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Exploring the evolution, trends and scope of microalgal biochar through scientometrics

Nageshwari Krishnamoorthy, Abhijeet Pathy, Aastha Kapoor, Balasubramanian Paramasivan *

Department of Biotechnology & Medical Engineering, National Institute of Technology Rourkela, Odisha 769008, India

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ABSTRACT

The recent surge in biorefinery facet and prerequisite management of colossal amount of algal residues after extraction of value-added products, has provoked researchers to focus on the state-of-the-art material, microalgal biochar. This manuscript is a scientometric research of microalgal biochar conducted between 2009 and 2021, using CiteSpace 5.8.R1. Ten significant scientometric attributes namely, annual publication outcome, co-authorship network, co-author country network, author co-citation network, document co-citation network, journal co-citation network, co-author institution network, research grant analysis, subject category analysis and co-occurring authors keywords were investigated to identify the progression and advancements in microalgal biochar research. China, USA, and India are the leading contributors to this field with several established government research grants to promote this discipline. Algal Research is one of the top-echelon journals contributing to this field in terms of publication outcomes. The research on microalgal biochar has escalated in the last decade with focus on various production techniques, process optimization and enormous applications in medical and energy sectors. Yet, more focus on scale-up of the technology, life cycle and technoeconomic analysis, and thorough understanding of the effect of influential parameters is necessary to commercialize and engineer the biochar. Through a detailed examination of co-occurring keywords, this article attempts to recognize the frontiers, research gaps and emerging aspects in this domain.

1. Introduction

Owing to the rapid industrialization and population boom of past two centuries, there has been mounting pressure on the available natural resources like land, water and air. Coupled with explosive rise in levels of pollution largely due to anthropogenic activities; there has been increasing energy consumption and demand. While conventional sources of energy like coal and petroleum are widely used, the reserves of the same are depleting rapidly. Besides, their use has been continually contributing to air pollution, water pollution and effects as serious as the global warming. The world is now looking up to unconventional sources of energy like solar, wind and hydropower but these are saddled by drawbacks like installation cost and maintenance upkeep, strict wind speed requirements, availability of large area and purported ecological and social disbalance respectively [1]. Such constraints and demands have lately shifted the spotlight on the use of sustainable alternatives for coal such as biochar, hydrochar etc.

Biochar is a carbonaceous porous solid produced through controlled heating between the ranges of 300–800 °C via different techniques like pyrolysis, hydrothermal carbonization (HTC), torrefaction etc. [2–4]. Amongst these techniques, conventional pyrolysis and its newer modifications like microwave assisted pyrolysis are shown to produce lower yield of char with increasing temperature while techniques like HTC and torrefaction offer advantages like reduced operational costs and enhanced properties like higher calorific value (as in case on hydrochar) [5,6].

While trees, agricultural residues, waste residues, energy providing perennial crops like maize, rapeseed etc. typically produce greater amount of various biofuels (liquid, gas and solid) with high calorific values, the need for land, maintenance and elaborate extraction and processing vastly adds to the cost of the biofuel produced [7]. Counted amongst primary sources of biomass, algae seem to have intrigued the interest of researchers and industry alike with its high content of lipids, proteins, carbohydrates and other secondary metabolites like pigments [7–9]. Algae is regarded as a third generation of biofuels that has unique capacity to utilize carbon dioxide from atmosphere and solar energy for meeting the growing demands of heat, power and fuel [10]. Microscopic photosynthetic units abundant in aquatic ecosystem as varied as

* Corresponding author.
E-mail address: biobala@nitrkl.ac.in (B. Paramasivan).

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freshwater and saline, algae are broadly classified into microalgae and macroalgae based on their size and into Chlorophyceae, Phyophyceae and Rhodophyceae based on their pigment.

Besides the algae's ability to sequester carbon dioxide, its high environmental tolerance, ease of growth, high growth rate, maintenance and extraction of biomass, comparatively lower costs involved also make it a very lucrative source of energy generation [11–13]. Upon thermal treatment of algal biomass, it is seen that dehydration is followed by decomposition of carbohydrates into anhydro sugars and furfurals, proteins into amines and some liquid olefins and lipids into aliphatic and aromatic hydrocarbons (in that order) as the temperature is increased from 25 °C to over 750 °C. The main products of such thermal treatment of biomass are bio-oil, syngas and residual biochar [14,15]. While bio-diesel and syngas from algae has been intensively researched, the usage of the residual biomass (containing entrapped carbohydrates and proteins) via various thermochemical techniques is an upcoming field of interest due to the versatility of the products [16,17].

Properties of biochar like carbon content, heating value, surface area, zeta potential, O/C, H/C, N/C ratios etc. are determined primarily by the parent biomass composition and the underlying process parameters like temperature, residence time and heating rate of the thermal treatment technique undertaken [2,3,18]. The algal biochar surface is shown to have been decorated with basic functional groups which contribute to high cation exchange capacity and high pH, both of which provide it an edge over lignocellulosic derived biochar [19]. Further, the presence of aromatic structure, free electrons of phenolic and amine groups, presence of trace elements (e.g., Ca, Na, K, P, Mg etc.), also add to the unique adsorbent properties of algal biochar [20]. As a result, algal biochar potentially finds use in applications like organic metal ion, pharmaceuticals, and inorganic pollutants removal from environment and wastewater, soil amelioration, supercapacitor, coal fuel replacement, struvite precipitation, CO_2 sequestration etc. [21,22]. Lately, process optimization and genetic engineering efforts have been initiated in the direction of yield and property enhancement to obtain algal biochar that not only caters to specific demands but also fits well within the economically feasible industrial arena [23]. Such advances in the field can be efficiently monitored through state-of-the-art techniques like scientometric analysis.

Scientometric analysis is an advanced bibliometric analysis, used to objectively map knowledge of a particular field through available scientific documents. The quantity and quality of the published articles are taken into consideration to evaluate the progress, research gaps and scopes of a given field of research [24]. Several articles in the recent decade have undertaken scientometric analysis to study the evolution of various fields through various scientometric attributes and visual patterns obtained from the analysis [25,26]. The aim of this paper is to conduct a scientometric analysis for the field of microalgal biochar from the year 2009 to 2021. CiteSpace, a java-based software was used to analyze the bibliometric datasets in our field of interest and visualize in the form of network patterns, trends and scientometric parameters. Distinct aspects of datasets such as annual publication rate, contribution from authors, countries, institutions and journals, keyword analysis, co-citation analysis of documents and authors, research grant analysis and subject category analysis were studied through various node types in the software. The visual and parametric outcomes will aid in comprehending the development of the research field, the paradigm shifts, interdisciplinary advancements, research gaps and various scientific frontiers.

2. Methodology

2.1. Data collection and processing

The data published on microalgal biochar till 20 August 2021 were obtained from well-known indexed databases, such as Web of Science® (WoS) and Scopus®. These repositories are considered highly reliable for their accurate bibliographic and citation data. They comprise of a huge dataset of STM (Scientific, Technical and Medical) journals, which can be retrieved and accessed in various file formats. In spite of enormous research carried out on biochar, the prime search topic was limited to microalgal biochar to gain deeper insights on this emerging field. After a series of iterations and keyword combinations, a set of keywords including “microalgae AND biochar” were used to search the data relevant to thermochemical conversion of microalgal biomass for various applications. The data was segregated such that the keywords appeared in either title, keywords or abstract and all the research conducted till date on microalgal biochar (2009–2021) to better comprehend the evolution, recent trends and scope in this research.

