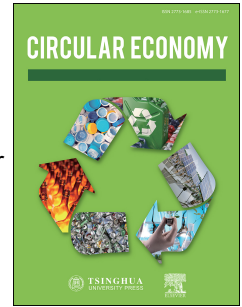


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Microalgae as potential agents for biochar production: Future of industrial wastewater treatment

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Review Article**Microalgae as potential agents for biochar production: Future of industrial wastewater treatment**Sayantani Ghosh^a, Sulagna Das^a, Avirup Panja^a, Alexei Solovchenko^b, Priyanka Jha^{c,d*}^aAmity Institute of Biotechnology, Amity University, Kolkata Campus, West Bengal 700135, India^bBioengineering Department, Faculty of Biology, M.V. Lomonosov Moscow State University, Moscow GSP-1, 119991, Russia^cDepartment of Biotechnology, Lovely Faculty of Technology and Sciences, Lovely Professional University, Punjab 144411, India^dDepartment of Intellectual Property and Rights, Division of Research and Development, Lovely Professional University, Punjab 144411, India

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Abstract: Diverse industries like breweries, textiles, paper & pulp, mining, chemical & nuclear, and food processing generate huge amounts of wastewater which can be toxic. This wastewater, rich in both organic compounds and inorganic salts, suspended solids, heavy metal ions and other pollutants should be properly treated before discharging into the environment. Recent studies demonstrated the efficiency of microalgae-based treatment. Microalgae are efficient in this regard since they produce photogenerated oxygen oxidizing the pollutants and toxin degrading enzymes, readily consume organics, and uptake/adsorb other pollutants. The current bottlenecks for microalgal bioremediation are high costs and low energy efficiency. The resulting biomass can be utilized for producing various forms of bioenergy via assorted traditional as well as modern techniques such as hydrothermal carbonization, pyrolysis, and torrefaction. One of the valuable outputs of these processes is biochar which is rich in nutrients and is capable of ion exchange. Therefore, it finds potential application in agriculture e.g., for revamping soil fertility and in wastewater treatment as adsorbent removing organic and inorganic pollutants. Here, we review novel processes designed for microalgae-based wastewater treatment with an emphasis on biochar production and utilization. Special attention is paid to the characterization of the physicochemical properties of biochar to maximize its targeted applications.

Keywords: Biochar; Microalgae; Wastewater; Bioremediation; Photobioreactor; MFCs

1. Introduction

Pharmaceuticals, heavy metals, pesticides, dyes, and surfactants, among other organic and inorganic contaminants, are routinely discharged into water bodies by numerous sectors. These pollutants are frequently transformed into a recalcitrant form resistant to natural degradation. Because of their harmful effects on ecosystems, the discharge of untreated contaminants into the environment is a major issue.

The number of pollutants leaking into the environment is diminished by wastewater treatment. To address wastewater effectively, it is crucial to implement treatment systems specifically designed for the unique composition of wastewater from each source, supporting microbial agents utilized in treatment. Conventional wastewater treatment procedures include chemical precipitation, activated charcoal adsorption, ion exchange, chemical reduction, and filtration. These strategies effectively reduce the total carbon and nitrogen levels in waste streams. One of the most common methods of wastewater treatment is biofiltration. The biodegradation of contaminants by microorganisms adhering to the filter medium is the basic working principle of biofiltration. Wastewater is generated by various facets of human activity. The energy consumption of wastewater treatment facilities (WWTPs) contributes to 3% of global power consumption, and this share will rise as the wastewater treatment rate rises (Nguyen et al., 2022).

Microalgae, the unicellular photosynthetic microorganisms, have high carbon fixing capacity with simultaneous evolution of photogenerated oxygen. At the same time, many microalgal species can consume organic compounds as an additional or sole source of carbon and energy. These features have been leveraged by applying microalgae in wastewater treatment, particularly for removing organic pollutants. The availability of artificial cultivation methods for these microorganisms either in open systems like raceway ponds (Mehariya et al., 2021) or closed systems like photobioreactors (Chen et al., 2011) or other advanced systems like algal turf scrubber using wastewater as growth medium makes this process efficient. Recently, membrane photobioreactors (MPBR) have been designed that allow cost-effective and efficient cultivation of microalgae along with its pre-harvesting in wastewater (Praveen et al., 2016). Industrial wastewater which is rich in organic matter (volatile fatty acids, dyes, etc.), nitrogen, phosphate, and heavy metals can serve as a source of nutrition for cultivating microalgae. The microalgal biomass generated from the wastewater treatment process is abundant in organic matter, making it a valuable substrate for the production of renewable energy sources such as biofuels, biogas, and biochar. (Ghayal & Pandya, 2013; Fig. 1). Biochar can also be used as bio-fertilizer to improve the fertility of the soil and help in soil amendment (Liu et al., 2017). Biochar is also applied in carbon

sequestration and as catalyst in various processes such as biofuel production (Chi et al., 2021).

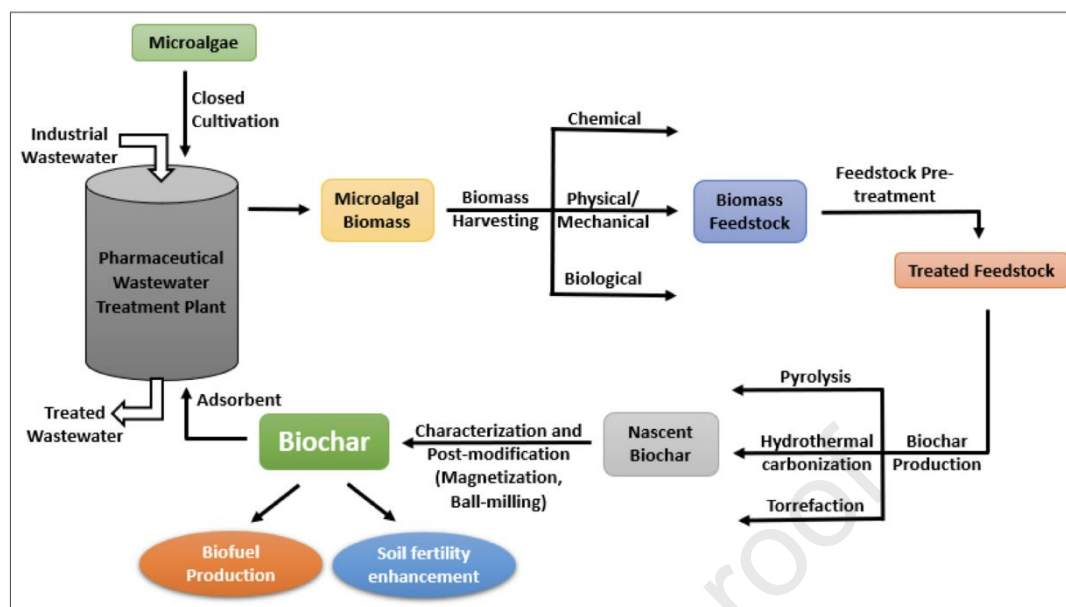


Fig. 1 Overview of biochar production from wastewater (Circular economy schematic diagram).

This review focuses on the production of biochar from algal biomass obtained from wastewater treatment plants via pyrolysis, hydrothermal carbonization, and torrefaction. Among these, pyrolysis is the most used technique where the biomass is thermally decomposed at high temperatures in an anaerobic environment (Soria-Verdugo et al., 2017); whereas, torrefaction, an emerging technique, is a milder form of pyrolysis carried out at lower temperatures around 300 °C (Yu et al., 2017). The temperature of pyrolysis and the heating rate are the main factors giving rise to different types of pyrolysis such as fast and slow pyrolysis (Brindhadevi et al., 2021). Studies have been carried out to compare the relative efficiencies of using different biomass at varying pyrolysis conditions producing biochar with varying yields and properties (Sekar et al., 2021). The biochar produced varies widely in its properties based on parameters such as biomass composition, pre-treatment conditions, conversion temperature, and residence time (Yaashikaa et al., 2020).

