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A review on algae-mediated adsorption and catalytic processes for organic water pollution remediation

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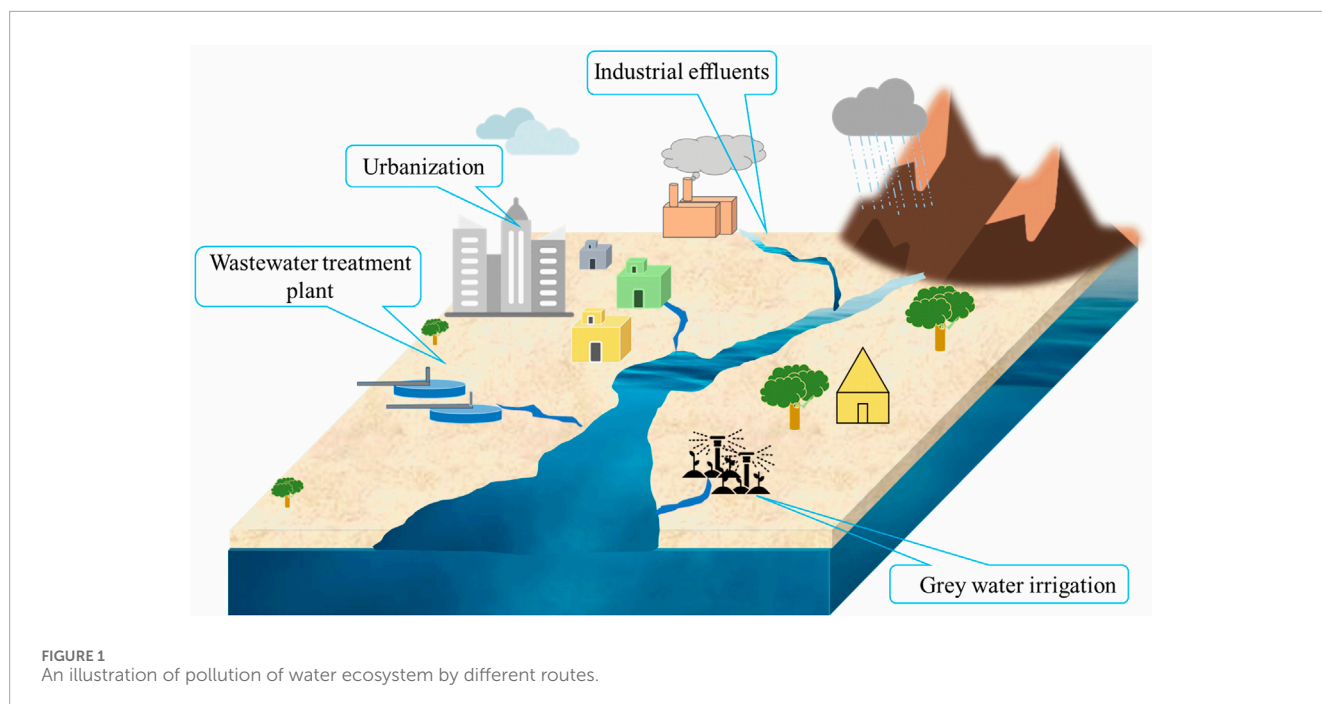
Wastewaters consist of organic pollutants that have environmental concerns. Wastewaters are treated by different methods, but efficient, low-cost, and sustainable techniques still need to be developed. Algae-based water pollution remediation techniques are considered to be sustainable approaches. This review exclusively discusses the facets of macro and microalgae in the treatment of organic toxicants. The current trends of algae-mediated water treatments have been discussed under adsorption and degradation methods. A focus on algae fuel cell, algae mediated activation of oxidizing agents, Fenton-like reactions, and photocatalysis was given. The need of algae-based adsorptive and catalytic materials was mentioned. The role of algae in the synthesis of catalysts which were employed in pollutant removal methods was also explained. The integrated algae-mediated water treatment techniques were also highlighted. The toxicant removal performances of different algae-based materials in the water medium were summarized. The conclusion and future prospects derived from the literature survey were described. This review will be helpful for researchers who are working in the field of sustainable water pollution remediation.

KEYWORDS

wastewater treatment, algae technology, nanomaterials, biosorption, bioremediation, bio-catalysis, algae fuel cell

1 Introduction

Natural water ecosystems such as lake (Luarte et al., 2022), river (Qin et al., 2019) and sea (Sanganyado et al., 2021) are seriously polluted owing to the discharge of multiple kinds of chemical pollutants including inorganic species and organic compounds. For



instance, the existence of 22 kinds of volatile organic compounds in Poyang lake water (sampling points = 28) was identified (Qin et al., 2019). Methylene chloride was found to be a predominant pollutant (708.19 ng L^{-1}) in this study. Another study has found that the organo-chlorine (polychlorinated biphenyls) and organo-bromo (polybrominated diphenyl ethers) compounds are present (used European eel as indicator) in Rasa River, Croatia (Kljakovic-Gaspic et al., 2023). Jiang et al. (2023) have determined the presence of phenolic compounds, polycyclic aromatic hydrocarbon and organochlorine compounds in the Yongding river basin (sampling points = 15). The composition and concentration of organic pollutants are found to be different in different regions of the Yongding river basin. The occurrence of organochlorine compounds in Mediterranean Sea water were also reported by using deep-sea organisms (*Chondrichthyes*) (Consales et al., 2023). Organic pollutants occur in surface and ground waters by direct discharge of industrial effluents (Singh et al., 2022), urbanization, wastewater treatment plants (Jiang et al., 2023), grey water irrigation (Turner et al., 2019) and other human activities (Li et al., 2021). An illustration of pollution of water ecosystems is given as Figure 1. Harmful organic pollutants such as antibiotics, pesticides, phenolics compounds and azo dyes show harmful effects including stroke, carcinogenicity, allergies, reproductive, neurological, and behavioral effects (Dev et al., 2023; Monisha et al., 2023). Hence, it is essential to remove those harmful pollutants from the water. But it is not an easy procedure owing to good stability and recalcitrant behaviors of these pollutants.

Several water treatment techniques such as biological, physical (evaporation, filtration, and reverse osmosis), and chemical (precipitation, catalytic oxidation and reduction, electrochemical techniques, ion-exchange) methods were established in recent decades (Rai et al., 2022). Traditional water treatment techniques consist of multiple stages to eliminate organic pollutants, and

these techniques need huge space, energy and capital expenditure. Expensive chemicals are employed for different purposes including oxidizing reagents, precipitating agents, and catalysts. These undesirable features urge the researchers to develop more efficient and inexpensive techniques to treat organic pollutants in water. Industries also need sustainable and eco-friendly techniques to treat their effluents. It should be also mentioned that the United Nations Sustainable Goal 6 regards the access of safe drinking water by all (United Nations, 2024). It is possible by decreasing water pollution through sustainable water treatment techniques.