2.2. Bibliometric analysis

The datasets were acquired in RIS (Research Information Systems) and plain text formats from Scopus ® and WoS ®, respectively and fed in to CiteSpace 5.8.R1, a Java-based software used to visualize patterns and trends using bibliometric references. The software uses pathfinder network scaling (sparsification technique to extract important structures of any graph/network) and co-citation analysis theory (similarity measure of documents that are cited together) to segregate the data into distinct disciplines of research commonality. Selection conditions like time slicing (range and years per slice), text processing (term sources like title, abstract etc. and term types), node types (author, reference, country etc.), pruning and visualizations were pre-defined and the data was analyzed for ten main scientometric attributes such as annual publication outcome and document type, network of co-authors' countries, co-authorship network, author co-citation network, document co-citation network, network of co-occurring author keywords, network of co-authors' institutions, research grant analysis, journal co-citation network and co-occurring subject categories.

2.3. Data interpretation through scientometrics

Scientometrics including citation count (CC), citation frequency (CF), citation burst (CB), sigma, betweenness centrality (BC), clustering, modularity silhouette value can be used to analyze the network provided by the software. A brief definition or description of these node and cluster characteristics are shown in Fig. 1a. CC, CF, CB, BC and sigma are node characteristics in a network, whereas clustering, modularity and silhouette value indicate cluster characteristics. Higher value of these metrics denotes high strategic importance in the network. Visualization parameters such as node size, distance between the node and thickness of links can help in better understanding of the relationship within an entity. Node size, label size and thickness of the link directly correspond to the amount of contribution of collaboration made by or between the entities. However, the distance between the nodes is inversely proportional to the research similarity or collaboration between the nodes. Interpretation of the network can provide information on the growing research interest, knowledge gaps, emerging trends and way forward in struvite research [27,28].

3. Results and discussion

3.1. Annual publication output analysis

As per the search results from the databases, 172 documents from Scopus ® and 213 documents from WoS ® published on microalgal biochar were obtained. All the documents were converted to similar file formats and duplicates were removed. At the end, 363 unique documents of microalgal biochar were finalized for further analysis. It was found that the thermochemical properties of microalgae were first explored in the early 2000's, where the authors adapted slow pyrolysis conditions for conversion of microalgal biomass into several products

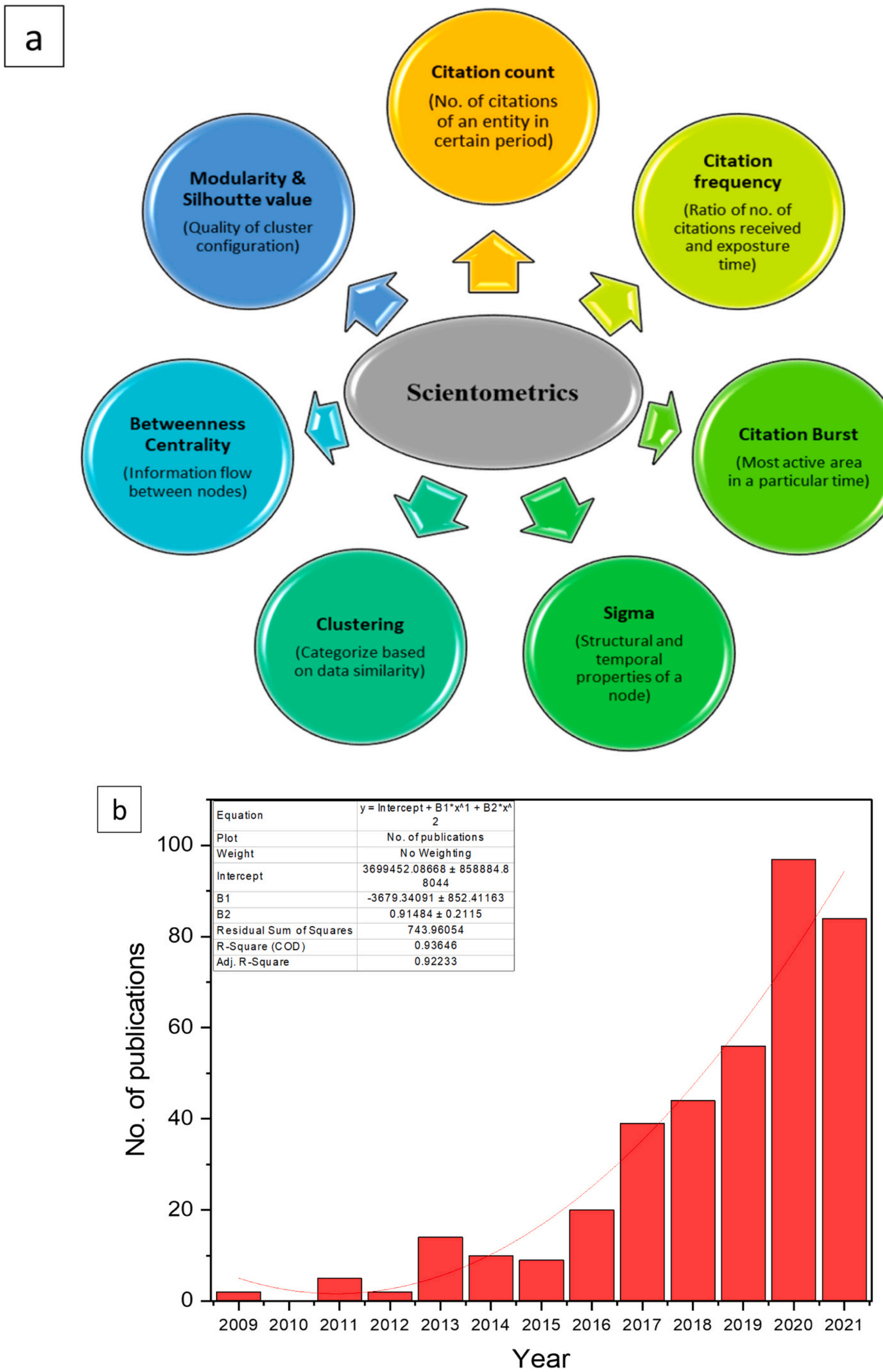

Fig. 1. a) Scientometric parameters used for analysis in CiteSpace 5.8.R1 b) Annual publication count of microalgal biochar (keyword: microalgae AND biochar) between 2009 and 2021.

like biochar, syngas, and bio-oil. The yield of biochar obtained was found to be greater than 33 % of the total weight of the sample. Since then, the interest in this field of study grew which is evident from the increase in publication rate through the years. Excluding the initial qualms, the focus on microalgal biochar has escalated with a leap from the year, 2013. A slight decrease in the publication count of 2021 can be observed as the data collection for the scientometric study was performed on 20 August 2021 (Fig. 1b). Most of the published documents were research articles (93.4 %), followed by review articles, proceedings papers, book chapters and others.