However, before the conversion the biomass needs to be pre-treated which can be carried out using physical, chemical, or biological methods. The resulting biochar is characterized based on its physicochemical, surface, and elemental composition properties to determine its suitability for the desired function (Sekar et al., 2021). Post-treatment techniques like magnetization (Liu et al., 2019), ball milling (Lyu et al., 2018), and corrosive treatments such as acid, alkali, and oxidation are used, among others, for upgrading the resultant biochar (Zheng et al., 2019).

This review focuses specifically on biochar, is to highlight its wide range of applications. Biochar, a carbon-rich charcoal of any biomass (Yu et al., 2017b), serves as a cost-efficient and eco-friendly solution to a variety of pressing issues of the current times. Having a porous surface, biochar is an

excellent adsorbent for treating wastewater and other organic and inorganic waste management (Chen et al., 2019, Braghiroli et al., 2018).

The microalgae-biochar coupling process offers a promising and effective approach to wastewater treatment by leveraging the unique strengths of both components. Microalgae play a crucial role in capturing and assimilating wastewater nutrients and pollutants, thereby reducing pollution levels (Chen et al., 2018a). Moreover, the biomass generated during this process can be converted into biochar through oxygen-free processes. Biochar, known for its large surface area and high absorption capacity, can be reintroduced into wastewater to remove heavy metals and other organic pollutants, resulting in a closed-loop system. In this system, microalgae thrive in wastewater, absorbing nutrients and contaminants to purify the water. The biomass produced is then transformed into biochar using pyrolysis or hydrothermal carbonization. This biochar can be reused in the treatment process to adsorb additional pollutants, thereby enhancing the efficiency of wastewater treatment (Chen et al., 2018b). This closed-loop coupling system shows great promise for industrial and municipal wastewater treatment systems, offering a more sustainable and cost-effective solution (see Fig. 1).

Over the last two decades, biochar, with its huge potential, has grabbed the attention of researchers. Previous reviews highlighted either the conversion of microalgal biomass to biochar or the applications of microalgae in wastewater treatment. This review aims to integrate these two important fields and fill in the gap between obtaining biochar from wastewater treatment and using it for the same purpose. It will provide a perspective on how industrial wastewater can serve as both the sink and source of biochar.

2. Effects of industrial wastewater components and biochar production techniques on treatment efficiency and sustainability

Various organic and inorganic contaminants such as pharmaceuticals, heavy metals, pesticides, dyes, and surfactants, from different industries, are discharged regularly into the water bodies. These contaminants frequently undergo transformation into recalcitrant forms, rendering them highly resistant to natural decomposition processes. The untreated discharge of such pollutants into aquatic ecosystems presents a critical challenge due to their significant adverse effects on ecological balance. Various dyes and heavy metals (like Fe, Co, Mn, Cu, Mo, Zn, etc.), mainly from the tanneries, mines, and metal processing industries, are responsible for binding to the surface of microorganisms and then penetrating inside the cell to cause harmful chemical reactions that disrupt their normal function. Wastewater from the pharmaceutical industry harbors different types of contaminants ranging from antibiotics and active biomass to phenols and polyaromatic hydrocarbons, which are more harmful than inorganic contaminants (Kumar et al., 2018). It may also contain toxins or antibiotics promoting the selection of microorganisms carrying drug-resistance genes in natural habitats, these pollutants may

also enter the food chain through the aquatic organisms. Among the macronutrient pollutants, organic carbon (C), nitrate and nitrite nitrogen (N), and phosphorus (P) are the major contributors. These latter two macronutrients are responsible for the eutrophication of the water bodies negatively affecting aquatic biota. The fluoride-rich wastewater leaching into the groundwater reserves results in major health issues such as dental fluorosis and kidney disorders (Yadav et al., 2019). Industrial waste streams frequently contain microplastic particles, partly from packaging, threatening aquatic and terrestrial lifeforms.

For many years, traditional techniques for treating industrial wastewater have relied on pyrolysis and hydrothermal carbonization. Pyrolysis involves heating organic materials without oxygen, and is known for producing high-quality biochar with a well-developed pore structure. This porous structure enhances the biochar's ability to adsorb contaminants, making it highly effective in wastewater treatment. Besides this, a significant initial investment in equipment and energy is often required which acts as a barrier in this long-term employment. This makes the process energy intensive, however, research has shown that the byproducts generated during this process like bio-oils and syn-gas can be used thereby reducing the overall emissions and making the process more sustainable (Tarelho et al., 2020).

In contrast, hydrothermal carbonization takes place in a water-rich environment at lower temperatures, resulting in biochar with different properties, including a higher retention of nutrients. The effectiveness of biochar in adsorbing heavy metals or organic pollutants can vary based on the method used, directly influencing its suitability for specific industrial wastewater treatment applications (Yang et al., 2023). This process involves lower initial costs and can operate at lower temperatures, but the biochar produced using this technique may require additional processing. As a result, the utility spectrum is reduced compared to pyrolysis. Additionally, since fewer byproducts are generated, the environmental benefits are also reduced in this method.

3. Bioremediation techniques in wastewater treatment

Bioremediation or biological degradation of impurities present in wastewater depends on a wide range of factors such as characteristics, concentration, and toxicity levels of the contaminants; retention time, temperature, and other conditional parameters maintained during the degradation process as well as the efficiency of the microbial strain used for the process (Shah & Shah, 2020). Based on these factors, various bioremediation techniques have evolved over the years (see Table 1), some of which are elaborated upon in the following discussion.

Table 1

An overview of various bioremediation techniques

| Method | Efficiency | Application | Reference |
|--------------------------|--|---|---|
| Activated sludge method | 82% BOD, 88% COD, 96% NH ₃ , and 98% SS removal | Removal of antibiotics and pharmaceutical toxins | (Watkinson et al., 2007) |
| Anaerobic bioremediation | ~90% removal of COD | Nitrogen and NH ₃ removal | (Shi et al., 2017) |
| Membrane bioreactors | Not reported | Toxin removal by pressure-driven methods | (Giwa et al., 2017) |
| Bacterial bioremediation | ~80% removal of COD | Reducing COD, TDS, TSS, and sulphate levels | (Das et al., 2012) |
| Phyto-remediation | ~67% reduction in phenol concentration and ~90% removal of industrial dyes | Removal of heavy metals and industrial dyes, reduction in phenol concentration, toxin bioaccumulation | (Shah & Shah, 2020) |
| Fungal bioremediation | 75%–89% BOD and 61% COD removal | Synthetic recalcitrant effluent treatment | (Rana et al., 2017) |
| Phyco-remediation | >50% heavy metal removal and 92.2% biosorption capacity | Removal of heavy metals, biosorption of hydrocarbon, and industrial dyes | (Arumugam et al., 2018, Das et al., 2016) |

Note: BOD = biological oxygen demand; COD = chemical oxygen demand; TDS = total dissolved solids; TSS = total suspended solids.

Phytoremediation is the process of plant interaction be it physical, chemical, biological, or biochemical, with toxic pollutants in wastewater. The various interaction patterns have been studied to apply phytoremediation treatment for reducing phenol concentrations (Wang et al., 2015), removal of heavy metals such as cadmium, bioaccumulation of toxins (Shah & Shah, 2020), and biosorption of industrial dyes (Nath et al., 2014) from wastewater plants. Various fungal strains are useful in reducing the chemical oxygen demand (COD) of industrial wastewater (especially those from the distillery) (Ahmed et al., 2022). Some specific strains such as white rot fungus have been studied to reveal their capability to reduce BOD and COD from synthetic recalcitrant effluent sample solutions rich in tannic and humic acids (Bardi et al., 2017). More and more studies are being carried out to explore the biochemical potential of fungi for wastewater bioremediation (Olicón-Hernández et al., 2017).

Microalgae are highly efficient agents for wastewater treatment as they can capture carbon dioxide

and reduce the organic load from concentrated sources such as farm or food processing wastewater without using harmful chemicals (Arumugam et al., 2018). Microalgal cultivation systems based on immobilized cell culture can achieve high biomass densities by minimizing biomass wash-out and maximizing its concentration within a small cultivation volume. Such immobilized and biomass-based systems were shown to effectively remove nitrogen and phosphorus from the tertiary effluent of wastewater treatment plants (Zeng et al., 2012). What has rendered the process of phyco-remediation more valuable is the possibility of waste valorization via the utilization of the microalgal biomass obtained from the treatment plants. Over the years, this biomass, rich in organic constituents (such as carbon, nitrogen, and phosphorus), has found many interesting applications some of which are discussed below.