Microbes such as bacteria, algae, and fungi were applied in different water treatment techniques for the elimination of toxic organic pollutants from water medium (Rios-Miguel et al., 2023). Particularly, research studies on algae-mediated water treatment methods for organic pollution remediation have increased considerably during the last decade (from 2014 to 2024). According to the Scopus search (as on June, 2024), by using a keyword "algae + organic + water treatment", the number of research articles (year of publications is mentioned within the bracket) are found as 53 (2010), 93 (2014), 174 (2018), 189 (2022) and 145 (June, 2024). Reviews on algae-mediated water treatments were published by different research groups. Specifically, algae-based adsorption, bioaccumulation, and degradation of wastewater containing chemical pollutants were discussed in a review written by Bhatt et al., 2022. Martínez-Ruiz et al., 2022 have focused on microalgae-mediated remediation methods for the treatment of landfill leachate in their review article. In addition, the simultaneous generation of value-added products including fuel, plastics, and soil enhancers has also been discussed. A review, written by Deka et al., 2022 has been focused on algae-mediated microbial fuel cells developed for the degradation of toxic organic dyes. Khan et al., 2022 have performed a literature survey on the microalgal-derived biochars with their dyes and heavy metals removal

performances (biosorption). These review articles either focused on a particular algae-mediated water treatment technique or algae-derived materials. A review focusing on the application of algae and algae-based materials in different water treatment techniques for organic decontamination is rare.

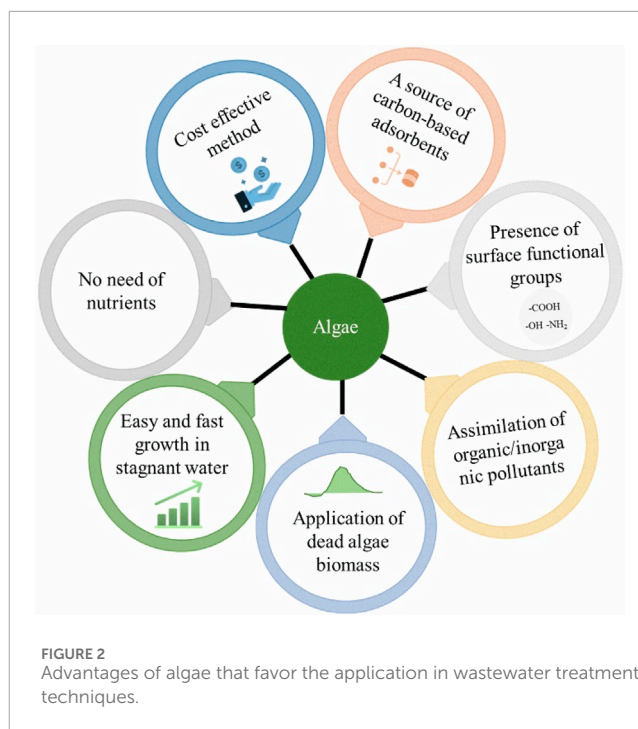
This review aims to explore the application of macro and microalgae in the treatment of water containing harmful organic toxicants including dyes, antibiotics and pesticides. Particularly, algae-mediated adsorption and catalytic degradation methods were targeted. Bare algae, modified and algae derived materials were particularly considered. The role of algae in different water treatments was highlighted. Future perspectives for algae-based water treatments were further proposed.

2 Algae for water pollution remediation

Algae are eukaryotic or prokaryotic (autotrophic) organisms that are generally classified into microalgae, and macroalgae based on their cellular types. They live in water environments, including ponds, lakes, rivers, oceans and wastewaters (Salman et al., 2023). Macroalgae are multicellular organisms, whereas microalgae are unicellular organisms. The lignin content of microalgae is low, and hence it can be treated by facile pre-treatment techniques. Microalgae can boom in effluents including industrial, domestic and salt water, since they utilize harmful inorganic and organic pollutants as nutrients for their growth. Microalgae also grow much faster and thus their availability is huge to harvest. Algae are used in food, health supplements, pharmaceuticals, energy storage, cosmetics, and biofuels (Biris-Dorhoi et al., 2020; Al-Ghamdi et al., 2023; Fernandez et al., 2023). The major components are fat, proteins, ash, lipids, and carbohydrates (Babich et al., 2022). The chemical composition of micro and macro is remarkably varied. Figure 2 displays the key advantages of algae which make them potential in water treatments. Photosynthesis ability and assimilation tendency to utilize organic pollutants (as a carbon source) made them efficient to apply in water treatment (Cuellar-Bermudez et al., 2017). Algae biomass possesses different surface functional groups which will be helpful to eliminate organic pollutants as well as inorganic contaminants (Bhatt et al., 2022). Algae can be cultivated in a wide range of aquatic environments with higher yields, and thus their availability is promising (Singh et al., 2021; van der Meer et al., 2023). Adsorbents derived from algae are possessing high porosity, stability, and functional groups which are vastly needed features of an adsorbent (Khan et al., 2022). Dead algae biomass can also be used for the decontamination of polluted waters. The utilization of dead algae is beneficial since they are not affected by the toxicity of the pollutants.

3 Algae-based wastewater treatments

Algae have been potentially used in various techniques to remove organic contaminants from water. In this section, algae-mediated adsorption and catalytic degradation methods were particularly discussed (Figure 3).



3.1 Algae-based adsorbents

3.1.1 Algae as biosorbent

The biomass of algae has suitable features to adsorb harmful organic as well as inorganic entities from their aqueous solutions (biosorption). Biosorption is a cheap, effective, and high-performance method for wastewater treatment (Ramesh et al., 2023). The algae cells consist of various functional groups like amino ($-NH_2$), carboxyl ($-COOH$), and hydroxyl ($-OH$), which are responsible for algae's sorption ability in water medium (Khan et al., 2022). There is no need to supply nutrients and maintain special conditions for dead algae biomass. Adsorption can occur between pollutants and the pre-treated algae biomass via chelation/complexation, ion exchange, or hydrogen bonding between pollutants. The following pretreatment is required to have algae biosorbent: First, algae are collected from natural or industrial sites, washed with plenty of potable water (to abolish extraneous particles), cleaned with pure water, dried (under natural sunlight or in a hot air oven), milled and then sieved to achieve the desired particle size (Mokhtar et al., 2017). The drying process may take some hours to a few days (Mokhtar et al., 2017; Elgarahy et al., 2023). Different algae species have been harvested and employed as sorbent for capturing harmful organic molecules in simulated contaminated water (Table 1).

