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Algal Biochar: An Advance and Sustainable Method for Wastewater Treatment

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ABSTRACT
The thermochemical process of various biomass results in the formation of a common by-product known as biochar. Biochar can be defined as a pyrogenic black carbon material obtained through different thermochemical routes of carbon-rich biomass in an inert atmosphere. The physico-chemical properties of biochar greatly influence its multidisciplinary applications like carbon sequestration, enhancement of soil fertility, wastewater remediation etc. However, in recent times, emergence of third generation feedstocks i.e., algal biomass for production of biochar has gained significant importance due to its suitable and unique features. After the extraction of particular valuable products, the algal residues can further be transformed into biochar, biofuel and biogas by several thermochemical technologies like pyrolysis, hydrothermal liquefaction, torrefaction and hydrothermal carbonization. Hence, the present review discusses about characteristics differentiation between conventional and algal biochar, various thermochemical methods for production of biochar, working mechanism of biochar responsible behind adsorption of various contaminants and its implementation in wastewater remediation purposes. In addition, it further highlights some key challenges that still require investigation for a wide scope and commercialization in upcoming future.
Keywords: Biochar; algal biomass; thermochemical; wastewater remediation

1. INTRODUCTION

At present, water pollution is becoming a major matter of concern for our society as the several types of pollutants either organic or inorganic discharged from industrial wastewater or sewage are an actual ultimatum to the environment. For instance, the leaching of pollutants into groundwater from industrial water or sewage can lead to fatal health issues to our biological systems. In addition, the presence of heavy metals like cadmium, aluminium, iron, arsenic, manganese, zinc and lead can also cause consequential health problems if detected in drinking water at above permissible limits (Hesham et al., 2021). Therefore, to overcome such issues, emergence of cost-effective and environment friendly technologies is a matter of prior concern for scientists and technologists. On that account, various technologies like electroplating, reverse osmosis, ion exchange, membrane processes, precipitation, irradiation, cold plasma technology etc. has been employed (Inyang et al., 2016; Bisht et al., 2021; Gururani et al., 2021; Bhatnagar, 2019). However, most of these methods have high cost of operation and generate disposal issues due to production of large toxic sludge and hence are not acceptable for implementation on large scale. Contrastingly, adsorption is an extensively proposed method for the removal of various heavy metals. The reason behind this fact is its cost effectiveness, high efficiency, and large availability of different adsorbents. Nonetheless, existing studies have confirmed the possible potential of several bio sorbents in remediation of many toxic metals from wastewater. Therefore, there has been a growing interest in analysis of tremendous biomass feedstock due to their renewability, wide availability, cost effectiveness and environment friendly nature (Bordoloi et al., 2017).

Recently, several raw biomass feedstocks like safflower seeds, wood, bamboos, pine-wood, sawdust, rice straw and other lignocellulosic plant materials have been utilized for production of biochar but inventing reasonable biomaterials accompanied by sophisticated potential of biochar is still a major challenge in field of wastewater remediation (Singh et al., 2021). Now-a-days scientists are investigating sustainable and renewable techniques worldwide and with regards to this, aquatic biomass being an eco-friendly and rich source of energy has gained remarkable interest (Abbasi and Abbasi, 2010). In general, algal biomass is basically utilized for generation of renewable energy sources because cultivation of algal species on non-arable land possesses an active role in the phenomenon of carbon sequestration, minimizing emission of greenhouse gases and reveals great efficacy of photosynthesis in contrast with other lignocellulosic biomasses, thus appearing as an efficient and renewable source of energy for industrial applications (Sevda et al., 2019; Bordoloi et al., 2020). Apart form algal biochar, studies have also analysed promising potential of algal strains in sustainable bioremediation of heavy metal pollutants (Nanda et al., 2021). Furthermore, production of biochar from algae is a type of carbon-negative process that seizes around 87% of carbon thus helping in its long-term storage. Therefore, due to such reasons, algal biomass can be a sustainable and potential feedstock for production of beneficial biochar.