The capability of microalgae to corroborate bacterial microbiota in pollutant removal and to donate electrons during metabolization of the pollutants has led to the development of bio-electrochemical systems known as microbial fuel cells (MFCs) (Gajda et al., 2015). Research has led to the development of different types of algae-based MFCs (Table 2). Studies of integrated systems consisting of MFCs with photo-bioreactors for wastewater treatment have shown promising results for the removal of ammonia and phosphates and reduction in COD (Yang et al., 2019a). Wang et al. (2010) confirmed the potential of using MFCs with algae-assisted cathode for simultaneous carbon removal from wastewater, power generation, and biodiesel production without mechanical aeration.

Table 2

Types of algae-based MFCs

| Type | Power density produced (mW/m ²) | Reference |
|------------|---|------------------------|
| Normal MFC | 116 – 140 | (Arun et al., 2020) |
| PAMFC | 153 | (Gouveia et al., 2014) |
| SMFC | 38 – 48 | (Wang et al., 2014) |
| MCC | 125 | (Wang et al., 2010) |

Note: PAMFC is short for photosynthetic algae microbial fuel cell; SMFC is short for Sediment-type algae microbial fuel cells and MCC is short for Microbial carbon capture cells.

Microalgae feature potentially high lipid yield, superior growth rate, they require a minimum land area for cultivation, can grow in a wide variety of climatic conditions and have a non-competitive nature

to food or fodder crops, and can even utilize wastewater as their source of nutrition (Laurens et al., 2017). As mentioned above, they are also great bio-sequesters and have excellent capacity to fix carbon (Sydney et al., 2010). All these have urged scientists to exploit the potential of microalgae as feedstock for bioenergy production (Chandra et al., 2019). The microalgal biomass obtained from the wastewater treatment plants is being utilized to produce different value-added products such as biofuels, biofertilizers, and biochar. This provides dual benefits of not only being an alternative to costly microalgae-based systems aimed solely at biofuel production but also valorization of the waste (Olguín, 2012).

Simultaneous application of algal biomass for wastewater treatment and sustainable bioenergy generation is a comparatively new field with a wide range of advantages such as cost-efficient treatment of industrial wastewater, reduction of fossil fuel dependency, energy security, controlling greenhouse gas emissions, and an overall environmental protection (Allen et al., 2018). It faces various challenges like proper optimization of the entire system, suitable strain selection with high sequestration capacity and biomass productivity, prevention of contamination, presence of growth inhibitors in the wastewater, pre-treatment, and loss of nutrients from wastewater which needs to be resolved (Shukla et al., 2017).

4. Production methods of biomass to biochar

With the growing interest in biochar for a wide range of applications, biochar production by biomass conversion increased. The most widely used method for this purpose is thermochemical conversion. Some of the commonly used techniques under this methods are: gasification, pyrolysis, torrefaction, and hydrothermal carbonization (Yaashikaa et al., 2019). To yield the maximum amount of biochar, the production technique should be suitable for the type of biomass used, and the conditions under which processing is carried out, such as temperature, rate of heating, and residence time, must be ideal. These conditions are critical because they have the potential to influence the physical and chemical states of biochar during the manufacturing process. The processing conditions greatly impact the biochar that is converted from plant biomass, as the process encompasses the loss of weight of the biomass (Barreto, 2018). The weight loss process is initiated with the loss of water around 100 °C, and is trailed by the breakdown of cellulose, hemicellulose, and lignin above 220 °C, and is concluded by the burning of carbonaceous compounds (El-Naggar et al., 2019).

4.1.1 Hydrothermal carbonization

Hydrothermal carbonization (HC) is a thermochemical conversion process that produces a solid, coal-like material from biomass. It has been utilized in various sciences for nearly a century, primarily to mimic the usual process of coal formation in the laboratory. In recent years, hydrothermal

carbonization has garnered significant attention as a promising biomass conversion technology to address the growing demand for efficient biomass utilization. Research and development initiatives have been launched to evaluate its feasibility and explore additional application opportunities. (Sharma et al., 2020).

HC is also an exothermic process that involves dehydrating and decarboxylating the biomass input to lower its oxygen and hydrogen content (as measured by the molecular oxygen to carbon and hydrogen to carbon ratios). This is accomplished by exposing a suspension of biomass in water to 180 – 200 °C for several hours at saturated heat. To distinguish the result from dry processes like pyrolysis and gasification, the product created by the hydrothermal process is referred to as hydrochar.

The biomass is suspended in water and placed in a closed reactor during the process. To preserve equilibrium, the temperature is steadily elevated. Different products are formed at various temperatures, as stated: below 250 °C hydrothermal carbonization produces biochar, and at temperatures between 250 and 400 °C hydrothermal liquefaction produces bio-oil. The hydrolyzed product goes through several processes like isomerization, fragmentation, and dehydration, to create the intermediate product, 5-hydroxymethylfurfural, and its derivatives. Additionally, intramolecular dehydration, polymerization, and condensation are used to produce hydrochar (Gollakota et al., 2018). The mechanism is challenged by the high molecular weight of lignin and its dynamic existence lignin degradation is started by dealkylation and hydrolysis processes, which produce phenolic byproducts like syringols, catechols, and phenols. The char at the end is created by repolymerization and cross-linking of intermediates. Similar to pyrolysis, hydrochar is produced from the lignin components that are not dissolved in the liquid phase. (Funke & Ziegler, 2010).

4.1.2. Pyrolysis

It is an anaerobic process involving the thermal decomposition of organic materials at temperatures ranging from 250 °C to 900 °C. This method serves as an alternative way to convert waste biomass into valuable products such as bio-oil, syngas, and biochar (Shen, 2020). Lignocellulosic components, including lignin, hemicellulose, and cellulose, undergo reactions such as cross-linking, fragmentation, and depolymerization at specific temperatures, resulting in solid, liquid, and gaseous byproducts. Unlike the gaseous byproducts—carbon dioxide, carbon monoxide, hydrogen, and syngas (C1–C2 hydrocarbons)—char and bio-oil are produced as solid and liquid substances, respectively. Fast pyrolysis is defined as a direct thermochemical process that converts solid biomass into liquid bio-oil with high energy potential. It is characterized by a rapid heating rate of biomass particles (>100°C/min) and short residence times for both biomass and pyrolysis vapors (0.5–2 s) at high temperatures. In contrast, slow pyrolysis has a slower heating rate (approximately 57°C/min) and an extended residence

time (over 1 h). As a result, slow pyrolysis produces a greater yield of char compared to other pyrolysis and carbonization techniques (Shen, 2020).

4.1.3. Torrefaction

This is a relatively new technique for producing biochar, involving a form of mild pyrolysis performed at a low heating rate. Various decomposition methods are used to remove oxygen, moisture, and carbon dioxide from the biomass in an anaerobic, inert atmosphere at elevated temperatures of approximately 300 °C. This process modifies the properties of biomass, including particle size, moisture content, surface area, heating rate, and energy density. Several methods for torrefaction exist: (a) Steam torrefaction, where steam is applied to the biomass for approximately 10 min at temperatures below 260 °C. (b) Wet torrefaction, also known as HC, occurs when biomass is immersed in water for 5–240 min at temperatures between 180 °C and 260 °C. (c) Oxidative torrefaction involves the oxidation of biomass using gaseous oxidizing agents, which are subsequently burned to generate heat energy. This heat energy is used to reach the desired temperature (Kwoczynski & Čmelík, 2021).

Torrefaction is a form of incomplete pyrolysis that occurs under specific conditions: a temperature range of 200–300 °C, a residence time of less than 30 min, a heating rate below 50 °C/min, and an anaerobic environment. The dry torrefaction process comprises several stages, including heating, drying, torrefaction, and cooling (Vogt et al., 2012).

4.2. Characterization of the physicochemical properties of biochar to maximize its targeted applications

Biochar possesses numerous beneficial properties that lead to its wide range of applications, which are discussed in a later section of this chapter. Modifying biochar by changing properties such as surface functional groups, pore structures, specific surface area, and stability may enhance its effectiveness for various applications (Wang et al., 2019).