The inferences from the Table 1 are as follows: Algae biomass can be obtained from natural environments, including coastal regions and ponds, and is also possible to cultivate in laboratories (Gul et al., 2019; Tukarambai, 2022). The biosorption capacity of a particular algal species is dependent on the molecular structure of organic pollutants. For instance, *Ulva fasciata* adsorbent showed different adsorption capacity towards rhodamine B and methyl orange dyes in water (Elgarahy et al., 2023). Similarly,

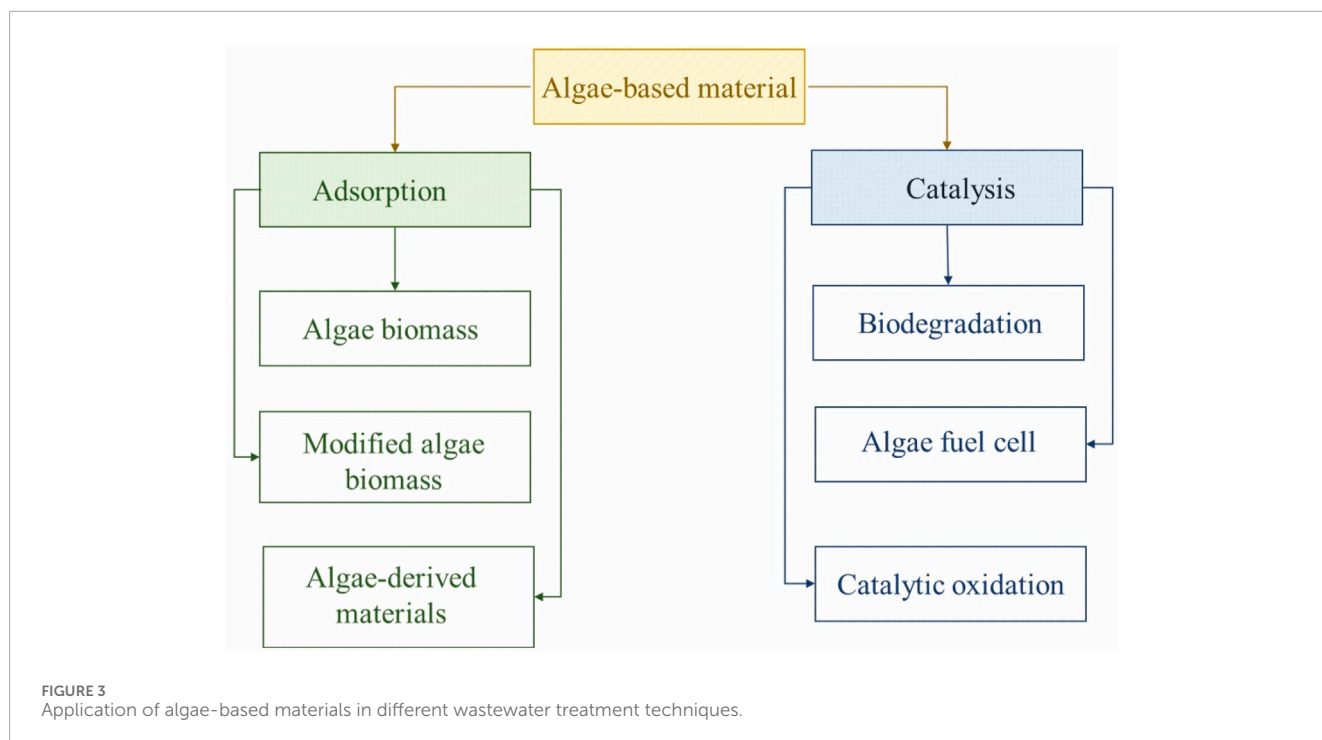


FIGURE 3 Application of algae-based materials in different wastewater treatment techniques.

Codium decortiatum based adsorbent has shown difference in the adsorption capacity of crystal violet and Congo red dyes under the same conditions (Oualid et al., 2020).

Algae biosorbent's performance can be further enhanced by applying ultrasonic treatment. By employing ultrasonic wave illumination (frequency = 35 kHz), the *U. fasciata* adsorbent could adsorb rhodamine B and methyl orange from water within 30 min, while the maximum adsorption equilibrium time without ultrasonic treatment is 180 min (Elgarahy et al., 2023). Algae adsorbents remove organic pollutant molecules via binding modes like hydrogen bonding, ionic attraction, and $n-\pi$ stacking (Abdulhameed et al., 2022; Yadav et al., 2022; Fontoura et al., 2017). The biosorption performance is dependent on the type of algae. An example, Mokhtar et al. (2017) have used red (*K. striatum*, *K. alvarezii* and *E. spinosum*), green (*C. lentillifera*), and brown (*S. polycystum*) algae as adsorbents for capturing methylene blue from water medium. Among others, *E. spinosum* showed the best methylene blue adsorption performance.

3.1.2 Modified algae as adsorbents

Algae like brown algae have water soluble organic compounds (carbohydrates, and pigments) that dissolve in water during biosorption (Bulgariu and Bulgariu, 2016). It causes secondary pollution and thus it is essential to modify the algae biomass (Rocha de Freitas et al., 2018). Generally, acid, salt, and organic molecules have been used for the modification process, thereby decreasing organic leaching from algae biomass. Further addition of chemical compounds has also been attempted (Bulgariu and Bulgariu, 2016). For example, Cobas et al. (2014) have pretreated the *F. vesiculosus* by using a solution of calcium chloride (CaCl_2), potassium chloride (KCl), or magnesium chloride (MgCl_2) (algae:salt solution = 2.5:50). The pre-treated algal was used for

the treatment of Sella solid blue, Sella solid orange, burdeuox, and special violet (leather dyes). About 88% of targeted dyes have been eliminated by 0.84 M CaCl_2 -treated *F. vesiculosus* sorbent (pH = 5.69 and algae dosage = 1.37 g). Lebron et al. (2019) conducted a research study in which methylene blue was removed from water by using modified *Fucus vesiculosus*, *C. pyrenoidosa* and *Spirulina maxima*, separately as adsorbents. Zinc chloride (ZnCl_2) and phosphoric acid (H_3PO_4 , 85%) were used as modifying agents, whereas the time and temperature for the chemical modification process are 24 h and 28°C respectively. This modification step causes the formation of oxygen-containing chemical moieties (carboxylic groups) on the surface of algae biomass. The carboxylic group has $\text{pK}_a = 4.5$, and thus it will be in an anionic state (deprotonated form), which can interact with the cationic methylene blue molecule effectively. Furthermore, the thermal stability of algae has also been improved. The H_3PO_4 -modified *F. vesiculosus* showed adsorption capacity of 1,162.9 mg g^{-1} (equilibrium time = 40 min). In this study, the biosorbent's dosage, equilibrium time, and pH of the medium were 2 g L^{-1} , 4 h, and six, respectively. In another study, 96% sulfuric acid-treated *Laminaria japonica* (a brown alga) was applied as a biosorbent in the adsorptive elimination of methylene blue from its solution (Shao et al., 2017). Sulfuric acid treatment leads to the formation of lactonic groups via the reaction between amino acids and sodium alginate. At the optimized experimental conditions (biosorbent = 0.6 g L^{-1} ; pH = 6; contact time = 60 min; temperature = 308 K), acid treated *L. japonica* biosorbent exhibited the highest methylene blue adsorption capacity of 549.45 mg g^{-1} , while untreated *L. japonica* biosorbent showed 418.41 mg g^{-1} . The mode of methylene blue interaction with biosorbent was determined to be complex formation and ionic attraction.

Alkali treated algae biosorbents have also been reported. For instance, *Ulva Lactuca* treated with calcined eggshell powder

TABLE 1 Studies on the algae biomass biosorbents and their adsorption activities.