Biochar is defined as a pyrogenic black carbon rich solid material obtained through various biomass feedstocks and is regarded as one of the most promising bio sorbents that has attracted an increased interest in recent years because of its great adsorption capability with respect to different environmental contaminants (Goswami et al., 2016; Joshi et al., 2021a; Joshi et al., 2020; Joshi et al., 2021b). Moreover, for obtaining biochar form biomass residues, various thermochemical routes like pyrolysis, gasification, hydrothermal carbonization and hydrothermal liquefaction have been practised (Kumar et al., 2020a). Therefore, the present review highlights basic characteristics difference between conventional and algal biochar involving different thermochemical technologies employed for its production. In addition, the mechanism involved behind adsorption of different contaminants has also been discussed followed by its implementation in wastewater remediation. The review further enlists some key challenges that still require investigation for a better and large-scale commercialization of algal biochar

2. CHARACTERISTICS OF ALGAL BIOCHAR

The term "biochar" has been invented by uniting two phrases i.e., "bio" signifying "biomass" and "char" signifying "charcoal" (Singh et al., 2021). It can be described as "a pyrogenic solid and black carbon substance obtained through thermo-chemical conversion of numerous biomass feedstocks, including forest and agricultural residuals such as manure, wood, leaves etc. under an inert or oxygen limited atmosphere at temperature of below 900℃ and further having its direct association with terms like renewable fuel, soil amelioration and carbon sequestration" (Godlewska et al., 2017; Kambo and Dutta, 2015). In recent years, biochar because of its cost-effectiveness, environment-friendly nature and great potential for various contaminants remediation has received an increasing interest of scientists and researchers. This solid black carbon material is distinguished by spongy structure, huge specific surface area in combination with liberal functional groups such as carbonyl, carboxylic, hydroxyl, ester, pyridine-N, phenolic, quaternary-N and pyrrole-Na that lays down it as an appropriate adsorbent for wastewater remediation purposes and it further owns tremendous economic and environmental advantages. Nonetheless, the physical and chemical characteristics of biochar is greatly influenced by number of factors like processing conditions, biomass type etc. and algal biochar shows significant differences in physical and chemical characteristics as compared to those obtained from lignocellulosic biomass (Pathy et al., 2020).

For instance, biochar obtained from macroalgae or microalgae is substantially alkaline in nature which rises from 7.6–13.7 to 8.7–3.7 and it further reveals distinctive properties such as increased hydrogen, ash and nitrogen content, low carbon content and cation-exchange capacity, high heating value and electrical conductivity as compared to the biochar derived through lignocellulosic biomass. In addition, biochar yield from macroalgae and microalgae ranges from 8.1–62.4% and 20–63% followed by fixed carbon content of 1.7–27% and 4.9–29.10%, respectively. The proportion of volatile matters is around 44.80% and elements like Mn, Na, Zn, K, Cu, Fe, Ca are present in total ash content of algal biochar (Singh et al., 2021). Moreover, the size of biochar obtained from algal species ranges from 10 to 100μm along with an irregular porosity of 1μm and has low surface area as compared to that of lignocellulosic biochar (Pathy et al., 2020). Unlike other biochar derived from wood-based materials, algal biochar further exhibits very high exchangeable nutrient content mainly due to ash and nitrogen content (Roberts et al., 2015). Therefore, all these exclusive characteristics differentiate novel algal biochar form lignocellulosic biochar and increase its implementation on a wider scale. Table 1 further highlights some common differences in physical and chemical characteristics of conventional and algal biochar

Table 1: Characteristics comparison of algal and conventional biochar

S. No.	Properties	Algal biochar	Conventional biochar	References
1.	Carbon	16.41%	60-80%	Palanisamy et al., 2017; Kumar et al., 2020b
2.	Hydrogen	0.36%	2.42%	Palanisamy et al., 2017; Wijitkosum and Jiwnok, 2019
3.	Nitrogen	2.3%	1.37%	Palanisamy et al., 2017; Wijitkosum and Jiwnok, 2019
4.	Volatiles	44.80%	12.3-60.6%	Singh et al., 2021; Kumar et al., 2020b
5.	pH	High (7.6-13.7)	Low (3.5-11.3)	Singh et al., 2021; Kumar et al., 2020b
6.	Cation exchange capacity	High	Low	Chen et al., 2020
7.	Surface area	Low	High	Pathy et al., 2020; Masoumi et al., 2021
8.	Heating value	High	Low	Singh et al., 2021
9.	Porosity	Irregular	Porous	Pathy et al., 2020; Masoumi et al., 2021