3.2. *Co-authorship network and citation analysis*

The co-authorship network provides information on both directed and undirected connections between authors around the world. Around 328 authors have collaborated (links: 546) and contributed to microalgal biochar research with WH Chen from Taiwan possessing the highest number of publications (18 documents). One of the review papers, “Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): A state-of-the-art review” published in collaboration with Quang-VuBach from Vietnam in Bioresource Technology journal has received a citation count of 142. The paper mainly focused on common kinetic models for predicting the thermal decomposition characteristics of microalgae required for designing of pyrolyzer and process optimization. WH Chen remains as a pivotal point between several research groups that actively contribute to this area of research in microalgal biochar. His collaboration with authors, V Ashokkumar and G Kumar mainly involved integrated algal biorefinery aspects of biodiesel, bioenergy and biochar production along with metallic iron conversion. On the other hand, research groups of JS Chang and PL Show have worked on adsorption of dyes and phenolic compounds like p-nitropheneol on microalgal reside derived biochar and analyzing the mechanisms behind adsorption. The second-highest contributing author, SH Ho from China has 12 publications and has concentrated on adsorption of heavy metals like cadmium on microalgal biochar.

Apart from these established collaborations, there are several independent research groups who have focused on novel aspects of microalgal biochar research and secured high impact. Joshu Chang and his team have experimented on combining wet torrefaction and microwave-assisted heating for production of biochar from *Chlorella vulgaris* ESP-31 and *Chlorella* sp. GD and reducing sugar for bioethanol production. A Pugazhendhi, T Mathimani and B Zhang have teamed up to shed light on activation strategies and pre-treatment techniques to utilize microalgal biochar as effective catalysts in several applications. In addition, they have focused on catalyzing bio-oil production through hydrothermal liquefaction (HTL) using biochar [29]. Similarly, research group of P. Balasubramanian have developed a machine learning algorithm using eXtreme Gradient Boosting (XGB) to predict algal biochar yield with significant process parameters along with proximate and ultimate analysis features [30].

Cluster analysis showed that only one major cluster named "microalgae *Nannochloropsis oceanica*" (cluster #0) was formed with a modularity (Q) of 0.9396 and weighted mean silhouette score of 1. The cluster name is determined by the document possessing strongest citation burst. Both the metrics indicate the structural integrity and quality of cluster configuration and changes when there is an inclusion of significant research into the cluster. Fig. 2 also shows the links or collaboration between the authors in the cluster and their period of contribution.

3.3. Network of co-authors' countries analysis

Scientometric analysis with country as the node type generates a network of co-authors' countries that have worked on microalgal biochar. Fig. 3 gives the cluster of countries where the size of the node and country name correspond to the amount of input made to this research field. A total of 76 countries around the world have contributed to this research with 155 established links or collaborations. China (Peoples R China) tops the list with 95 published documents followed by USA (70 documents) and India (41 documents). Australia secures the top rank by bursts with a value of 5.62. In case of sigma (ranges from 0 to 1), USA has the highest value of 0.58, implying the importance of temporal and structural properties of this node in the cluster.

The purple dots present at the conjunctions away from the main cluster are turning points (pointed black arrows) that denote the transformation of research from existing methodologies to exciting, novel ventures (Fig. 3). For instance, England has stood out from current ideologies by focusing on thermochemical conversion techniques other than pyrolysis such as HTC, HTL and supercritical water gasification (SCWG) for pre-treatment of microalgal biomass to produce biochar, bio-oil, and syngas products. From this point, countries like Columbia and Mexico have started to work on these aspects of microalgal biomass conversion.

Cluster analysis showed that the largest cluster, hydrothermal liquefaction (cluster #0) includes contribution from 13 countries with a silhouette value of 0.675. The most active citer to his cluster is Hyungseok Nam from Korea, whose work involves algal biomass conversion through HTL and pyrolysis to study if the biochemical composition is suitable for use as a fuel. The second-largest cluster, hydrochar sorption (cluster #1) comprises of 9 countries which have explored this research area and contains with a silhouette value of 0.832. It is also noteworthy that the names of these clusters denote some of the emerging areas of microalgal biochar research.

3.4. Document co-citation analysis

Document co-citation analysis in CiteSpace reveals documents which have received the highest citation in any field of study. Though not directly related to microalgal biochar, "The technological and economic

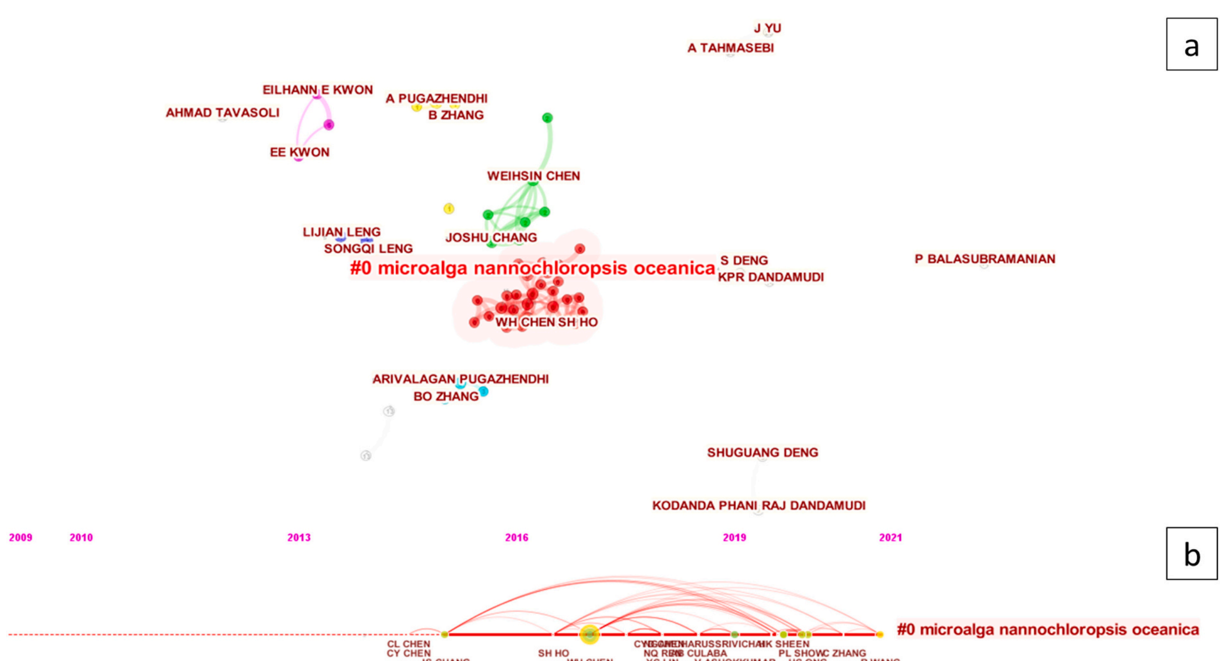

Fig. 2. a) Cluster view b) timeline and cluster analysis of co-authorship analysis network of microalgal biochar research (2009–2021).