Algae species	Collection point	Pollutant	Adsorbent dosage	Time (min)	Isotherm model	Adsorption capacity (mg g ⁻¹)	References
<i>Ulva fasciata</i> Delile	Mediterranean sea	Rhodamine B Methyl orange	30 mg	60	Langmuir isotherm	144.92 196.04	Elgarahy et al. (2023)
<i>Sargassum Tenerrimum</i>	Rushikonda beach	Eosin yellow	0.4 g	60	Freundlich isotherm	5.18	(TukaramBai et al., 2021)
Microalgae	Research Laboratory	Crystal violet Methylene blue	80 mg L ⁻¹	5.2	Langmuir isotherm	243.0 297.1	Abdulhameed et al. (2022)
<i>Euchema Spinosum</i>	Algae factory	Methylene blue	1.4 g L ⁻¹	60	Langmuir isotherm	833.33	Mokhtar et al. (2017)
<i>Fucus vesiculosus</i>	Amlwch port	Methylene Blue Rhodamine B	100 mg	420	Langmuir isotherm	200 166.66	Yadav et al. (2022)
<i>Chlorella pyrenoidosa</i>	Green Gen company	Rhodamine B	0.1 g	120	Sips isotherm	63.14	Denardin da Rosa et al. (2018)
<i>Scenedesmus</i> sp.	Research Laboratory	Acid Blue 161	20 mg	240	Freundlich isotherm	83.2	Fontoura et al. (2017)
<i>Phormidium animale</i>	Research Laboratory	Acid Red P-2BX	4 g L ⁻¹	1,440	Langmuir isotherm	100	Gul et al. (2019)
<i>Sargassum tenerrimum</i>	Coast region	Methylene Blue	0.1 g	120	Temkin isotherm	95.82%	Tukarambai et al. (2021)
<i>Codium decorticatium</i>	Agadir bay	Crystal violet Congo red	1.5 g L ⁻¹	120	Langmuir isotherm	278.46 191.01	Oualid et al. (2020)
<i>Chromochloris zofingiensis</i>	Research Laboratory	Methylene blue	1 g L ⁻¹	60	Langmuir isotherm	135.423	Bayat et al. (2023)
<i>Hormophysa triquetra</i>	Coast region	Crystal violet	0.02 g	24 h	Langmuir isotherm	181.8	Bibi et al. (2023)

has been prepared for the separation of cationic (methylene blue) and anionic (Congo red) dye molecules from their mixture solution (Qulatein and Yilmaz, 2023). Also, when compared to untreated *Ulva Lactuca*, calcined eggshell-treated *Ulva Lactuca* presented a maximum (methylene blue) adsorption capacity of 2000 mg g⁻¹ (Langmuir isotherm) within 15 min. The adsorption of methylene blue and Congo red is effective in alkaline and acidic conditions, respectively. This study also reported that the adsorption of methylene blue involved ionic interaction and intermolecular hydrogen bonding, whereas Congo red's adsorption was attributed to hydrogen bonding that happened between the hydroxyl and the amine (-NH₂) groups.

Algae doped iron (II, III) oxide (Fe₃O₄)/chitosan composite was synthesized via a two-step approach, and the resultant biocomposite has been used to adsorb Direct Red 31 and Direct Red 28 from water (Solanki et al., 2022). About 94% of Direct Red 31 removal efficiency was reported when the biocomposite dosage, contact time, and initial pH is 0.6 g L⁻¹, 10 min, and 5, respectively. In the case of Direct Red 28, 90% removal efficiency was obtained under the following conditions: biocomposite dosage

= 7 g L⁻¹; adsorption time = 20 min; and pH = 3. A copper (Cu)-benzenetricarboxylic acid/sulphated *U. fasciata* composite (specific surface area = 950 m² g⁻¹) was constructed for the selective adsorption of methyl orange and methylene blue in an aqueous solution (Abdelhameed et al., 2020). Within 10 min, the adsorptive removal efficiency toward methylene blue and methyl orange was 97% and 68%, respectively. By following the Langmuir model, the adsorption capacity obtained for methylene blue and methyl orange is 162 and 72 mg g⁻¹, respectively. An effective capturing of methylene blue by this composite adsorbent was determined by electrostatic attraction.

3.1.3 Algae-derived adsorbents

Carbon-based adsorbents were synthesized using algae biomass, since it is possible to harvest more algal biomass per unit volume (Chen et al., 2022). Biochar synthesised from algal biomass has shown good activity in wastewater treatment. For example, phycocyanin-extracted algal bloom biomass was utilized to synthesize hydrochar via hydrothermal carbonization (Zhang et al., 2017). According to Langmuir's isotherm, the obtained hydrochar

(4 g L⁻¹), displayed a maximum malachite green (100 mg L⁻¹) adsorption capability of 89.05 mg g⁻¹. The functional groups present in hydrochar are actively participating in the adsorption of malachite green. Further, *Caulerpa scalpelliformis*-derived biochar was applied in the adsorption of remazol dyes from the water (Gokulan et al., 2019). The optimum adsorbent dosage, pH, dye concentration, and temperature are reported as 2 g L⁻¹, 2, 0.05 mmol L⁻¹ and 30°C, respectively. The order of adsorption efficiency of biochar derived from *C. scalpelliformis* is Remazol brilliant orange 3R > Remazol brilliant blue R > Remazol brilliant violet 5R > Remazol black B. On the other hand, *Undaria pinnatifida* dried powder (Yao et al., 2020) was used to synthesize activated biochar [activating agent = potassium hydroxide (KOH)] and used in the adsorption of few selected dye molecules. The surface area and functional groups of synthesised biochar is 1,156.25 m² g⁻¹ (volume = 0.67 cm³ g⁻¹) and hydroxyl/carbonyl, respectively. The adsorption capacities obtained for activated biochar towards malachite green, methylene blue, and rhodamine B is 4066.96, 841.64, and 533.77 mg g⁻¹ respectively. Diffusion, van der Waals attraction, hydrogen bonding, π - π stacking and electrostatic attraction are the major adsorption modes on the biochar adsorbent.

The activated carbon was obtained from *Sargassum oligocystum* at a carbonization temperature of 500°C (3 h) (Foroutan et al., 2019). The obtained activated carbon was coupled with Fe₃O₄ nanoparticles, and the resultant composite adsorbent has been applied for methylene blue and methyl violet elimination. The adsorbent dosage, contact time, ultrasonic frequency, and pH of this adsorption experiment were followed as 0.15 g/100 mL, 50 min, 45 kHz, and 7, respectively. The determined adsorption capacities of this composite adsorbent toward methylene blue and methyl violet are 60.60 and 59.88 mg g⁻¹ (Freundlich isotherm), respectively.

The biochar was synthesised by using a mixer (weight ratio = 1:2) of algal biomass (major stains = *Spirulina* sp., *Chlorella* sp., *Synechocystis* sp., and *Scenedesmus* sp.) and a kombucha-symbiotic culture of bacteria and yeast (Pathy et al., 2022). The carbonization temperature used for composite synthesis is 500°C (45 min). About 500 mg g⁻¹ of malachite green adsorption capacity was reported for the composite adsorbent.