3. THERMOCHEMICAL TECHNOLOGIES FOR ALGAL BIOCHAR PRODUCTION

An exponential increase in demand of algal biochar for various applications has pushed scientists forward for inventing advanced technologies for converting algal biomass into suitable and sustainable biochar. With respect to this, thermochemical conversion is the commonly known practised route for attaining the desired purpose and it basically involves methods like pyrolysis, torrefaction, hydrothermal carbonization and hydrothermal liquefaction. However, the selection of specific technique is highly affected by numerous factors like desired properties of final product, type of feedstock (either dry or wet), etc. and yield of desired product further varies with the type of method employed. In addition, the process conditions like temperature, heating rate, residence time etc. should also be optimum as they greatly influence the chemical and physical states of final product.

Pyrolysis is an often-investigated thermochemical route for converting various feedstock biomasses into biochar due to its yield, speed, operating conditions and simplicity. Current studies have also mentioned that pyrolysis is further related with production of flexible products i.e., liquid, that are comparatively easy to handle in contrast with other thermochemical conversion technologies (Sekar et al., 2021). Moreover, pyrolysis is defined as the thermochemical decomposition method in which biomass is exposed to elevated temperature of about 300–650℃ in an oxygen free atmosphere. It basically results in the generation of three major products namely, biochar, bio-oil and non-condensable gases and is further categorized into flash, fast, slow, hydrolytic, catalytic and microwave assisted pyrolysis on the basis of operating parameters. However, in among all theses, slow pyrolysis led to maximum solid yield of 25–35%, hence is regarded as major process for biochar production (Kambo and Dutta, 2015). Similarly, hydrothermal liquefaction is also a type of thermochemical route which includes exposure of biomass feedstock to moderate temperature of around 200-374°C under a high pressure of 5–20 MPa in an inert environment and leads to generation of biochar, biocrude oil, gaseous product and aqueous phase. Furthermore, this process involves about more than 70% of carbon conversion from feedstock as biochar or bio-oil and the char yield ranges from 2 to 70% (Ponnusamy et al., 2020).

Hydrothermal carbonization is also another advanced thermochemical route that has gained attention for hydro-char production due to its cheapness and eco-friendly nature. It involves transformation of carbohydrate in biomass into solid and carbon-rich product known as hydro-char at temperature of around 180-260℃. Additionally, this specific method occurs in self-generated pressure of around <10 bar in water as solvent and results in maximum yield of product by using short time period and low energy expense. Hence, it offers a benefit to potentially use residue of algal biomass therefore converting it into valuable products (Yu et al., 2017). Moreover, torrefaction is defined as a thermochemical process carried out at temperature of around 200–300 °C in atmospheric pressure under an anaerobic atmosphere. In this process, a moderately degraded solid biomass with maximum carbon content known as torrefied char is produced. This method involves thermal pre-treatment of biomass leading to removal of volatiles by various decomposition reactions thus upgrading quality of biomass. It has been stated that solid yield of around 51.3–93.9% can be obtained in residue of microalgae after torrefaction at temperature of 200–300 °C along with residence time between 15 min to 1h (Singh et al., 2021). Fig 1 depicts different thermochemical routes along with their reaction conditions for conversion of algal biomass into biochar.