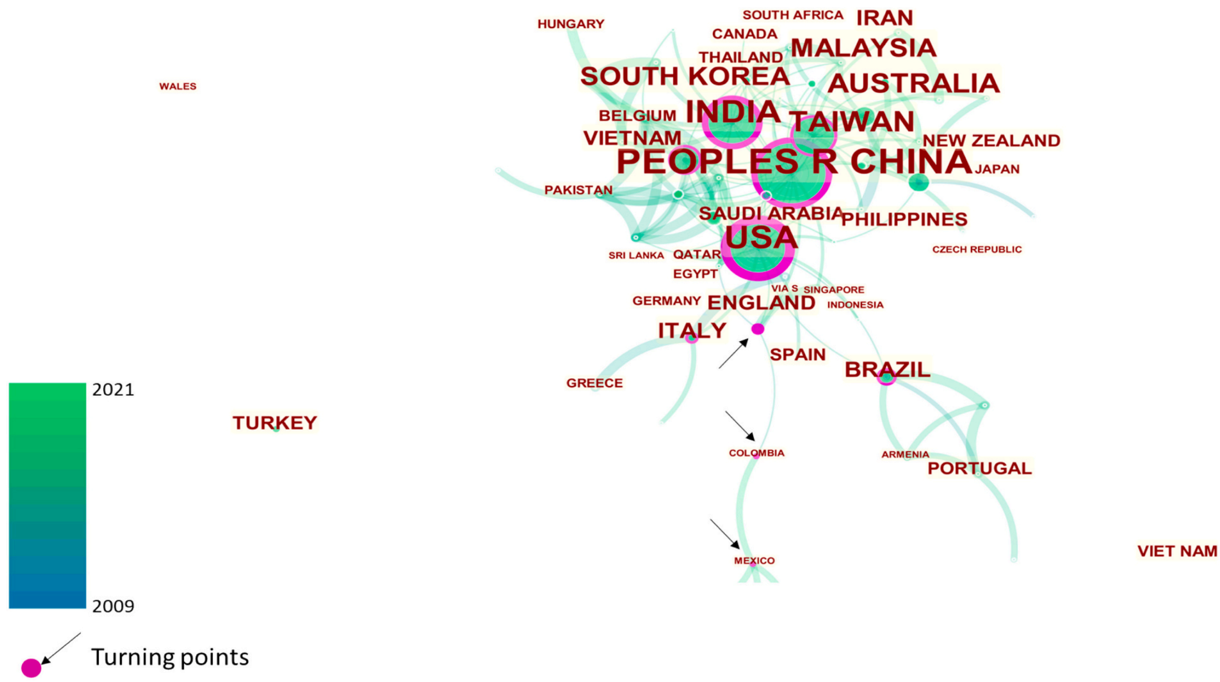

Fig. 3. Cluster view of co-author country analysis with significant turning points in microalgal biochar research between 2009 and 2021.

prospects for CO_2 utilization and removal" published by Hepburn and his group in Nature journal, has the highest citation count of 213. This article discusses utilization of microalgae-based products and biochar as efficient means of CO_2 sequestration from atmosphere and soil carbon sequestration, respectively. This is followed by article "Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production" published by Kaige Wang and his team in Bioresource Technology journal with a count of 188. Table 1 gives the list of top 15 most cited articles in microalgal biochar research. It can be seen from the cluster view that the documents were distinctly segregated based on its citing articles. This shows that the articles vary in their primary focus, covering various aspects of this field.

3.5. Network of co-author's institutions

Scientometric analysis of the institute contribution to certain research will be helpful for young researchers who are seeking opportunities to pursue a career in this field of interest. Analysis for the contribution of various institutions to microlalgal biochar research was performed using node type 'institution' in CiteSpace. The top 5 institutions contributing to this research were found to be (1) National Cheng Kung University, Taiwan (15 documents), (2) Tunghai University, Taiwan (8 documents), (3) National Chin-Yi University of Technology, Taiwan (7 documents), (4) Chinese Academy of Sciences, China (7 documents), (5) Arizona State University, USA (8 documents). It is noteworthy that most of the institutes contributing to this emerging research are public universities. The universities in Taiwan seem to be major contributors whose interest in this field grew recently after 2015. It can be understood from the pennant diagram that Taiwan universities have a well-established network amongst them and between renowned universities around the world. Also, Fig. 4a portrays the relevance and specificity of the query. For instance, the research aspects of universities

Table 1
List of top 10 most cited articles that published in microalgal biochar research from the year 2009–2021.

Sl. no.	Title of the paper	Authors & year of publication	Published journal	Citation count	Centrality
1	The technological and economic prospects for CO_2 utilization and removal	Hepburn C et al., 2019	Nature	213	49
2	Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production	Wang K et al., 2013	Bioresource Technology	188	13
3	Thermal characterization of microalgae under slow pyrolysis conditions	Grierson S et al., 2009	Journal of Analytical and Applied Pyrolysis	168	1
4	Biochar properties regarding to contaminants content and ecotoxicological assessment	Oleszczuk P et al., 2013	Journal of hazardous materials	159	13
5	Lignocellulosic biorefinery as a model for sustainable development of biofuels and value added products	Bhowmick et al., 2018	Bioresource Technology	159	43
6	ZeroWasteWater: short-cycling of wastewater resources for sustainable cities of the future	Verstraete et al., 2011	International Journal of Sustainable Development & World Ecology	151	4
7	Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): a state-of-the-art review	Bach et al., 2017	Bioresource Technology	142	32
8	Comparative study on pyrolysis of lignocellulosic and algal biomass using a thermogravimetric and a fixed-bed reactor	Yuan et al., 2015	Bioresource Technology	141	8
9	Promising pathway for algal biofuels through wastewater cultivation and hydrothermal conversion	Roberts et al., 2013	Energy & Fuels	96	13
10	Fast microwave-assisted pyrolysis of microalgae using microwave absorbent and HZSM-5 catalyst	Borges et al., 2014	Bioresource Technology	94	9