3.2 Algae-mediated degradation of organic pollutants

3.2.1 Algae-mediated dye degradation/reduction

The assimilation tendency of algae towards the dissolved chemical pollutants in water is the basis for algae-mediated pollutants' degradation methods (Rai et al., 2022; Satya et al., 2023). Generally, the live algal cells are added to polluted water and kept for certain days under optimized conditions. The algae absorb the organic pollutants from the water via their cell walls and use them as nutrients for their growth (Bhatt et al., 2022). The absorbed organic pollutants are converted into simple molecules via different metabolic pathways, thereby giving polluted water its cleanliness (Bhatt et al., 2022). The removal of pollutants can be monitored by withdrawing solution from the reactor and subjecting it to analysis using analytical methods such as UV-visible spectroscopy and chromatographic techniques (Moradi et al., 2021; Hu et al., 2021). Different harmful organic pollutants were

degraded by different algae species. For example, in order to treat atrazine (C₈H₁₄ClN₅) aqueous solution, *Chlorella* sp. has been used by Hu et al., 2021. *Chlorella* sp. culture was exposed for 8 days to pure atrazine and atrazine treated solutions (40 and 80 μ g L⁻¹). Atrazine solution was initially treated by (0.1 g L⁻¹) titanium dioxide (TiO₂)-mediated photocatalytic process for 60 min under an ultraviolet lamp (250 W). The removal efficiency in 40 and 80 μ g L⁻¹ of atrazine solutions was determined to be 83.0% and 64.3%, respectively. The removal efficiency of a pure atrazine solution has been found to be higher than that of a prior degraded atrazine solution. This study has found that the atrazine' degradation products inhibited the photosynthetic ability of *Chlorella* sp. by suppressing light harvesting. On the one hand, the direct green 6 (C₃₄H₂₂N₈Na₂O₁₀S₂) dye molecules were degraded by live and dead cells of *Spirulina platensis* (Moradi et al., 2021). Compared to dead cells, live *S. platensis* cells have the possibility of being re-used for the degradation of direct green 6 dye with no loss of activity. In addition, the generation of valuable products like polyhydroxybutyrate is also enhanced.

It has been explored that the addition of redox mediators (organic compounds) further accelerates the algae-mediated degradation process. Meng et al., 2014 have determined that the acid red 27 (C₂₀H₁₁N₂Na₃O₁₀S₃) decolorization (reduction) efficiency of *Shewanella* algae was improved by anthraquinone-2,6-disulfonate or humic acids as redox mediators, even in saline conditions. It should be mentioned that the addition of chemicals (redox mediators) may increase the cost of the treatment method. Algae have also been coupled with other microorganisms like bacteria to explore the sustainable water treatment technique (Khoo et al., 2021). A synergistic effect was observed when algae coupled with microbes, thereby boosting the degradation performance (protocooperation). As an example, a mixture of *Chlorella sorokiniana* XJK (algae) and *Aspergillus* sp. XJ-2 (fungus) has been used for the degradation of disperse red 3B, and the degradation process gave low toxic degradation products (Tang et al., 2019). About 98.09% of the degradation rate was obtained for this consortium. The participation of manganese peroxidase and lignin peroxidase in the degradation of disperse red 3B has been confirmed. Li et al. (2022) have also investigated the performance of an algae (*Chlorella*) and bacteria consortium in the decolorization of simulated coloured (disperse red 3B) water (pH = 7.8). The degradation efficiency and chemical oxygen demand (COD) removal efficiency of the algae-bacteria consortium were reported as 90% and 91%, respectively. Algae particularly degraded the dye molecules, whereas the degradation by-products were further decomposed by bacteria.

3.2.2 Algae fuel cell

The capability of algae to grow in different wastewaters makes it possible to utilize them in fuel cells. Algae fuel cells are used for generating electricity and instantaneous treatment of polluted water (Deka et al., 2022). In an algal fuel cell, the anodic compartment consists of organic compounds (pollutants) which will be oxidized by biofilm that attached to the anode and produce electrons and protons. Both electrons and protons travel through the algal cathode by means of circuit connection and an ion selective membrane, respectively. At the cathode, protons are reduced to water in the presence of oxygen molecules (Figure 4) (Deka et al., 2022).

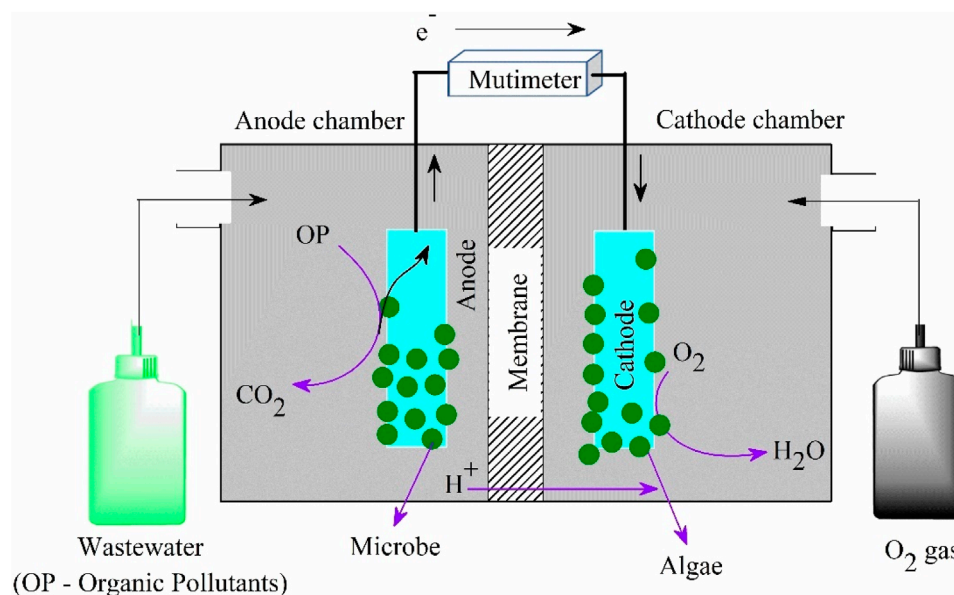


FIGURE 4
A pictorial diagram of algae fuel cell and its working mechanism.

Researchers have employed various industrial wastewaters in algae fuel cells for effective treatment. In a study, landfill leachate diluted with domestic wastewater was taken into an algae/carbon fibre brush cathode chamber, whereas the anode chamber was filled by domestic wastewater added with sodium acetate (CH_3COONa) (Nguyen et al., 2017). The reported COD removal at the anode and cathode chambers is 97% and 52% (10% leachate), respectively. In addition, algae growth at the cathode chamber also favoured the successful elimination of ammonium ($98.7\% \pm 1.8\%$ for 10% leachate, 5 days) and phosphorus (80.28% for 5% leachate, 5 days) in highly diluted landfill leachate. But it has been determined that the COD removal efficiency was decreased by adding a high volume of landfill leachate. Noticeably, the highest potential of this fuel cell was 300 mV, when the leachate concentration is 5%. On the other hand, the photo-cathode algal fuel cell containing *Chlorella vulgaris* was used to treat wastewater and generate electricity concurrently (Commault et al., 2017). The maximum removal rate of COD and ammonium is $0.19 \text{ g L}^{-1} \text{ d}^{-1}$ and $5 \text{ mg L}^{-1} \text{ d}^{-1}$, whereas the highest power density was reported as $34.2 \pm 10.0 \text{ mW m}^{-2}$ (without *C. vulgaris* = $15.6 \pm 9.7 \text{ mW m}^{-2}$).