4.2.1 Functional groups

The surface of biochar has various functional groups, including carboxylic, amine, hydroxyl, amide, and lactonic groups, which enhance its sorption capabilities. The primary factors influencing the presence of these functional groups on the biochar surface are temperature and the type of biomass used (Li et al., 2017a). Furthermore, an increase in parameters such as pH, porosity, and surface area may lead to a decrease in these surface functional groups. The most commonly employed characterization techniques are Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) (Brewer et al., 2014).

4.2.2 Surface area and porosity

The sorption capacity of biochar is greater when it possesses a large surface area and high porosity. The porous surface of biochar develops during the dehydration phase of the pyrolysis process, particularly when water loss increases at high temperatures (Brewer et al., 2014). The pore size of biochar can be analyzed using scanning electron microscopy, with pore diameters varying from less than 2 nm to over 50 nm. Biochars with micropores are not suitable for pesticide adsorption from wastewater (Safaei Khorram et al., 2016; Varjani et al., 2019). Without the activation process, biochar is less porous and has a smaller surface area. The activation process is performed during the manufacturing process to increase the biochar's porosity and surface area (Jain et al., 2016).

4.2.3 Biochar stability

The carbon sequestration capability of biochar is evaluated based on its stability and resistance to soil degradation caused by both biotic and abiotic factors. Numerous studies have been performed to assess and evaluate biochar stability (Spokas, 2010). This can be analyzed through the temperature used during the pyrolysis process (Cross & Sohi, 2013). However, this prediction is both misleading and evident. Traditionally, proximate analysis has been used to evaluate the types of coal, moisture, charcoal, ash, and fixed carbon (C). Biochar stability is typically assessed using three different methods: (a) quantifying or qualifying the carbon structures of biochar, using parameters such as aromaticity; (b) assessing stable carbon through thermal, chemical, or thermochemical methods, including thermal degradation and chemical oxidation; and (c) incubating biochar in soil to model carbon mineralization (Leng et al., 2019). Although biochar has numerous applications, the current methods for measuring its stability do not yield reliable results. Therefore, developing new techniques to assess biochar stability could enhance its effectiveness in climate change mitigation.

Table 3 presents the analytical techniques employed to characterize biochar. The various physical and chemical reactions performed to optimize biochar properties (Wang & Wang, 2019) and enhance their efficiencies are discussed below. Additionally, Table 4 provides a comparison of the most commonly used modification techniques (Yang et al., 2019b).

Table 3

Characterization techniques for biochar

| Technique | Property analyzed |
|---|---|
| BET model of multilayer adsorption* | Surface area; pore size distribution |
| Energy dispersive X-ray spectroscopy (EDXS) | Distribution of chemical elements (molar fraction of chemical composition analysis) |

| | |
|--|---|
| Extended X-ray absorption fine structure (EXAFS)** | Evaluation of poly-aromatic structure |
| Fourier transform infrared spectrometry (FTIR) | Surface functional group analysis |
| Nuclear magnetic resonance (NMR) | Carbon aromaticity determination |
| Scanning transmission electron microscopy (STEM) | Internal or surface morphology analysis |
| X-ray photoelectron spectroscopy (XPS) | Valence state of chemical elements |
| X-ray diffraction (XRD) | Crystalline phase of carbon |

*Developed by BET (Brunauer, Emmett, and Telle); **Region of spectrum in X-ray adsorption spectroscopy (XAS)

Table 4

Comparison of the different biochar modification techniques

| Modification type | Effects |
|---------------------------|--|
| Acid modification | Increases polarity, hydrophilicity, and adsorption capacity |
| Alkali modification | Increases pore volume and surface area; improves hydrophobicity; enhances capacity for VOC adsorption |
| Metal impregnation | Improves catalytic performance, magnetic properties, heavy metal, and organic pollutant removal capacity, thermal stability; increases SSA |
| Mineral impregnation | Increases ion-exchange capacity and lead removal capacity |
| Carbonaceous modification | Enhances surface area |
| Steam modification | Improves catalytic activity and microporosity; increases surface area |

5. Biochar applications for industrial wastewater treatment

Biochar has a microporous surface, which enables it to function as an excellent adsorbent for various pollutants in wastewater. Additionally, its functional groups contribute to its ion exchange properties, facilitating the removal of heavy metals. Biochar derived from different feedstocks exhibits distinct properties that can be applied to a wide range of pollution control applications. This section emphasizes the diverse uses of spent microalgal biomass-based biochar in wastewater treatment.

Biochar, similar in functionality to activated carbon, effectively removes both organic and inorganic pollutants from wastewater (Fig. 2; Qambrani et al., 2017). Various optimization techniques,

such as mineral impregnation, blending with chitosan, and increasing pyrolysis temperature, can enhance biochar's capacity to remove heavy metals such as Cd^{2+} , Ni^{2+} , copper, and lead (Hussain et al., 2017). Additionally, the diverse functional groups of carbon, sulfur, and metallic oxides present on the surface of biochar contribute to the mineralization of petroleum contaminants in industrial wastewaters (Chen et al., 2019). Biochar derived from microalgal biomass, owing to its high content of oxygen-containing functional groups, exhibits a strong adsorption capacity for Cu^{2+} (Regmi et al., 2012) ions from industrial wastewater.

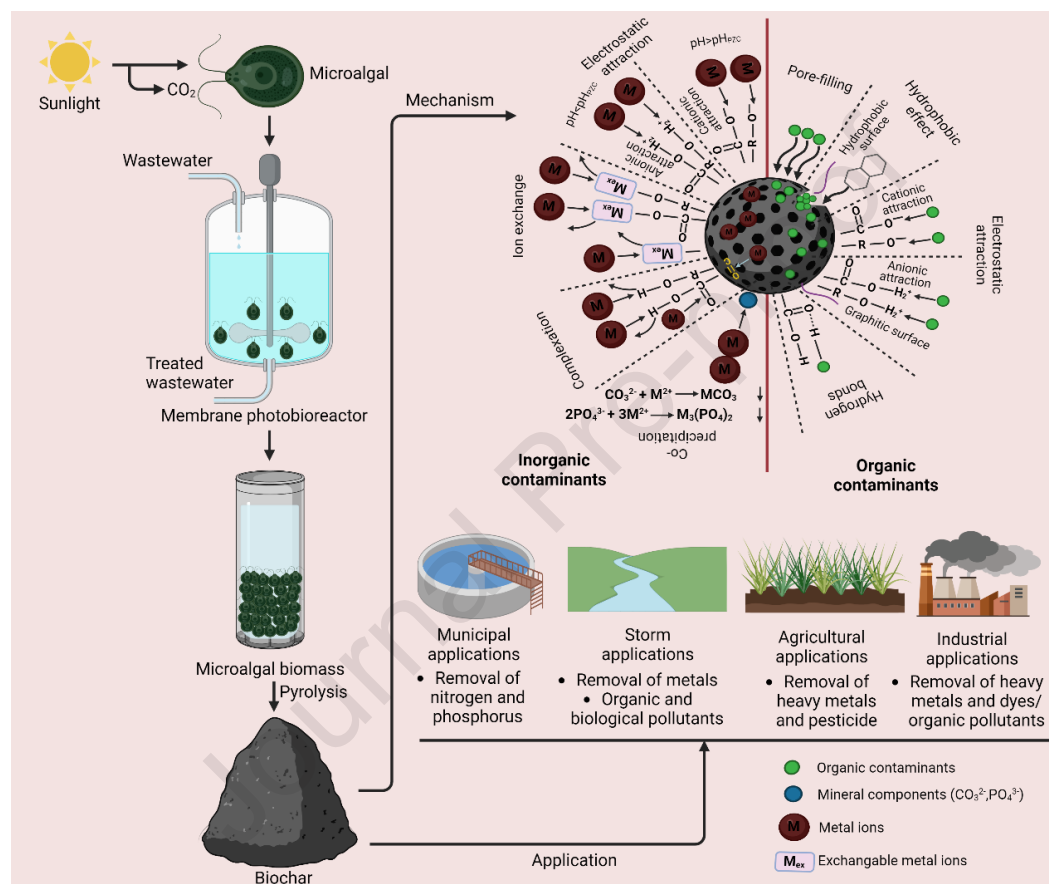


Fig. 2 The mechanism by which biochar removes organic and inorganic contaminants from industrial wastewater and its various applications

A series of studies indicate that biochar produced from activated wastewater sludge is highly effective in removing inorganic phosphorus and nitrogen, including NH_4^+ and PO_4^{3-} ions, from wastewater treatment plant effluent (Yin et al., 2019; Yang et al., 2018b). Ajmal et al (2020) suggested that magnetically modified biomass-derived biochar enhances the removal efficiency of phosphate ions from wastewater. Recent research highlights the diverse applications of modified biochars in conjunction with other technologies for on-farm irrigation wastewater remediation techniques, including pathogen removal (Chaukura et al., 2020). Table 5 summarizes some of the most commonly used types of biochar, made from various industrial wastes, their properties, and the pollutants they remove.