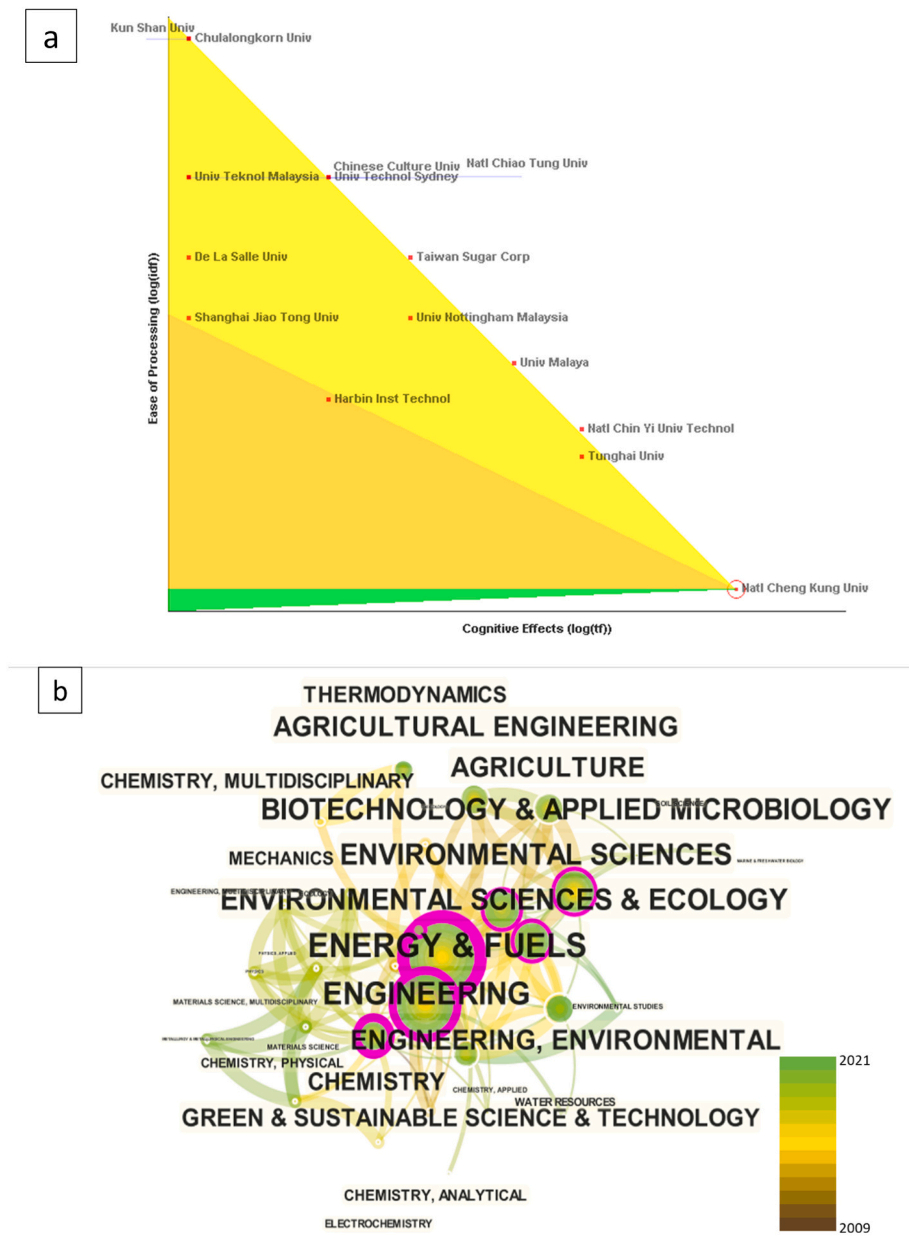

Fig. 4. a) Pennant diagram showing the collaboration of National Cheng Kung University, Taiwan with other institutes worldwide b) Cluster view of co-occurring subject category analysis of microalgal biochar (2009–2021).

present in the mid portion of the diagram are more relevant and specific to the seed (National Cheng Kung) university, which is determined on the basis of co-citation.

3.6. *Research grant analysis*

Research grants play a substantial role in research by motivating and boosting the interests of scientists to perform significant study in a particular field. Scientometric analysis was performed to make researchers aware of the common research grants that fund studies related to microalgal biochar. The results showed that National Natural Science Foundation of China (NSFC) sponsored projects on the context, production of various value-added microalgal products through pyrolysis have secured the highest number of publications (37 documents) from 2009 to 2021. This organization is an affiliated to State Council of China, the chief administrative authority of the People's Republic of China, which is followed by Ministry of Science and Technology Taiwan, the Government Ministry of Republic of China (8 documents). It is noteworthy to mention that most of the grants obtained are from government funding organizations than private. In addition, it promotes international collaboration between researchers working in similar areas of interest. It is an affirmative sign and encouraging fact that the importance of carry forwarding the research of microalgal biochar is acknowledged by various government establishments around the world.

3.7. *Co-occurring subject category analysis*

Subject category analysis of a particular research area gives a broad perspective on what sectors the research is mainly focused in. In case of microalgal biochar, most of the research aspects were fixated around "Energy & Fuels" (113 documents), followed by "Engineering" (83 documents) and "Environmental Sciences & Ecology" (54 documents). Fig. 4b shows the cluster view of the subject categories involved in microalgal biochar research. In energy & fuels category, the authors mainly considered microalgal pyrolysis as a process of producing sustainable fuel alternative. Biochar, bio-oil and syngas produced were analyzed for suitability of characteristics like heat of combustion and utilization as fuel. In engineering perspective, aspects like process parameter optimization and designing of catalysts to extract specific value-added products from microalgae like polysaccharides, proteins and pigments were focused. Researchers working in environmental sciences & ecology sector give importance to microalgal culturing to recycle nutrients and mitigate greenhouse gas emissions. Also, the application involves direct use of microalgal biochar as fertilizers, soil amendments and adsorption of pollutants like dyes, antibiotics and heavy metals. In recent years, categories like 'Electrochemistry' (4 documents) and "Water Resources" (4 documents) are emerging. Electrochemistry involved testing the potential of microalgal char as supercapacitors or energy storing devices, which is emerging as a high value-added application. The high specific surface area, electrical conductivity, and mechanical stability of microalgal biochar enhances its double-layer capacitance by absorbing electrolyte ions compared to biochar-based electrodes produced from lignocellulosic biomasses [31]. While the Water Resources category focused on the treatment of various nutrient-rich wastewaters using microalgal biochar.

3.8. *Journal contribution analysis*

Analysis of journal co-citation network in CiteSpace provided insights on the journals which have contributed to microalgal biochar research since its occurrence. As per the citation count, "Bioresource Technology" secures the top rank with 50 articles published on pyrolysis of microalgae for production of value-added products. Following this, journals "Science of the Total Environment" and "Fuel" have published 14 documents each. "Algal Research" is one of the top 10 journals contributing to microalgal biochar research with 'Life cycle assessment of a microalgae biomass cultivation, bio-oil extraction and pyrolysis processing regime' as its most cited article'. This analysis will help researchers working on algal char to gain an overall idea on the journals that focus on their area of interest. Table 2 gives the list of top 10 journals that have contributed to microalgal biochar from 2009 to 2021.

Table 2
List of top 10 journals that have most contributed to microalgal biochar research from the year 2009–2021.