Instead of a single fuel cell, an integrated algal fuel cell has also been proposed for efficient water treatment. A microbial fuel cell integrated with algae biofilm (*Scenedesmus quadricauda* SDEC-8) has been constructed by Yang et al., 2018 to remove nutrients (nitrogen, phosphorous) and COD from domestic wastewater and produce electricity simultaneously. The total nitrogen, phosphorous, and COD removal efficiency is 96.0%, 91.5%, and 80.2%, respectively. The performance (power density = 62.93 mW m^{-2}) of this integrated device is found to be better than that of a sole microbial fuel cell or algae biofilm. Hou et al., 2020 have coupled an anaerobic digestion tank (as anodic chamber) with algae-assisted microbial fuel cell to treat food wastes which consist of food preparation leftovers

as well as uneaten food. The algae and its concentration were *Golenkinia* sp. SDEC-16 and 150 mg L^{-1} , respectively. About 89% COD removal rate was observed for this coupled technology. In order to treat mariculture effluent (antibiotics, phosphate, and heavy metals), a constructed wetland–microbial fuel cells/electroactive bacteria–algae biofilm/siphon aeration technology was developed by Wang T. et al. (2023). By this integrated technology, about $97.38\% \pm 3.62\%$ sulfamethoxazole and $80.99\% \pm 1.3\%$ chemical oxygen demand removal efficiencies were obtained (voltage = of $354 \pm 23 \text{ mV}$).

Recently, Yang et al. (2021) have fabricated a triple-chamber fuel cell that is composed of two cathodic and one anodic compartment for the elimination of Cu^{2+} ions, nitrogen, COD from synthetic wastewater along with electricity production. The removal efficiency reported for Cu^{2+} ions, nitrogen, and COD is 99.9%, 79%, and 84.1%, respectively. Algae takes the ammonium, while the as-formed nitrogen oxides are removed in the dark by the cathode. The maximum power density achieved by this fuel cell was 420 mW m^{-2} .

It should be mentioned that the algae mediated fuel cells and its integrated technologies not only remove pollutants/wastes but also showed considerable advances in the production of electrical energy (Mahmoud et al., 2022).

3.2.3 Algae-derived catalyst for dye degradation

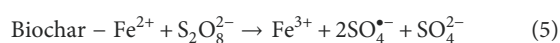
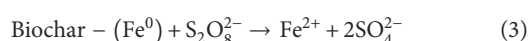
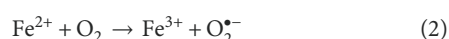
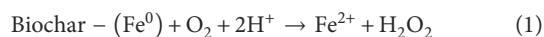
Algae have been used as carbon sources, thereby synthesizing different carbon-based catalysts. The performances of algae-derived catalysts in the degradation of organic pollutants in water were given in Table 2.

Table 2 clearly reveals that the alga-derived carbon and nanomaterial-based catalysts perform better in catalytic oxidation (activation of peroxymonosulfate and peroxydisulfate species), Fenton-like processes, and photocatalysis. The degradation mechanisms were highlighted below:

TABLE 2 Algae derived nanoparticles and their catalysis performance in the removal organic pollutants.

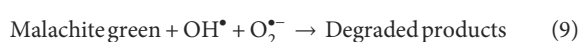
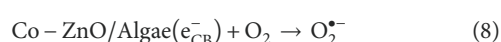
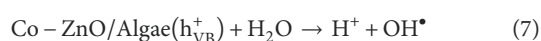
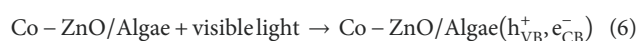
Alga source	Catalyst	Type of catalyst	Catalyst dosage	Pollutant	Condition	Reaction time (min)	Removal performance (%)	References
Alga	Algal biochar/La/Cu/Zr nanocomposite	Photocatalyst	0.1 g	Malachite green (250 mL, 2×10^{-6} mol L ⁻¹)	Solar light illumination	300	94	Sharma et al. (2019)
Taihu blue algae	Nitrogen-doped algal carbocatalyst	Peroxymonosulfate activation	40 mg	Methylene blue (20 mg L ⁻¹ , 200 mL)	Peroxymonosulfate (30 mg)	60	99	Wang et al. (2022)
<i>Undaria pinnatifida</i>	Boron-doped seaweed biochar	Peroxymonosulfate activation	100 mg L ⁻¹	Diclofenac	Peroxymonosulfate (0.5 mM)	30	100	Annamalai and Shin, (2023a)
<i>Sargassum duplicatum</i>	Boron-doped biochar	Peroxymonosulfate activation	1.0 g L ⁻¹	Polycyclic aromatic hydrocarbons	Peroxymonosulfate (1×10^{-4} M)	12 h	93	Hung et al. (2022)
Blue algae	FeO _x /biochar	Peroxydisulfate activation	200 mg L ⁻¹	Tetracycline (100 mL)	Peroxydisulfate (1 mM)	30	98.2	Yin et al. (2023a)
<i>Sargassum</i>	Co-ZnO/algae	Photocatalysts	0.05 g	Malachite green (5 mg L ⁻¹)	150 W Metal-halide lamp	10	100	Rabie et al. (2020)
Taihu blue algae	Fe ₃ O ₄ /activated biochar	Fenton-like catalyst	10 mg	Methylene blue (200 mL, 100 mg L ⁻¹)	H ₂ O ₂ (2 mL)	30	~99.97	Mi et al. (2023)
Enteromorpha	Iron single-atom catalyst	Fenton-like catalyst	5 mg	Naproxen (50 mL)	Peroxymonosulfate (1.0 mM)	30	96	Yin et al. (2023b)
algae mud	N-doped algal biochar	Peroxydisulfate activation	2.0 mg L ⁻¹	Tetracycline (100 mL, 50 mg L ⁻¹)	PDS (100 μL, 1.0 mol L ⁻¹)	60	86.4	Yin et al. (2023c)
<i>Spirulina platensis</i>	Ni/ZnO/ZnS/microalgae	Photocatalysts	0.5 mg mL ⁻¹	Methylene blue (10 mg L ⁻¹)	Artificial (light intensity = 680 ± 10 lx)	180	88.9 ± 1.4	Serrà et al. (2020)
<i>Enteromorpha prolifera</i>	Cobalt ferrite (CoFe ₂ O ₄)/biochar	Peroxymonosulfate activation	0.1 g L ⁻¹	Lomefloxacin Hydrochloride (100 mL, 10 mg L ⁻¹)	Peroxymonosulfate (0.1 mM)	30	>82	Wang et al. (2023b)
<i>Spirulina platensis</i>	<i>Spirulina</i> carbon dots	Photocatalysts	—	Reactive Red M8B	Sunlight	6 h	95.5	Palanimuthu et al. (2023)
<i>Undaria pinnatifida</i>	Seaweed-derived biochar	Peroxymonosulfate activation	0.1 g L ⁻¹	Tetracycline	Peroxymonosulfate (0.5 mM)	60	100	Annamalai and Shin, (2023b)
<i>Spirulina</i>	Nickel ferrite (NiFe ₂ O ₄)/N-doped carbon nanoflakes	Photocatalysts	0.1 g L ⁻¹	Congo Red Rhodamine B (30 mL)	5 W LED bulb (λ = 450 nm)	40 35	96.51 98.83	Patar et al. (2024)
Microcystis sp.	N & S-doped carbon nanosheets/CeO ₂	Photocatalysts	10 mg	Isothiazolone (5 mg L ⁻¹ , 100 mL)	300 W Xe lamp	90 min	95.4	Hu et al. (2024)