Table 5

Adsorption capacity of biochar for wastewater pollutants

| Feedstock | Modification | Contaminant removed | Removal capacity (mg/g) | Mechanism of removal | Reference |
|-------------------|--|-------------------------------------|-------------------------|---|--------------------------|
| Paper mill sludge | Oven dried and acid washed | As ⁵⁺ | 34.1 | Chemisorption | (Cho et al., 2017) |
| Sewage sludge | Stirred and heated | As ⁵⁺ ; Cr ³⁺ | | Chemisorption | (Agrafioti et al., 2013) |
| Swine manure | Chemically modified | Tetracycline; Imidacloprid | | π - π interaction; pore-filling | (Jin et al., 2016) |
| Green waste | Dried and HCl modified | Cd ²⁺ | 6.72 | Chemical adsorption | (Zhang et al., 2018b) |
| Chitosan | - | Ciprofloxacin | | Hydrophobic interaction, H-bonding | (Afzal et al., 2018) |
| Bagasse | Anaerobically digested | Sulfamethoxazole | 1.6 | π - π EDA interaction | (Yao et al., 2018) |
| Sawdust | Iron and zinc doped | Tetracycline | 86 | Site recognition and competition bridge formation | (Zhou et al., 2017) |
| Wood waste | MgO modified | NH ⁴⁺ | 47.5 | Struvite precipitation | (Xu et al., 2018) |
| Hardwood | Acid wash and water wash | Phosphorous | 1.2 | Adsorption and surface precipitation | (Dugdug et al., 2018) |
| Maple wood | Dried and H ₂ O ₂ modified | Pb ²⁺ | 43.3 | Complexation by O ₂ functional groups | (Wang et al., 2018) |
| Cottonwood | HTC + LDH | Phosphate groups | 386 | Surface adsorption | (Zhang et al., 2014) |
| Willow wood | Acid wash and water wash | Phosphorous | 1.93 | Adsorption and surface precipitation | (Dugdug et al., 2018) |
| Pine wood | Oven dried and milled or Ni/Fe-LDH* modified | As ³⁺ | 1.56 | Electrostatic attraction; surface complexation with hydroxyl groups | (Wang et al., 2016) |

| | | | | | |
|---------------------------|--|-------------------------------------|-------|--|--------------------------------------|
| Rice husk | Washed and Polyethylene-imine modified | Cr ⁶⁺ | 435.7 | Amino group facilitated surface adsorption | (Rajapaksha et al., 2018) |
| Wheat straw | Mg-Fe LDH* | NO ₃ ⁻ | 24.8 | Surface adsorption and interlayer anion exchange | (Xue et al., 2016) |
| | Acid wash and water wash | Phosphorus | 1.06 | Adsorption and surface precipitation | (Dugdug et al., 2018) |
| | Pristine | NH ₄ ⁺ | 2.08 | Chemical bonding and electrostatic interaction | (Yang et al., 2018a) |
| Switchgrass | Magnetization | Metribuzin herbicide | 39.5 | H-bonds and electrostatic attraction and | (Essandoh et al., 2017) |
| Sugarcane harvest residue | MgO particle impregnated | NH ₄ ⁺ | 22 | Struvite crystallization, electrostatic attraction, and π - π interactions | (Li et al., 2017b) |
| Peanut shell | Washed, dried, milled and MgO treated | Pb ²⁺ ; Cd ²⁺ | 36 | Non-specific and specific outersphere surface complexation | (Wan et al., 2018) |
| Banana peels | Oven dried | Pb ²⁺ ; Cu ²⁺ | 75.99 | Ion-exchange, precipitation and electrostatic attraction | (Zhou et al., 2017, Li et al., 2017) |

*LDH = layered double hydroxides

5.1 Dairy and agroindustry

Nutrient-rich dairy wastewater is often used for irrigation to supply essential nutrients to crops at relatively low costs. However, its high organic load poses significant threats to groundwater and nearby water bodies. Studies have explored the potential of biochar, produced from locally available excess biomass, to recover excess nutrients from dairy wastewater while contributing to carbon sequestration and enhancing soil fertility (Ghezzehei et al., 2014). The effectiveness of biochar in removing organic and inorganic pollutants from dairy wastewater treatment plants is influenced by its polarity index, aromaticity index, and SSA (Braghiroli et al., 2018).

Agricultural wastewater with a high organic load can be effectively treated using biochar in

conjunction with biofilter technology, resulting in significant reductions in COD and TSS, as well as the recovery of essential nutrients (Manyuchi et al., 2018). Research by Zheng et al. (2019) indicates that modified biochar, engineered with AlOOH additions, can effectively retain phosphorus from secondary-treated wastewater, allowing for its recycling and reuse. Additionally, biochar can remediate pesticide-rich agricultural discharge (Dai et al., 2019). Different preparation conditions and biomass feedstocks, such as almond and maize straw, along with various modifications such as π - π interaction, hydrophobic interaction, and pore-filling (Wang et al., 2020), facilitate the adsorption of harmful pesticides including thiacloprid (Zhang et al., 2018a), imidacloprid (Jin et al., 2016), dibromochloropropane (Klasson et al., 2013), and triazine pesticides such as atrazine and simazine (Zheng et al., 2010).

5.2 Municipal wastewater

Biochar derived from digested sludge and pyrolyzed at 450 °C serves as an excellent adsorbent for ammonium in municipal wastewater (Tang et al., 2019). Additionally, studies have indicated that digested sludge biochar can be used as a catalyst for the ozonization of wastewater biorefineries and for reducing the organic load (Pessôa et al., 2021). Upgrading residential units with on-site sewage treatment facilities by incorporating low-cost biochar adsorbents has shown promising results in the removal of polar and hydrophilic contaminants (Blum et al., 2019). Recent advancements in technology that use constructed wetlands (CW) and biofilters (BF) for treating municipal wastewater, with biochar as their substrate, have demonstrated promising results in contaminant removal (Deng et al., 2021). Biochar derived from alder (*Alnus* sp.) has been reported to effectively remove nitrogen and phosphorus from pretreated municipal wastewater when used as a substrate in CWs (Kasak et al., 2018). In contrast, rice husk biochar has shown efficacy in removing bacteriophages from municipal sewage when used in BFs (Yin et al., 2017).