Rank	Journal name	No. of articles published	Most cited article
1	Bioresource Technology	50	Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production
2	Science of the Total Environment	14	Algae as potential feedstock for the production of biofuels and value-added products: Opportunities and challenges
3	Fuel	14	Concomitant extraction of bio-oil and value added polysaccharides from *Chlorella sorokiniana* using a unique sequential hydrothermal extraction technology
4	Energy	11	Catalytic deoxygenation co-pyrolysis of bamboo wastes and microalgae with biochar catalyst
5	Energy Conversion and Management	11	Microalgae from wastewater treatment to biochar - Feedstock preparation and conversion technologies
6	Journal of Cleaner Production	8	Biochar, a potential hydroponic growth substrate, enhances the nutritional status and growth of leafy vegetables
7	Energy & Fuels	7	Promising Pathway for Algal Biofuels through Wastewater Cultivation and Hydrothermal Conversion
8	Journal of Analytical and Applied Pyrolysis	7	Thermal characterization of microalgae under slow pyrolysis conditions
9	Biomass Conversion and Biorefinery	6	Biochar production from sewage sludge and microalgae mixtures: properties, sustainability and possible role in circular economy
10	Algal Research	5	Life cycle assessment of a microalgae biomass cultivation, bio-oil extraction and pyrolysis processing regime

3.9. *Co-occurring author keyword analysis*

Co-occurring keyword analysis is an alternative strategy to get to know about multiple aspects of any research field such as evolution, knowledge gaps and future prospects. Research on microalgal biochar since its advent was analyzed using several scientometric attributes. Other than microalgae and biochar (keywords used in search), 'biomass' and 'pyrolysis' have the highest citation counts of 143 and 122, respectively. The top four keywords with strongest citation bursts are 'lipid', 'water', 'refining' and 'chemical composition' with strengths 3.56, 3.27, 2.94 and 2.74, respectively. These keywords have also secured high sigma values of 1.03, 1.03, 1.04 and 1.01. In terms of centrality, keywords 'microalga' (0.12), 'biofuel' (0.11) and 'carbon' (0.11) top the list. Clustering analysis revealed the list of clusters based on title, author, keyword and category. The largest five clusters were labelled enhancing copper ion (#0), domestic wastewater (#1), thermal characterization (#2), fixed-bed reactor (#3) and heavy metal ion (#4) (Fig. 5). These are the aspects in which most of the research on microalgal biochar has been carried out from 2009 to 2021. The names of the clusters are given on the basis of strongest citation burst received by the article.

The largest cluster, #0 consisted of articles focusing on HTL, HTC, nitrogen transformation and adsorption behavior studies for several acid-basic dyes and heavy metals using microalgal biochar. Arun et al. [32] enriched the bio-oil produced as a result of HTL of *Chlorella vulgaris* with liquid-liquid extraction for use as transportation fuel. In addition, the biochar synthesized was used as an adsorbent to recover nutrients and remove organic pollutants from wastewater. Another innovative study was carried out by Chabi et al. [33], wherein the authors used electrocoagulation based harvesting technique to modify the surface of *Chlorella* sp. with aluminum-boron electrodes. The biochar produced by hydrothermal conversion had mesoporous structure suitable for adsorbing tetracycline. Cluster #1 included articles on cultivation of microalgae in wastewaters and utilization for various value-added products. Also, studies on sustainability of generation of solid algal products, carbon footprints, life cycle energy and environmental life cycle assessments were discussed. Following this, research on the characterization and comparison of products obtained from various thermochemical processes such as fast pyrolysis, slow pyrolysis, HTL etc. were carried out (cluster #2). Articles on various reactor designs were present in cluster #3 including fixed-bed reactors, conical spouted bed reactors etc. were counted in.

Though the large cluster comprises enormous record of the research on microalgal biochar, small clusters also play a significant role in the role due to the presence of articles with strong citation bursts. These concepts can also be considered as emerging aspects of this field of research. For example, cluster #10 emphasized on the use of lipid or pigment extracted algal residue for thermochemical conversion. Cluster #12 highlighted the development of novel techniques like microwave heating in integration with conventional techniques to enhance the product quantity and quality. A detailed review on the evolution of the field, research gaps to be focused and budding prospects of microalgal biochar is conversed in the upcoming sections.

3.9.1. *Evolution of microalgal biochar research*

Getting piqued from the famous "Terra Preta" soils of Amazon basin,

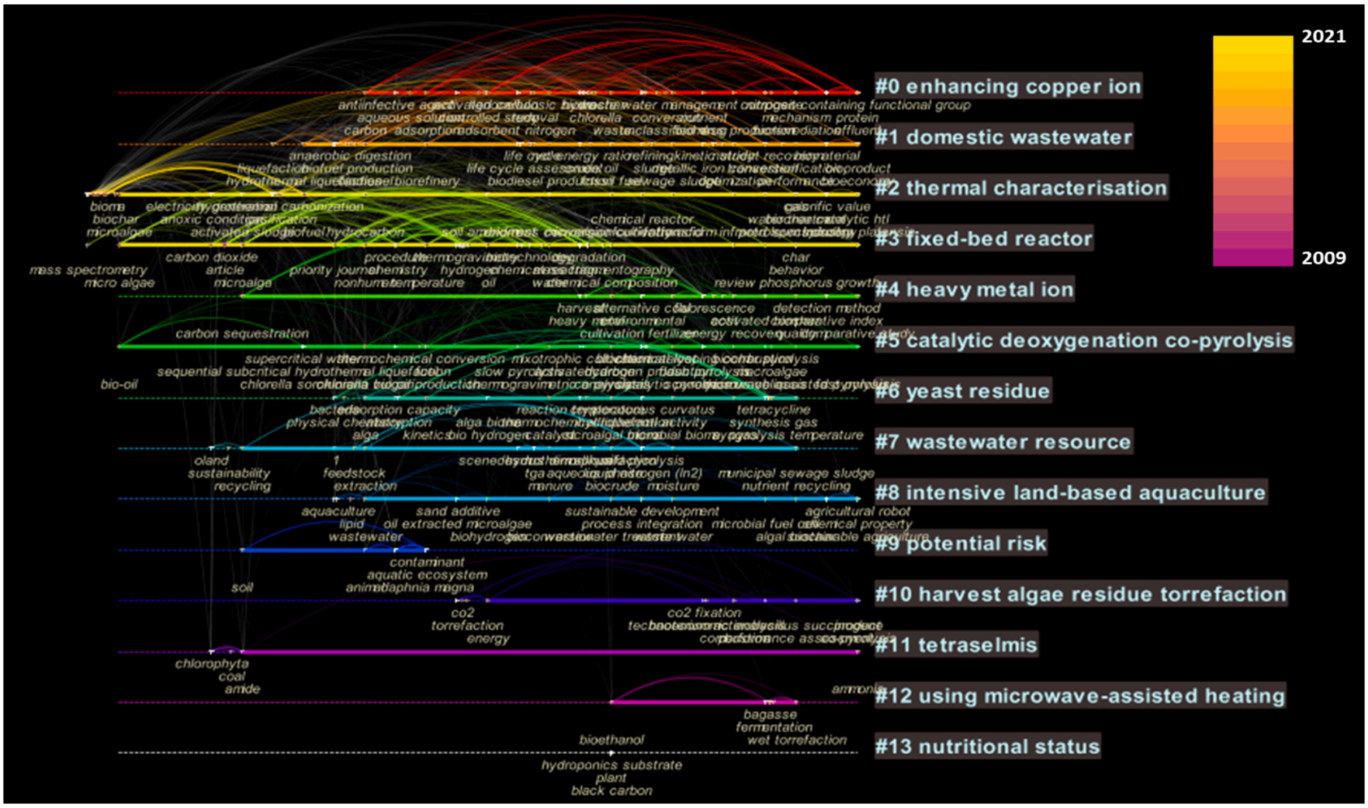

Fig. 5. Timeline view of co-occurring author keyword analysis of microalgal research with segregated cluster categories between 2009 and 2021.