(a). Activation of oxidant: A persulfate activation mediated decomposition of tetracycline in presence of FeO_x (Fe^0 + iron oxide)@Z700 (algae-derived biochar) composite was explained as follows: FeO_x @Z700 accelerated the cleavage of O–O bond in persulfate ($\text{S}_2\text{O}_8^{2-}$), and subsequent production of $\text{O}_2^{\bullet-}/\text{SO}_4^{\bullet-}$ radicals which led to the decomposition of tetracycline (Yin et al., 2023a). This study has reported that the $\text{Fe}^0/\text{Fe}^{2+}$ system played a key role in the production of $\text{O}_2^{\bullet-}$ and $\text{SO}_4^{\bullet-}$ radicals (Equations 1–5) (Yin et al., 2023a).



(b). Fenton-like reaction mechanism was reported for iron (III) oxide (Fe_2O_3)/Taihu blue algae-derived activated biochar composite catalyst in the methylene blue degradation reaction (Mi et al., 2023). Under the catalytic reaction conditions, the functional groups present in the biochar and metal sites favoured the production of persistent free radicals (carbon-centered free radicals) which led the Fe(III)-complex formation, and subsequently generated Fe(II) ions. Hydroxyl radicals were efficiently generated by Fe(II) ions via the hydrogen peroxide (H_2O_2) decomposition. Thus, the generated hydroxyl radicals effectively decomposed the methylene blue.

(c). The photocatalytic degradation pathway of malachite green by cobalt (Co)-doped zinc oxide (ZnO)/algae/visible light system was described by the following manner (Rabie et al., 2020): The incident visible light photons induced the creation of holes and electron which are responsible for degradation of malachite green (Equations 6–9).



Alternatively, algae-derived carbon catalysts were also modified with suitable reagents to enhance their catalytic activity. Recently, *Spirulina* biomass has been used to synthesize potassium permanganate (KMnO_4)-modified biochar, which was employed in the catalytic oxidation of malachite green in water (Zhu and Zou, 2022). The modified biochar has a porous structure (pore

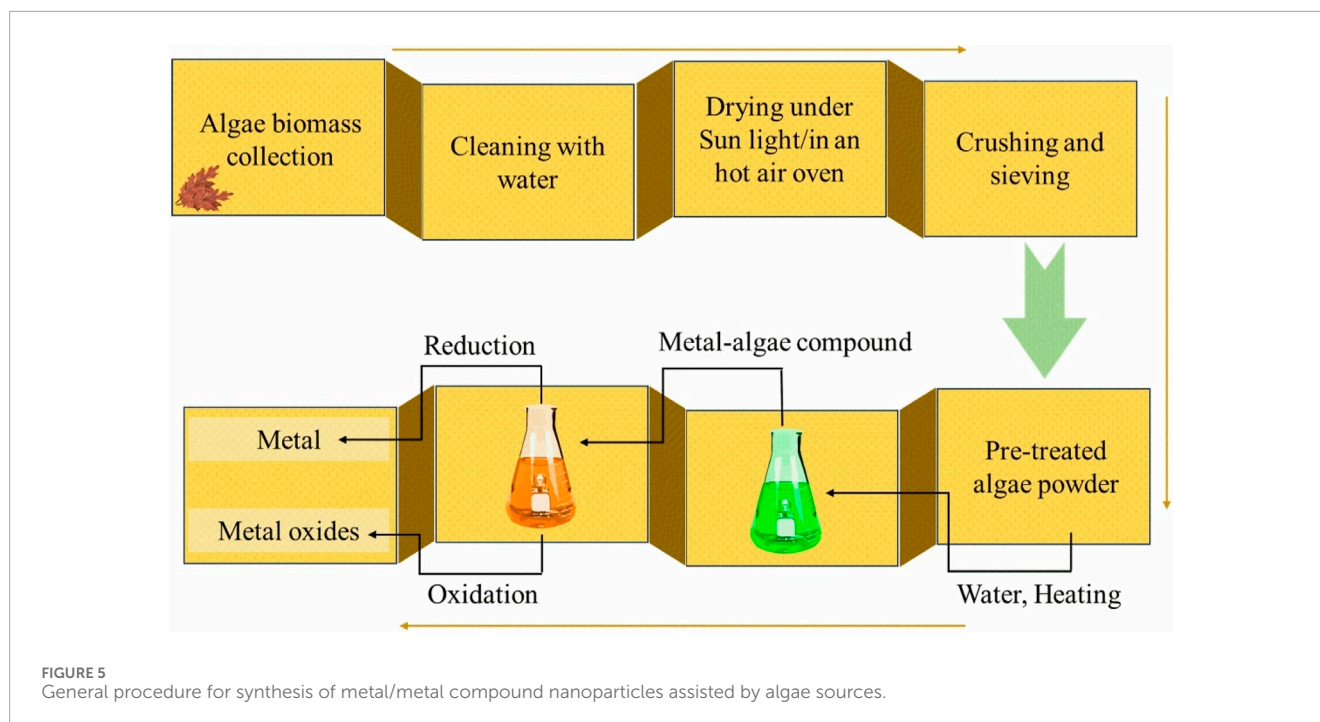
diameter = 22.596 nm) with a surface area of $2.766 \text{ m}^2 \text{ g}^{-1}$ and showed remarkable catalytic activity in the presence of 5 mmol L^{-1} H_2O_2 towards the oxidation of malachite green. The malachite green oxidation efficiency (8000 mg L^{-1}) was found to be 99% within the reaction time of 30 min.

3.2.4 Algae-mediated synthesis of catalysts for dye degradation

Nanomaterials have a relatively larger surface area, tunable surface groups, and charges, which are desirable for good catalysts (Nasrollahzadeh et al., 2021). Extracts of algae have been extensively used to synthesize nanomaterials, including metals and metal compounds (Khan et al., 2022). The major role of algae extract is as a complexing/reducing agent and capping agent to yield nanoparticles with high stability. Algal extracts contain fats, proteins, carbohydrates, and polyphenols that are accountable for the reduction and stabilization of nanoparticles. The general procedure involved in the algae-extract assisted synthesis of nanomaterials is illustrated in Figure 5.