5.3 Textile industry

Textile industry wastewater primarily contains organic contaminants such as harmful dyes and heavy metals. Studies have shown that negatively charged biochars can effectively interact with positively charged dyes in alkaline environments (Ambaye et al., 2021). Ion exchange with cationic organic pollutants such as dyes (Hassan & Carr, 2018), physical adsorption (both monolayer and multilayer) of heavy metal ions on the porous biochar surface, electrostatic interactions between pollutants and oxygen-containing functional groups on the biochar surface, precipitation of insoluble biochar-heavy metal complexes, and contaminant complexation with biochar through adsorption,

functional group binding, π - π interactions, or metal bridge formation are among the primary mechanisms by which biochar removes pollutants (Fig. 2). Additionally, biochar derived from food waste has been investigated for its ability to adsorb dyes from textile industry wastewater (Parshetti et al., 2013). Certain textile dyes, including crystal violet, malachite green, and congo red, which are resistant to conventional degradation methods (such as oxidation, aerobic digestion, and photo-degradation), have been shown to be effectively adsorbed by biochar obtained from macroalgae (Lin et al., 2018). Cationic dyes, such as methylene blue, exhibit strong π - π interactions with the biochar surface and have been found to be extensively adsorbed by biochar derived from switchgrass, which is produced at high pyrolysis temperatures (Park et al., 2011). Additionally, this switchgrass-derived biochar has also been reported to effectively adsorb other anionic dyes, including Congo Red and Orange G (Enaime et al., 2020). Furthermore, nanoporous biochar derived from bamboo cane and biochar from pecan nutshells have demonstrated the ability to adsorb wool carpet dyes, such as Lanasyne Gray and Lanasyne Orange, as well as Reactive Red 141 from water (Pradhananga et al., 2017; Zazycki et al., 2018). Studies have also highlighted the effectiveness of *Gliricidia* biochar in adsorbing crystal violet from aqueous solutions (Wathukarage et al., 2019). Similarly, corncob biochar modified with H_2SO_4 has demonstrated the ability to decolorize and remove various dyes and chemicals from textile wastewater through chemisorption (Sonu et al., 2020). Additionally, another study indicates that NaOH-activated biochar, produced by pyrolyzing *Sterculia alata* fruit shells, exhibits a significantly enhanced capacity for removing Patent Blue V dye, with the potential for multilayer adsorption (Giri et al., 2020). A sustainable and cost-effective technology that combines biochar with layered double hydroxide (LDH) composites has demonstrated potential for decolorizing dye-contaminated water (Zubair et al., 2021). Additionally, studies have reported the use of biochar as a composite catalyst for the degradation and mineralization of wastewater dyes (Sutar et al., 2022). Another recent study investigated the efficacy of an algal biochar-based nanocomposite (nAgBC), derived from *Spirogyra* sp., for treating wastewater contaminated with organic dyes such as Congo Red (Shaikh et al., 2022).

While numerous studies have explored the various applications of biochar in wastewater treatment, this technology has not yet been widely adopted, primarily owing to optimization challenges, because most research has been performed at the laboratory scale. Difficulties in adjusting operational and working parameters are considerable barriers to the broader application of biochar in wastewater treatment. Furthermore, existing studies (Varjani et al., 2020) indicate the need for further research on the governing factors of the adsorption process and the stability of biochar.

5.4 Tannery industry

The tanning industry generates various potentially hazardous pollutants, including heavy metals

such as Hg, Cd, Cu, Pb, Al, and Cr (Ballén-Segura et al., 2016), along with salts, sulfides, acids, and lime sludge (Zhao & Chen, 2019). Nutrient-rich secondary effluents containing nitrogen and phosphorus can lead to the eutrophication of water bodies. The properties of biochar not only facilitate the removal of organic and inorganic contaminants through filtration but also create suitable conditions for the rapid growth of microalgal biomass. This biomass further reduces heavy metal concentrations (Das et al., 2017) and decreases nitrogen levels, phosphorus, ammonia, and COD levels of the discarded wastewater (Sforza et al., 2020). Studies indicate that alkali-activated biochar (A-HTCB) derived from switchgrass, along with biochar produced from hydrothermally carbonized pinewood (Huang et al., 2015), also aids microalgae in adsorbing heavy metals and metal ions such as Cr³⁺.

5.5 Pharmaceutical industry

Pharmaceutical industry wastewater contains a diverse array of harmful organic contaminants, including drugs (such as paracetamol), antibiotics, enzymes, expired medications, hormone disruptors, food additives, endocrine-disrupting compounds, detergents, flame retardants, plasticizers, and personal care products. The disposal of these contaminants has raised considerable toxicological concerns for both human health and the environment (Nunes et al., 2017). Research has investigated the potential of both spherical and non-spherical biochars—derived from pure carbohydrates (like glucose) and lignocellulosic wastes (such as pomelo peel waste), respectively—for the removal of these drugs (Ocampo-Perez et al., 2019). Biochar can adsorb antibiotics such as tetracyclines and sulfonamides through electron donor–acceptor interactions with the functional groups on its surface (Peiris et al., 2017). Furthermore, biochar derived from Fe–Zn-doped sawdust and digested bagasse has been shown to effectively remove sulfamethoxazole (SMX) and tetracycline (TC) via π – π interactions, site recognition, competition, and bridge enhancement (Yao et al., 2018). Another study highlights the potential of biochar composites with LDH for the removal of caffeine and other antibiotics, including carbon tetrachloride, diclofenac sodium, SMX, TC, and paracetamol (Zubair et al., 2021). Biochar derived from *Arundo donax* through microwave-assisted pyrolysis has also been shown to effectively remove SMX (Bartoli et al., 2016). Magnetic biochar made from potato leaves and stems, coated with humic acid, has demonstrated the ability to adsorb various fluoroquinolones, including ciprofloxacin, enrofloxacin, and norfloxacin (Zhao et al., 2019). A recent study reviewed the application of sludge-based biochar for adsorbing a wide range of pharmaceuticals from wastewater through various mechanisms (Ihsanullah et al., 2022). Additionally, another recent study investigated the potential of biochar produced from plant sources such as *Eucommia ulmoides* and sugarcane bagasse and peanut shells in extensive removal of pharmaceutical pollutants such as SMX, naproxen, and norfloxacin (Monisha et al., 2022).

6. Economic and sustainable integration of biochar and microalgae-based wastewater treatment

Indeed, wastewater presents not only a challenge but also a resource for cultivating microbial biomass and producing value-added products. In addition to organic compounds that facilitate microbial growth, most types of wastewater contain various inorganic nutrients, such as nitrate and phosphate, which can be used by microalgae. Several factors, including (solar) light intensity, pH, temperature, and nutrient availability, influence the growth rate and patterns of microalgae. The biochemical oxygen demand (BOD) of wastewater can be reduced through the microalgal uptake of urea, phosphates, and metals such as magnesium, zinc, lead, cadmium, and arsenic. When treating wastewater, the microalgal biomass generated can be used to produce carbon-neutral products such as bioplastics, biofertilizers, animal feed, biofuels, and exopolysaccharides. This approach not only addresses the issue of wastewater treatment but also combines it with microalgal biorefinery, generating revenue and promoting a sustainable circular bioeconomy. This review will highlight contemporary and innovative strategies for using microalgae to reclaim nutrients from industrial wastewater sources and convert them into value-added compounds. Additionally, relevant challenges will be briefly discussed, along with a techno-economic analysis of existing pilot-scale projects worldwide (Bhatt et al., 2022).

The conversion of microalgal biomass into biochar has recently attracted attention owing to its various applications (Javed et al., 2019). It is estimated that 380 billion cubic meters of wastewater is produced globally each year, with projections indicating an increase of up to 24% above current levels within the next decade and an increase of 51% by the middle of this century. From a commercial standpoint, resource efficiency is a critical factor, making microalgae-based wastewater treatment a promising example of effective waste valorization. Integrating the cultivation of mixotrophic microalgae in wastewater treatment with the hydrothermal conversion of microalgal biomass feedstock has emerged as an economically advantageous strategy within the circular economy framework. The COD-rich anaerobic digestate (wastewater) acts as an effective culture medium for microalgae. The thermo-chemical conversion of microalgal biomass produces valuable energy resources such as algal biofuels and biochar, which have various applications, as previously discussed (Li et al., 2018).

Traditional wastewater treatment systems face challenges such as high energy consumption, the release of surplus sludge, greenhouse gas emissions, and resource wastage, which considerably hinder the pursuit of carbon neutrality in WWTPs. Microalgae are increasingly recognized as a vital element of the circular economy and sustainable development. In particular, microalgae have emerged as promising organisms for remediating polluted water bodies. The effective treatment of wastewater and subsequent biomass production have been reported using microalgae from several genera, including *Chlorella*, *Anabaena*, *Spirulina*, *Dunaliella*, *Ankistrodesmus*, *Porphyridium*, *Botryococcus*, *Aphanizomenon*, *Haematococcus*, *Synechococcus*, *Arthrospira*, *Nannochloropsis*, *Chlorogloeopsis*,

Chlamydomonas, Scenedesmus, and Isochrysis. Microalgae exhibit various mechanisms, including adsorption, bioaccumulation, and biodegradation. These strains can degrade toxic substances through their diverse biological processes. By generating biomass while using contaminants, microalgal strains have proven to be valuable for applications related to the circular economy and sustainable development (Nagarajan et al., 2019).