it was in 1966 that Wim Sombroek first highlighted the presence, use and science behind biochar. Developing over the next five decades, biochar today is regarded as one of the products of biomass, a third-generation biofuel that has the potential to mitigate and liberate the populace from the economic, social and largely the environmental burden of continuous use of conventional coal and petroleum-based fuels and energy derivatives [34]. Sourced from feedstocks as varied as trees, crops, agricultural waste (lignocellulosic biomass), sludge, biomass-derived commodities and algae, biochar is a carbonaceous product produced by controlled heating of biomass between 300 and 800 °C [35,36]. Amongst various feedstocks algae has been of particular interest due to its high growth rate, flexibility of culture conditions, ability to sequester carbon dioxide, environmental sturdiness and unique physiochemical and morphological properties of biochar produced from its thermal treatment [5,34]. The evolution of microalgal biochar research is discussed below under three stages as the preliminary research, progression and current trends.

3.9.1.1. Preliminary research (2009–2014). Initial research were focused on the thermal characterization of microalgae, properties of char produced from the thermal conversion. The research was aligned more on deriving value-added product from the waste. For this conventional pyrolysis process was implemented. However, newer thermochemical techniques (such as HTL/HTC, torrefaction) have been developed over the years for the producing of algal char with the consideration of specific requirements (biomass harvesting/drying and biochar properties). Research on the effect of the experimental parameters (such as highest heating temperature, heating rate, and residence time) on algal biochar yield and optimized those parameters for enhancing the yield and properties of biochar [37]. Pre-treatment was introduced for improving certain aspects of algal biochar such as its surface area and its functional groups. Moreover, the first life cycle assessment of algal biochar (while evaluating the algal biorefinery process) was reported [38]. Even modifications of conventional pyrolysis like flash/fast for improving surface properties were reported [39].

3.9.1.2. Progression (2015–18). Comparative analysis of these processes discuss the advantage associated with different production techniques. For instance, slow pyrolysis is the front-runner which yields highest amount of biochar by employing heating rates of 0.1–1 K s^{-1} with a residence time of around 450–550 s. HTC besides being an inexpensive, fast process can produce char with higher carbon content at higher temperatures [40]. Microwave assisted pyrolysis is a mature, easy to scale up technology which also co-produces syn-gas and bio-oil along with char in minimal time and less energy uptake [41]. In case of torrefaction (dry and wet) it is reported that temperatures lesser than 250 °C and shorter residence times can produce chars with high calorific value (21 % increase), 61.5 % retention of energy from original biomass, reduced ash content and better hydrophobicity [42]. Moreover, the comparisons of different process were crucial to produce an application specific, cheap and yet effective char.

In this period, now the research was shifted from normal thermal conversion to catalytic thermal conversion, where the thermal conversion was carried out in the presence of different catalysts. Zeolites, or alkaline salts have been employed to produce char with enhanced properties like higher surface area, higher cationic exchange capacity, increased functionality increased adsorption, better pore structure, lower acid etc. [43]. With the progression of the algal biochar research, its comparisons with biochar produced from lignocellulose biochar was reported. Though algal char has lower HHV, surface area, CEC and carbon content than the conventional lignocellulosic biochar, the presence of (extractable) traces of elements like Na, Ca, Mg, K, S not only adds to the uniqueness of algal char but also adds to enhanced functionality that finds use in applications like soil ameliorant, catalysis, wastewater treatment, environmental remediation, coal fuel replacement, supercapacitor etc. [36].

Owing to its porous structure algal biochar has a high surface area that makes it suitable for remediation and adsorption-based applications. Further the pore structure and number can be enhanced by using catalysts like $CuCl_2$, alumina, zeolite etc. [2,3]. Doping with alkaline salts like KOH and co-combusting with various feedstocks tend to increase the functional groups on the char surface (in addition to phenolic and amine groups already present on the surface) [44]. These are together known to increase the pH, zeta potential and cation exchange capacity of char which opens up unexplored avenues of applications [4]. Besides dictating the C, O, N content of char temperature also affects the pH, cation exchange capacity and functional groups of chars. A significant number of research were now focused on producing engineered biochar, where more sophisticated and novel physical/ chemical modifications were performed and the engineered biochar was utilized in major environmental applications. Predominantly, the application was concentrated on remediating heavy metals, dyes, antibiotics, nutrients and emerging contaminates. Later on, the complex kinetics models were also developed and implemented to comprehend the thermo-chemical conversion of algal biomass [45].

3.9.1.3. Current trends (2019–21). Lately there have been considerable efforts to use synthetic biology tools like genetic engineering to produce algal strains that produce “designer char” [23]. Optimized process parameters and reactors are also being mulled to cut economic and environmental costs while increasing the efficient use of feedstock (concept of extracting value-added products from biomass as a pre-treatment – Biorefinery) and achieving higher yields of char with enhanced physiochemical and morphological properties. Apart from remediating the pollutants, the scope of algal biochar research is expanding to certain non-conventional areas.

In a nutshell, three main aspects of algal biochar are in the focus of the research community, production, characterization, and its application. The production of algal biochar and a desirable modification is evolving rapidly, several novel modifications (physical, chemical, and biological) have been done to algae for synthesizing the engineered char or composites of algae [46]. The choice of modifications is application specific, but not limited to it. Various other factors such as price, facile synthesis and environmental considerations also plays an important role in deciding the type of modifications. Further, secondary aspects in algal biochar research lies in its characterization. Previously, all the chars derived from wet biomasses are treated similarly, but with subsequent development it became clear that algae are different from other water originated biomass. Moreover, even the char derived from microalgae and macroalgae have significant differences [19]. In future, with development of more sophisticated characterization techniques, there is a high probability that the distinction between char of different microalgae will become clearer. And the last aspect is application. Currently, the majority of the application of algal biochar is limited to environmental field, and bioenergy domain. But with the advancement of biochar field in non-conventional applications, application of biochar will progress into non-conventional research. Biochar derived from algal are now being used in preparing cathode catalyst for using in microbial fuel cells [47], moreover, owing to its properties it has been also utilized as super capacitor and catalyst [46]. Further, the algal biochar is being used in preparing bio nano-particles and carbon dots [48]. These, advancement will open up a new research domain for it in sensing and bio medical applications (Fig. 6).

3.9.2. Research gaps

- The relationship between feedstock composition and biochar's physiochemical and morphological properties needs to be elaborated further to tailor-make biochar aimed at fulfilling specific applications.
- The presence of heteroatoms like N, O and S, on biochar's surface increases its applicability to fields as varied as sensor material and supercapacitors [49]. Hence ways to preserve/increase the presence of heteroatoms even at higher temperatures of production techniques is a challenge that needs to be worked upon.
- Effects of various thermochemical production strategies such as pyrolysis, HTL, and torrification, etc. on the yield and properties of biochar is yet to fully understood (on micro and macro scale) [5].
- Concept of “bio-refinery” (i.e., use of algal biomass residue for extraction of components like pigments, fatty acids and polysaccharides before char production) still needs to be explored further and incorporated into existing production processes of biochar while balancing a trade-off between effect on applicability of biochar and extraction of value-added products from feedstock.
- Optimization of effect of process parameters such as highest heating temperature, heating rate, and residence time needs to be studied in little depth, moreover, complex kinetics model needs to be implemented with the inclusion of various experimental features.