Some examples of nanocatalysts prepared by using algae extracts were discussed below. Silver (Ag^0) nanospheres with particle size of $10 \pm 2 \text{ nm}$ have been prepared by using *Caulerpa serrulate* (Aboelfetoh et al., 2017). The catalytic potential of silver nanospheres was tested in the reduction of Congo red molecules in water. The catalytic efficiency of silver nanospheres prepared at 95°C is 99.3% (time = 12 min). An aqueous extract of *Saragassum cervicornis* was prepared at 85°C – 90°C (1 h) and used to prepare palladium (Pd^0) nanoparticles via a reduction process (Anwar et al., 2021). Extracts of *Saragassum cervicornis* have been used as an alginate source that reduces palladium ions into palladium nanoparticles. The as-prepared palladium nanoparticles were used as a catalyst for the reduction of Congo red, methyl red, and methyl orange dyes in water. The catalytic reduction efficiency reported for methyl orange (catalyst dosage = $60 \mu\text{g } \mu\text{L}^{-1}$), Congo red (catalyst dosage = $40 \mu\text{g } \mu\text{L}^{-1}$), methyl red (catalyst dosage = $80 \mu\text{g } \mu\text{L}^{-1}$) is 99.66% (10 min), 99.25% (9 min), and 95.45% (10 min), respectively. Recently, bimetallic nanoparticles were also prepared efficiently using algae extract. The silver/palladium (ratio = 1:1) bimetallic nanoparticles with greater ultraviolet light triggered photocatalytic degradation efficiency in the Congo red dye degradation than the monometallic nanoparticles have been demonstrated (Al-Enazi, 2022). The algae extract employed to prepare mono and bimetallic nanoparticles is *Bacillariophyceae*. An extract was prepared by boiling a suspension containing 1 g of *Bacillariophyceae* powder in 100 mL of double distilled water at 60°C for 30 min.

Apart from metallic nanoparticles, metal oxides like copper oxide (CuO) and ZnO with high catalytic activities have been synthesized. For instance, CuO crystalline nanoparticles were prepared using *Cystoseira trinodis* extracts along with ultrasonic irradiation (Gu et al., 2018). The frequency and power of ultrasonic waves are 20 kHz and 400 W, respectively. The CuO nanoparticles (dosage = 50 mg) have been applied as a photocatalyst in the degradation of methylene blue (5 mg L^{-1} , 100 mL) in water. Under ultraviolet irradiation, the photocatalytic efficiency was 98%. The ZnO nanoparticles ($20 \pm 2.2 \text{ nm}$) were prepared by using *Chlorella* extract (Khalafi et al., 2019). The role of *Chlorella* extract as a reducing as well as stabilizing agent



was confirmed through Fourier transform infrared spectroscopic analysis. Hydroxyl groups in the algae reduce zinc ions (Zn^{2+}) into elemental zinc (Zn^0) nanoparticles, which subsequently undergo oxidation during the air-drying stage to form ZnO nanoparticles. Aggregation of ZnO nanoparticles would be avoided by biomolecules present in the algae extract. *Chlorella* extract-assisted synthesis ZnO nanoparticles display 97% photocatalytic dibenzothiophene degradation efficiency. The concentrations of dibenzothiophene and ZnO nanoparticles is 10 mg L^{-1} and 0.01 g , respectively. Copper sulfide (CuS) nanoparticles were synthesized by using *Chlorella ellipsoidea* extract which acted as a capping and reducing reagent (Borah et al., 2022). CuS nanoparticles have been utilized as an efficient sunlight-active photocatalyst for the (1 mL, 1 mM) sodium borohydride ($NaBH_4$)-mediated degradation of methylene blue in aqueous solution (25 mL , $1 \times 10^{-4} \text{ M}$), and the reported rate constant is 0.03692 min^{-1} (catalyst dosage = 1 mg).

It should be mentioned that a cadmium oxide (CdO)/ZnO nanocomposite with a particle size range of 20–50 nm was also prepared by precipitation approach in the presence of *Padina gymnospora* (Rajaboopathi and Thambidurai, 2017). Reactive Blue 198 degradation efficiency of CdO/ZnO in the presence of different light sources is 99.57% (natural sunlight), 95.2% (36 W fluorescent lamp, visible light), and 94.3% (15 W UV lamp, ultraviolet). The best photocatalytic performance was determined under sunlight irradiation (time = 15 min). The photocatalyst dosage, dye concentration, and volume are 0.5 g L^{-1} , 10 mg L^{-1} and 100 mL , respectively.

4 Conclusion and future prospects

Algae are potential materials in the treatment of organic pollutants in water due to their favorable properties such as

abundance, assimilation of pollutants as nutrients, high biomass yield, and fast growth. Different algae have been effectively employed in adsorptive and catalytic pollutant removal techniques. Algae biomass shows great biosorption capacity for organic pollutants. Algae types and ultrasound play a foremost role in the pollutant's removal process. Chemical treatment or the addition of nanomaterials remarkably improved the performance of algae. Biosorption of organic pollutants by algae occurs via physical and chemical interactions. Biochar, hydrochar, and activated carbon adsorbents with good adsorption capacity can be obtained using algae species. Redox mediators and microbes like bacteria and fungi can boost the degradation performance of algae and also provide other value-added products. Algae fuel cells are promising for wastewater treatment and power production. Light, concentration, and volume of wastewater, combined with other techniques and cell design, determine the performance of algal fuel cells. Integrated algae fuel cells might have much attention in water pollution remediation and energy production. Algae have been used as source materials for the synthesis of (catalyst in the activation of oxidizing agent, Fenton-like, and photocatalysis) catalysts, which have shown high performance in the degradation of organic pollutants. Further, algae-extracts also functioned as reducing and/or capping reagents in the preparation of monometallic, bimetallic nanoparticles, metal oxides (like ZnO, CuO), metal sulfides (like CuS), and composite nanocatalysts. Algae are being source materials and reagents in the development of adsorbents and catalysts. Effective utilization of algae-related adsorbents and catalysts might be beneficial in-terms of environmental protection and economic aspects, as it avoids usage of harmful chemicals and minimize harmful effects of algae.

Besides, further research studies are essential to determine the performance of algae-based adsorbents and catalysts in real wastewater treatment plants. Research can be focussed on the algae-mediated synthesis of sustainable nanomaterial-based adsorbents

and catalysts. More understandings are needed to explore the role of algae in nanomaterials synthesis. The biocompatibility of algae-derived nanomaterials needs to be evaluated. The removal performance of algae in the presence of nanomaterials must be studied using different kinds of organic pollutants. Research should be focused on the conversion of highly toxic algae into useful materials and pollutant adsorbed algae biomass. Research studies should also focus on the cost analysis of algae-based materials.

Author contributions

RS: Data curation, Formal Analysis, Methodology, Validation, Writing—original draft. SaR: Conceptualization, Formal Analysis, Supervision, Validation, Writing—review and editing. W-HC: Conceptualization, Formal Analysis, Investigation, Methodology, Supervision, Writing—review and editing. MS-M: Formal Analysis, Investigation, Methodology, Validation, Writing—original draft. TS: Formal Analysis, Investigation, Methodology, Supervision, Writing—original draft. AJ: Data curation, Investigation, Methodology, Project administration, Validation, Writing—original draft. SuR: Conceptualization, Formal Analysis, Investigation, Methodology, Supervision, Validation, Writing—review and editing.

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Conflict of interest

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