This work emphasizes the concept of a circular bioeconomy and the use of biochar as a practical solution for its effective organization. During the pyrolysis process, larger organic material particles break down into smaller atoms. These smaller atoms are subsequently released from the process as condensable vapors (oils), gases, and a substantial amount of heat. Factors such as heating rate, temperature, weight, time, the type of precursors, and the design and arrangement of the reactor influence the results. By developing closed-loop models in which waste from one process serves as input for another, small-scale manufacturing systems can be interconnected, fostering greater societal benefits and financial and environmental results within the circular economy (Fathianpour et al., 2018). For the development of new opportunities, it is essential to facilitate exchanges between alternative biochar production techniques and waste recycling. A circular bioeconomy has been established using waste from one processing industry to address contaminants in another, with the resulting product being used for soil remediation (Ubando et al., 2020). This approach has led to advancements in novel products and processes, as well as the potential for the creation of alternative businesses. High moisture content in important components leads to fluid formation, and even small amounts of water can pose a considerable risk because it increases the likelihood of producing more residue than oil. However, at higher temperatures ($>800^{\circ}\text{C}$) and with a faster heating rate, an increased amount of debris and vaporous materials is generated. Volatile compounds are released at a rapid rate during the initial phase of the process, around $250\text{--}300^{\circ}\text{C}$. For effective biochar production, methods that balance ease of use, energy conservation, and minimal emissions should be integrated into the local network, considering both technical and budgetary factors while recovering the biochar and heat produced. This application of the circular economy reduces waste while enhancing its value through various procedures and techniques. Research by Mohsenpour et al. (2021) indicates that incorporating microalgae in wastewater treatment has decreased the need for external nutrients by nearly 60%. Additionally, biochar produced through hydrothermal conversion, in contrast to traditional pyrolysis, achieves a 30% energy saving, which leads to lower operational costs and increased profitability. This approach can enhance the economic return by \$1,200 per ton (Mohsenpour et al., 2021). This, in turn, has lowered operational costs, resulting in annual savings of approximately \$50,000–\$100,000 for a medium-sized treatment plant. This integration provides a dual revenue stream for many industries, promoting both sustainability and broad economic benefits.

The economic viability of integrating biochar and microalgae-based wastewater treatment is greatly affected by policy frameworks. In many countries, government agencies offer subsidies or tax incentives for sustainable technologies that facilitate carbon sequestration and effective waste management. This financial support enhances the economic feasibility of these projects and accelerates the adoption of circular economy practices, ultimately contributing to broader environmental and economic goals.

6.1 Legislation requirements in EU and non-EU countries

Strict regulations are implemented in both developed and developing countries to manage and reduce carbon footprints across various industrial sectors. These laws focus on environmental policies designed to promote sustainability and climate action. Boiocchi et al. (2023) emphasized that essential standards for carbon footprint analysis include protocols such as the GHG Protocol, ISO 14064, ISO 14067, and PAS 2050. These policies, based on ISO standards, aim to lower greenhouse gas emissions and facilitate annual monitoring of carbon emissions.

Many EU countries have established certification frameworks for carbon removals to validate carbon sequestration activities across various industries, effectively monitoring emission rates in the wastewater sector. In contrast, the situation differs in non-EU countries. For example, in the USA, the Environmental Protection Agency regulates wastewater treatment plants under the Clean Air Act and the Clean Water Act. Conversely, countries such as India lack a robust legislative framework similar to that of other regions. However, the National Action Plan on Climate Change implements stringent controls across industries to reduce carbon emissions.

In the context of biochar production, various countries are developing legislation to promote and regulate its use, aligning with broader environmental goals such as the Circular Economy Action Plan and the Emissions Trading System in the European Union. These regulations aim to recognize and incentivize the carbon sequestration benefits of biochar, encouraging its adoption as a sustainable practice in agriculture and waste management (Singh et al., 2022). Consequently, biochar production is increasingly significant in efforts to reduce carbon footprints and foster long-term ecological sustainability, especially in the context of climate change mitigation.

6.2 Circular economy associated with biochar production

In recent years, extensive research has focused on the concept of the circular economy within the framework of sustainable development, particularly regarding wastewater treatment and its associated solutions, which represent emerging economic paradigms. The circular economy aims to minimize

waste and maximize resources by creating closed-loop systems where products, materials, and resources are reused, recycled, and regenerated (Fig. 3). This approach ultimately reduces environmental impact and enhances economic resilience. It encourages viewing wastewater not as waste but as a valuable resource that can be repurposed for other applications.

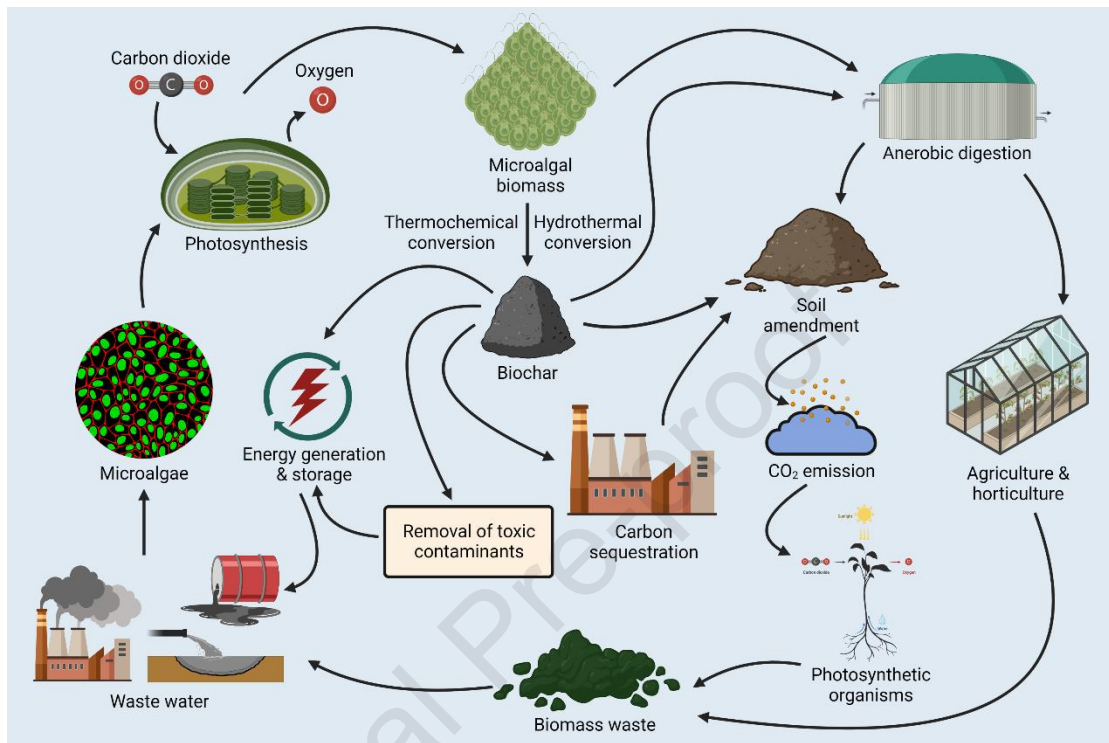


Fig. 3 Model for pioneering a circular economy in effective environmental management

The paper highlights the diverse applications of biochar. As a carbon-rich product derived from algal biomass, biochar is instrumental in advancing the circular economy, especially in wastewater treatment. It offers numerous advantages, including waste reduction and a lower environmental impact. Recent studies indicate that algal biochar can be effectively integrated into wastewater treatment systems, contributing to water purification and the production of algal biomass. The algal biomass has the potential to be converted into biochar in the future. This integrated system minimizes the reliance on chemical treatments, reduces environmental footprints, and offers greater sustainability over the long term. Furthermore, valuable byproducts generated during these processes can serve various important functions, including enhancing soil health and facilitating carbon sequestration.