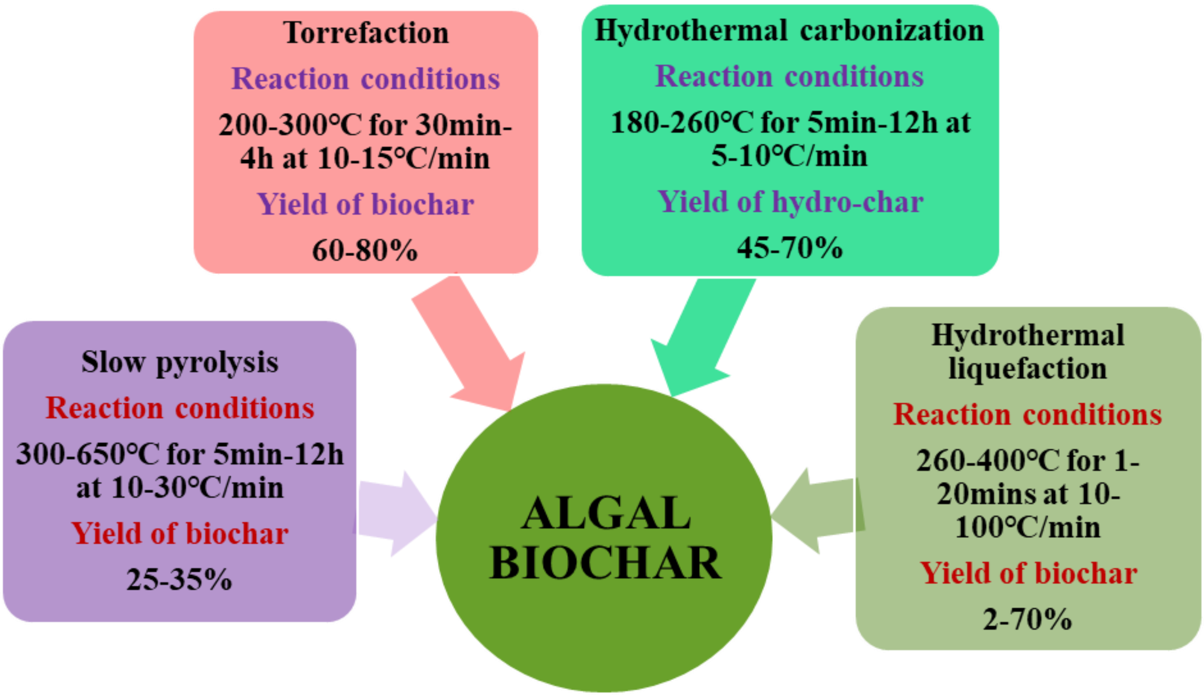

Fig 1. Thermochemical technologies for production of biochar from algal biomass

4. WORKING MECHANISM AND IMPLEMENTATION OF BIOCHAR FOR WASTEWATER REMEDIATION

Presently, water environment is degrading on a rapid rate due to rising economic development and related anthropogenic activities. Different type of pollutants such as nutrients, organic matter and heavy metals are constantly discharged into water bodies either by wastewater effluent or stormwater runoff hence causing its degradation which holds major threats to environment health and water security. Therefore, to deal with these, implementation of cost-effective technologies for treatment is a prior necessity (Guo et al., 2021). On that account, technologies like flocculation, electrochemical methods, coagulation, nanofiltration, membrane-related processes, ion exchange, ultrafiltration, precipitation etc. has been employed but are further associated with various flaws such as high energy consumption, generation of toxic sludge in large quantity and utilization of costly chemicals is a necessity in such methods (Singh et al., 2021). However, adsorption can be a novel and sustainable finding for overcoming such flaws as it is an economic process offering ease of operation and reveals high removal efficiency even at lower concentrations (Zhang et al., 2020). During adsorption process there is direct transfer of solutes into the unoccupied active binding surfaces (external) of biochar and allows diffusion of ions into the pores (internal) until there is saturation of equilibrium. Nonetheless, the adsorption process has been efficiently investigated as a cost-effective and easy method for removing various pollutants from wastewater or other aqueous solutions (Ahmad et al., 2013).

For attaining the desired purpose, algal biochar can be a successful adsorbent as algal cell wall is mainly composed of lipids, sugars, cellulose, proteins etc. which constitutes phenolic, carboxylic, ketonic, hydroxyl, aldehydic and other similar polar functional groups that can provide efficient adsorption binding sites and when biochar interacts with pollutants, the relation between pollutants and uncarbonized parts is associated to distribution whereas the carbonized part is associated to surface adsorption (Nautiyal et al., 2016; Dai et al., 2020). Moreover, existing studies have also investigated on the promising potential of algal biochar as a sustainable adsorbent for instance, Son et al., (2018) stated that as compared to biochar obtained from conventional pinewood sawdust, algal-based magnetic biochar revealed high efficiency in removing heavy metals and concluded magnetic algal biochar as an efficient tool for removal of pollutants. Likewise, Michalak et al., (2019) analysed that biochar obtained through Cladophora glomerata can be used as an efficient, cheap and renewable adsorbent for remediation of several metal ions from aqueous solutions or wastewater and excellent removal potential of 89.9%, 97.1% and 93.7% was observed for Cr(III), Cu(II) and Zn(II) ions, respectively. Utilization of various algal based biochar for wastewater remediation is given in Table 2.