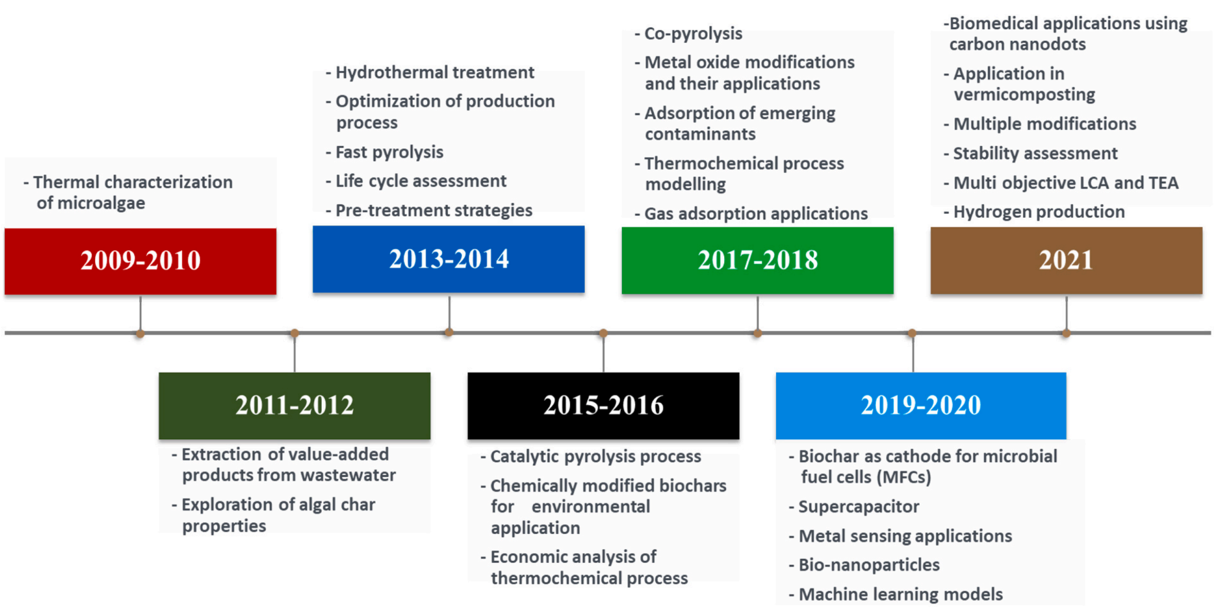

Fig. 6. Timeline showing the evolution of microalgal biochar research from 2009 to 2021.

Modelling would provide an idea about the properties of biochar produced at industrial scale.
- Effects of pre-treatment (like that of acid, heat etc.) on the yield of algal biochar demands comprehensive studies that elucidate the consequences of such treatment on conversion of liquid hydrolysates in feedstock to solid char product [50].
- Environmental impact of using biochar, (especially the by-products of biochar use like persistent free radicals, trace heavy metals, and small-molecular organic compounds like furans, dioxins, phenols etc. that are highly toxic for environment) need to be studied and researched so as to increase its eco-friendliness and safety.
- Majority of the application related to algal biochar has been performed at laboratory level, the application needs a scale up, and the challenges faced while implementing the application at a larger scale requires an in-depth discussion.
- Co-pyrolysis systems that use varied feedstocks along with algal biomass for char production need to be studied and developed as these are purported to have lesser energy demand and higher efficiency than singular systems that use only algae [51]. Besides the lower energy requirements and cost cut the biochar produced by such systems is said to have enhanced physiochemical properties that are flexible enough to be used for various applications.
- More studies related to life cycle assessment and techno economic assessment of algal biochar should be done. This will ensure the applicability of the production process at an industrial scale.

3.9.3. Emerging trends and future scope

- Co-combustion of varied feedstocks and catalytic pyrolysis with salts of alkali metals like KOH for production of biochar are being looked up as potential launchpad for introduction of intrinsic dopants in biochar that increase its porosity, surface area, Cation exchange capacity and catalytic properties [52].
- Techniques like HTL and torrefaction are being optimized to co-produce algal char as well as other bio-fuels like syngas and bio-oil. While taking lesser time, consuming lesser energy than conventional pyrolysis these methods also show immense potential to use wastewater streams and algal blooms (wet biomass) as feedstock that reduce cost as well as environmental impact of algae [36].
- Recent spin-offs of conventional pyrolytic techniques that use microwaves certainly present a very mature, easy to scale -up and flexible model (w.r.t addition of activators and catalysts to large quantities of biomass) for algal biochar production [53].
- Genetic engineering of algal strains to achieve higher strains of char and to produce “designer-char” that caters to specific working environments and applications is being actively pursued to cover unexplored areas of applications of char [23].
- Wet torrefaction, acid pre-treatment etc. are being studied and developed to increase the functionality of biochar and thereby it's use in various applications.
- Development and employment of a continuous process for algal biochar production is being pursued to increase the efficiency and productivity.
- Microalgae-derived biochar has been used for remediation of organic pollutants like dyes, rhodamine b, sulfamethoxazole etc. and heavy metals like cadmium, lead etc. from wastewaters [54–56].
- The green carbon dots synthesized from *Chlorella Sorokiniana* biochar was polymerized with $KMnO_4$ exhibited higher fluorescence intensity as suitable for chromium detection [57].
- In case of adsorption application of microalgal biochar, growth and harvesting phase of microalgae was found to impact the efficiency. The biomass obtained at mid-log phase showed best adsorption capacity of sulfamethoxazole [58].
- Microalgal biochar produced from microalgal consortium harvested through electrocoagulation-flotation was used as a seed agent to improve struvite crystallization [22].

4. Conclusion

Microalgal biochar is a fast-growing field with enormous environmental benefits such as carbon-sequestration, waste management and nutrient recovery. This scientometric analysis provides insights into the evolution and key emerging aspects of microalgal biochar research like integrated strategies of combining pyrolysis with microwaves; interdisciplinary, novel applications of algal biochar such as superconductors and carbon nano-dots for biomedical sensing; genetic engineering aspects to enhance productivity and nutrient value; agricultural fertilizer and simultaneous biogas production. Focusing on these above said directions on research gaps and emerging trends will ensure the commercialization and application of microalgal biochar in various sectors, while contributing to carbon-negative, circular bioeconomy.

CRediT authorship contribution statement

Nageshwari Krishnamoorthy: Conceptualization, Analysis, Writing - original draft preparation.
Abhijeet Pathy: Writing - original draft preparation.
Astha Kapoor: Writing - original draft preparation.
Balasubramanian Paramasivan: Conceptualization, Writing - reviewing and editing, Final approval.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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