Recent studies by Sun et al. (2022) indicate that the pyrolysis of algal biomass not only produces biochar but also generates bioenergy in the form of syngas and bio-oils. These energy-rich products can be used to create valuable items or fulfill other energy needs, thereby enhancing sustainability and self-sufficiency within the system. The production of biochar from algal biomass contributes to a circular economy by establishing a sustainable, low-waste framework that effectively uses all byproducts and closes the energy loop. In circular systems like this, biomass generated from microalgae-based

wastewater treatment can be further processed through pyrolysis to produce biochar, which can then be reused for wastewater treatment, thereby reducing the wastewater footprint (Boiocchi et al., 2023). These processes not only decrease the consumption of freshwater in these industries but also minimize waste generation and help maintain a clean environment. However, commercial challenges still exist, and ongoing research may provide effective solutions to address these issues.

6.3 Cost analysis

As new wastewater treatment technologies emerge, it is essential to perform comprehensive cost analyses for each to ensure effective large-scale implementation and economic viability for commercial use. The use of biochar derived from microalgae is being investigated as a promising, environmentally friendly, and sustainable alternative to existing technologies. While conventional treatment methods—such as activated sludge treatments, chemical treatments, and advanced oxidation processes—provide numerous benefits for wastewater management (Yu et al., 2017a), they often come with high installation costs and associated expenses, which can impede widespread adoption and large-scale implementation.

The estimated production cost of biochar from microalgae ranges from \$0.30 to \$0.70 per cubic meter, which includes expenses for cultivation, harvesting, and pyrolysis. This cost is considerably lower than the \$1.00–\$3.00 per cubic meter associated with advanced oxidation processes for wastewater treatment. Conversely, activated sludge systems are less expensive, costing approximately \$0.20–\$0.50 per cubic meter (Kaetzel et al., 2018). However, despite the cost advantage of activated sludge systems, they are associated with high energy consumption and persistent challenges related to sludge disposal after installation. These issues are not present in biochar treatment techniques. In activated sludge systems, energy consumption typically ranges from 0.6 to 2.0 kWh per cubic meter of treated wastewater, largely owing to the energy-intensive aeration processes required to maintain microbial activity (Garfi et al., 2017). In contrast, the biochar system reduces energy consumption by nearly 50% because microalgae naturally absorb CO₂ and produce oxygen, thereby decreasing the need for external aeration and lowering electricity usage.

In addition to its economic benefits, biochar production provides substantial environmental advantages. For example, biochar serves as a carbon sink, effectively sequestering carbon dioxide for prolonged periods, which can lead to the generation of carbon credits in various emissions trading schemes (Costa et al., 2023). Consequently, despite its initial higher cost compared to some conventional wastewater treatment methods, this approach contributes to long-term sustainability and environmental friendliness. It promotes closed-loop systems that are not only cost-effective in the long run but also complement traditional methods.

7. The cycle of microalgae-assisted wastewater as a source and sink for biochar

As previously discussed, microalgae are small aquatic plants increasingly recognized for their capacity to remove pollutants and excess nutrients from wastewater, making them a promising option for wastewater treatment and management. Furthermore, this microalgal biomass can be converted into biochar by heating it in an oxygen-deprived environment (Chandra et al., 2019). The biochar production process from wastewater-treated microalgae includes cultivating the microalgae in wastewater, harvesting and drying the biomass, and subsequently pyrolyzing the dried material to produce biochar, thereby achieving pollutant removal alongside biochar production (Enaime et al., 2020).

A primary advantage of using microalgal biomass from wastewater treatment plants to produce biochar is its effectiveness in improving water quality by removing pollutants and excess nutrients. Microalgae are recognized for their ability to absorb pollutants, including nitrogen, phosphorus, and heavy metals, rendering the water safe for discharge or reuse (Zeng et al., 2012). Moreover, converting microalgae to biochar reduces wastewater volume, facilitating easier treatment and management.

Another benefit of generating biochar from microalgal biomass in wastewater treatment plants is that it offers a sustainable and cost-effective alternative to conventional biochar production methods. This approach maximizes waste use because the refuse from water treatment plants is valorized rather than discarded. Moreover, the byproducts of the pyrolysis process, including bio-oil and syngas, serve as energy sources, enhancing the economic viability of the operation (Olguín, 2012). In addition, the biomass produced by microalgae is rich in energy, leading to biochar that is more stable and possesses a longer lifespan compared to biochar derived from other sources. This stability makes it a suitable material for soil amendment and carbon sequestration, enabling carbon storage that can last from hundreds to thousands of years (Sydney et al., 2010).

Biochar, characterized by its large surface area and high porosity, has the capacity to absorb a diverse array of waste products from water, making it a prime candidate for wastewater treatment (Fig. 3). A significant challenge in cultivating microalgae is supplying the necessary nutrients for their growth. Traditional nutrient delivery methods for microalgae come with limitations, such as high costs, potential environmental impacts, land requirements, and challenges in controlling nutrient levels (Allen et al., 2018). As previously mentioned, biochar can be produced from various biomass sources, including wood, straw, and agricultural waste, and it can contain essential nutrients such as nitrogen, phosphorus, and potassium, which are crucial for microalgae growth.

Thus, microalgae-assisted wastewater treatment serves as both the source and sink for biochar. The latter can be produced from microalgal biomass and used as an efficient, sustainable, and cost-effective method for wastewater treatment as well as a substrate for harvesting microalgae.

8. Challenges and environmental concerns

Microalgae-based wastewater treatment has emerged as a highly effective alternative to traditional wastewater treatment methods, although it faces certain challenges. While microalgae can use wastewater as a nutrient source for survival, wastewater treatment plants often lack the necessary nutrient composition to support optimal growth conditions for microalgae, consequently reducing their activity. Furthermore, bioremediation tends to be selective for biodegradable contaminants, limiting the scope of its applications. Another challenge is the problem of internal shading caused by surface microalgal growth, which restricts light penetration and inhibits growth in the culture medium (Bhatia et al., 2021). Additionally, microalgal cultivation in open raceway pond treatment plants is susceptible to contamination from protozoa and other microorganisms, which reduces biomass concentration. In a laboratory setting, contamination can be effectively managed using closed PBRs. However, the installation and maintenance of large-scale PBRs considerably increase cultivation costs. Likewise, pretreatment processes are not practical at a commercial scale.

Likewise, the use of biochar has raised several environmental concerns. Research performed by Khorram et al. indicates a potential risk of weed outbreaks caused by the reduced effectiveness of herbicides in soil treated with biochar (Safaei Khorram et al., 2018). Furthermore, the stability of biochar presents another critical issue that requires careful monitoring. As biochar weathers and ultimately degrades in the soil, it releases absorbed contaminants, which may lead to soil toxicity owing to the dissolution of organic pollutants or leaching of heavy metals, potentially disrupting the microbial community in the soil (Lian & Xing, 2017).

9. Conclusions

This review offers a systematic overview of microalgal wastewater treatment alongside the properties and functions of biochar, illustrating how the latter can enhance the former process and thereby act as a vital connection between these two increasingly relevant methods. Microalgae-based wastewater treatment has proven to be an effective approach for managing industrial wastewater. Likewise, the diverse applications of biochar in waste removal, bioadsorption, energy sequestration, and soil fertility restoration, as well as its potential in other areas, have attracted considerable interest from researchers worldwide. The time has come to fully integrate these two mechanisms to achieve maximum efficiency in wastewater treatment and eliminate various pollutants in an environmentally sustainable and bioeconomical manner. The cycle of biochar-assisted microalgae-based wastewater treatment produces biomass that can be pyrolyzed to generate biochar, which can then be reused for wastewater treatment or applied for other purposes, thus offering a much-needed solution to today's

environmental challenges. Despite significant success at pilot or laboratory stages, the practical application of biochar at commercial scales continues to encounter numerous limitations, requiring further research to address these challenges.

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Declaration of competing interest

The authors would like to declare that they do not have any potential conflict of interest.

CRediT authorship contribution statement

Sayantani Ghosh: conceptualization writing—original draft, investigation; Sulagna Das: conceptualization writing—original draft, investigation; Avirup Panja: Editing of the draft, investigation; Alexei Solovchenko: writing—review and editing; Priyanka Jha: conceptualization writing—original draft, supervision, writing—review and editing.

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