Table 2: Utilization of algal biochar for wastewater remediation

S. No.	Algal species used	Target organic or metal pollutant	Reference
1.	*Rhizoclonium riparium*	U(VI)	Wang et al., 2021
2.	*Ascophyllum nodosum*	Ciprofloxacin	Nguyen et al., 2021
3.	*Spirulina*	Methylene blue	Leng et al., 2015
4.	*Chlorella* sp.	Methylene blue and Congo red dye	Yu et al., 2021
5.	Blue green microalgae	Tetracycline	Peng et al., 2014
6.	*Scenedesmus quadricauda*	Cr(VI)	Daneshvar et al., 2019

U-Uranium; Cr-Chromium

5. FUTURE CHALLENGES AND SCOPE

An accelerated interest in valuable applications of biochar has generated interdisciplinary field for engineering and scientific research. Algal biochar can potentially be utilized in several areas like remediation of soil environment, energy storage, carbon sequestration, enhancement of soil fertility etc. and moreover, apart from these, it has been effectively utilized as a sorbent for removing various contaminants from wastewater including both inorganic as well as organic due to its special structure and large surface area. However, still there are many shortcomings that require further analysis and investigation so that the application of algal biochar as a bio sorbent for wastewater remediation can be commercialized successfully.

For instance, the cost effectiveness of this particular method and the reality that wastewater constitutes numerous impurities can obstruct the process because algal broth harvested from wastewater can constitutes several organic pollutants, heavy metals or symbiotic bacteria that may hysterically affect its successive applications and the elements of algae, like proteins can also differ crucially in wastewater thus possessing considerable influence on application and preparation of biochar products (Yu et al., 2017; Chen et al., 2020). In addition, the alleviation of number of chemicals utilized for biochar activation, means its optimization: altering agent ratio consequently reducing the production costs can also be regarded as a key challenge for future optimization of biochar. Other than this, the involvement of strong oxidants such as alkalis and acids for alteration at the time of biochar production, enforce possibility of secondary pollution to our environment. Therefore, organic acids such as citric acid, acetic acid or tartaric acid can be utilized as modifiers for producing more greener and cleaner biochar (Sun et al., 2015). Furthermore, defined relationships along with related working mechanisms must be prospected to efficiently prepare biochar, involving differences in sources of raw materials, pyrolysis technologies and activation methods. As discussed before, studies have also stated that persistence of compounds like free radicals, small-molecular organic components involving PAHs, polychlorinated biphenyls, pesticides, polychlorinated dibenzo-p-furans and dioxins, linear alkylbenzene sulfonates etc. can be harmful for environment. It is also necessary to balance and explore the advantages and toxicity of algal biochar in environment. Hence, little efforts are still required to identify the unexpected effect of algal biochar on our environment involving consumption of chemicals, energy or materials related with release into water, soil and air. Additionally, analysis of emerging technologies is also of utmost importance at initial stage. If not, advantages of the technology might be restricted while moving towards large scale application (Chen et al., 2020). Nonetheless, the concept of algal biochar can come up with a main stream for revenue generation shortly by energy production, carbon sequestration, utilization as bio sorbent including soil amendment and further development in the field of algal biochar will provide more environment sustainability in upcoming future.

6. CONCLUSION

In recent years, the application of algal based biochar for wastewater remediation purposes has gained an increased interest of scientists and researchers due to its beneficial characteristics and sustainability. In this review, characteristics differentiation between conventional and algal biochar, different thermochemical routes for biochar production and its implementation for wastewater remediation purposes along with working mechanism have been presented. This manuscript also highlights that the promising potential of algal based biochar for removing various contaminants from wastewater or aqueous solutions cannot be challenged. However, for an increased sustainable utilization and suitable applications, the properties of biochar demand further tailoring and enhancement because the more detailed study and understanding of biochar's structure and characteristics will be helpful in realizing its effectiveness as bio sorbent.

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