemical usage, energy savings, and the potential for resource recovery, making algae systems increasingly viable in the long term (Dutta et al., 2023) the outline of different processes involved in microalgae-based wastewater system to achieve sustainable development goals is shown in Figure 4.

9 Recommendation and future perspectives

Several investigations have been conducted to pave the way for industrial scale microalgae application by determining the associated processes and technologies. However,

- The transition from pilot to industrial scale activities frequently exposes microalgae to unfavourable conditions, resulting in significantly lower bioproduct yields. As a result, more studies and research are needed to ensure the monetary and environmental feasibility of integrating robust microalgae cells and bioprocess engineering methods. Further genetic or metabolic engineering research should be carried out to ensure the cultivation of genome-modified microalgal cells with improved characteristics related to unfavourable environment adaptation and higher performance for removing pollutants and bioproduct yields.
- Sorting microalgal biomass from treated wastewater after bioremediation is a significant challenge, particularly in suspended cultivation. To address this, securing microalgae cultivation to a media/supporter may be used, ensuring the separation process more accessible and decreasing hydraulic retention time.
- Only a few studies have been completed, so cost-effectiveness studies of microalgae-based wastewater treatment and assessments to traditional methods must be investigated. The lack of basic design and operation guidelines for microalgae-based wastewater treatment, on the other hand, encourages researchers to investigate harder to provide basic guidance and recommendations for enhancing the resilience and flexibility of microalgal strains to deal with different types of wastewaters.
- More research on incorporating microalgae into the biological treatment process, as well as a thorough understanding of the relationships between microalgae and existing bacteria in wastewater, is required.
- Before introducing microalgae, it is recommended to regulate the influents with adequate input and/or pretreat. Furthermore, the wide variety of nutrients and their strength in wastewater necessitate several pretreatments in order to produce an ideal balance of nutrients for the microalgae. In such cases, researchers should use optimised mixtures of multiple wastewater sources as a single, well-balanced nutrient media for microalgae.
- Assessing wastewater from industries and microalgae cultivation modes may differ depending on geographical zone due to variations in sunlight availability and temperature. As a result, colder zones should concentrate on photobioreactor-based microalgae cultivation with the goal of producing high-value-added products from microalgae grown on wastewater.
- The microalgae-based wastewater treatment processes and overall method monitoring (e.g., pH, temperature, microalgae cell conditions, BOD, and DO) are complicated operations that necessitate the development of innovative technologies such as online monitoring and remote control.

10 Conclusion

The bioremediation capabilities of microalgae in wastewater have been demonstrated and confirmed by recent and available literature studies. Microalgae are promising possibility for carbon capture technology because they have been shown to be effective at removing heavy metals and nutrients from various types of wastewaters. Microalgae have an accurately high potential to remove newly emerging contaminants. However, each species of microalgae has distinctive traits and the capacity to eliminate different kinds of contaminants. Because different types of microalgae have different inherent abilities, particularly nutrient uptake, tolerance for harsh or extreme environmental conditions, and competitive potential relative to native organisms, the response and development of different types of microalgae in wastewater also varies. The ultimate objective of wastewater treatment is to reduce the biochemical oxygen demand as well as organic, inorganic, and synthetic elements like high levels of ammonium, bicarbonate, phosphate, potassium, sulphur, heavy metals, dyes, pesticides, pharmaceuticals, and a wide range of pathogenic bacteria. Phyco-remediation, or the bioremediation of wastewater using algal species, can remove biological and chemical compounds using microalgae. High concentrations of nutrients found in domestic, industrial, and agricultural wastewaters encourage the growth of microalgae, reducing or even eliminating the need for supplemental feeding. After the consumption of heavy metals or toxic substances, algae do not cause secondary pollution. Even dead algal biomass can eliminate heavy metals from wastewaters through the biosorption process, though this method is less efficient than using live algae cells. Utilising algae to treat wastewater is a key component of new technologies. Molecular techniques are also used to develop novel algal strains with improved phyco-remediation capabilities. In order to increase the viability and compatibility of microalgae cultivated at full scale, more research is needed to examine the industrial scale of microalgae and the improvement of bioproduct quality. For the future advancement of microalgal technology, numerous experiments evaluating the removal effectiveness of a wide range of heavy metal ions by various microalgal strains either individually or in combination should be carried out. To increase the opportunities for the application of microalgal treatment in wastewater plants, more research on the integration of current treatment systems and microalgal treatment needs to be conducted and reported.

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PK: Writing–original draft. ND: Writing–original draft, Writing–review and editing. SB: Conceptualization, Supervision, Validation, Writing–original draft, Writing–review and editing.

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