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Integrating Biochar in Anaerobic Digestion: Insights into Diverse Feedstocks and Algal Biochar

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Abstract

This review article intends to report the advances in the production and application of biochar from macroalgae and microalgae and its utilization in anaerobic digestion (AD), aiming to achieve zero waste and promote a circular economy. Biochar, a carbon-rich material derived through the pyrolysis or gasification, offers environmental and agricultural benefits due to its stability and porosity. By incorporating biochar into AD systems, improved process efficiency, enhanced microbial activity, and nutrient retention can be achieved. An integrated approach on its production and application can minimizes biomass disposal impacts, generate renewable energy, and improve the soil and nutrient management. The use of macroalgae and microalgae for biochar production aligns with the sustainability principles, as these resources have high growth rates and there is no direct competition with the arable land. Thus, the focus of this article is to review the recent advances in biochar production from microalgae and macroalgae, factors influencing biochar properties, structure, characterization and mechanism of biochar action and the impacts of biochar addition on AD. It also evaluates the economic and environmental benefits, highlighting the role of this approach in achieving a zero-waste paradigm and supporting circular economy development.

Keywords: Biochar; Anaerobic digestion; Gasification; Pyrolysis; Circular economy; Zero waste; Sustainable development goals

1. Introduction

The development of circular economies and the search for environmentally friendly waste management techniques seem to be of great relevance in recent times. In this context, using renewable biomass resources such as macroalgae and microalgae show enormous promise for overcoming the difficulties connected with waste disposal and advancing the development of renewable energy sources. Making biochar from macroalgae and microalgae and then using it in AD procedures is one potential strategy (Boakye et al., 2019). The integrated system helps developing a zero-waste paradigm and the formation of a circular economy, in addition to providing a solution for waste valorization.

Seaweed, also known as macroalgae, is a plentiful marine resource that has historically are used for several applications, including food, feed, and fertilizers (Kumar et al., 2021). However, given to their quick growth rates and great biomass output, they can also result in huge biomass surpluses and environmental issues, if not adequately managed. Similarly, single-celled photosynthetic organisms known as microalgae have drawn interest as possible sources of biofuels and priceless bioactive substances (Sirohi et al., 2023). However, their extensive cultivation can produce substantial amounts of biomass wastes that are needed for novel utilization techniques.

Biochar is substance rich in carbon which is produced by the thermochemical processes such as pyrolysis or gasification of biomass. It has drawn tremendous attention for its many environmental and agricultural applications. Its surface shows high porosity and possesses large surface area and stability. Due to these properties, biochar is considered useful for soil applications as it retains moisture, helps in aeration, etc, which ultimately improve the health of the soil (Abhishek et al., 2022; Chen et al., 2022). It can also be used in a number of other processes such as AD to improve the biogas production (Li et al., 2020).

In the process of biological methanation under anaerobic conditions, the complex biomass (organic nature) is converted into biogas (a mixture of methane and carbon dioxide). Anaerobic microorganisms are generally used in the process to convert complex organic molecules into less complex ones such as methane and carbon dioxide. Numerous benefits may be attained by adding biochar made from macro- and microalgae to AD systems. First, by adding biochar, which due to its porous structure promotes microbial colonization and substrate accessibility, the process can become more stable and efficient (Zheng et al., 2017).

Second, through encouraging the establishment of microbial consortia and biofilm, biochar acts as a catalyst in biological methanation process, resulting the formation of biogas from the organic waste. Finally, the inclusion of biochar can help to immobilize and retain the crucial nutrients, thus, minimizing nutrient losses and improving the digestate quality.

An important step towards reaching the zero waste and promoting a circular economy is the incorporation of biochar produced from the macroalgae and microalgae into AD systems. The environmental effects of disposing of these biomass resources may be reduced by valorizing them, which also improves soil and nutrient management and produces renewable energy. Additionally, because macroalgae and microalgae have rapid rates of development, they do not compete with the arable land, and can be grown in a variety of aquatic conditions, including wastewater. Further, their use for the manufacture of biochar is consistent with the values of sustainability and resource efficiency.

This review intends to examine the current developments in the generation of biochar from macroalgae and microalgae and its application in biological methanation process. It further discusses the main determinants of biochar characteristics along with the strategies to optimize the pyrolysis and gasification processes. The influence of the addition of biochar on the performance of the AD process has also been assessed, in addition to the integrated approaches for potential economic and environmental advantages, emphasizing its contribution to the creation of a circular economy and a zero-waste paradigm for sustainable development.

2. Production of biochar from macroalgae and microalgae

Recent developments clearly indicate the versatility of algal feedstock as a promising resource for producing biochar with promising climate change mitigation potential and as an alluring carbon capture technique. Studies have explored this third-generation biomass-based (macroalgae and microalgae) biorefinery to get the maximum outcome with potential food-feed-environmental benefits. The thermochemical treatment technology for biomass offers numerous advantages, including minor footprint, efficient products formation and their isolation in short time, and also to treat different kinds of wastes and their mixtures when compared to other physical, biological and chemical treatment technologies (Chen et al., 2021). Pyrolysis (slow/flash/fast) and gasification as well hydrothermal treatment, specifically for the feedstock having high moisture (ca. 50% or more), dry/wet torrefaction, etc. are the most adopted and conventional methods that are used to produce biochar from macroalgae and microalgae (Akbari et al., 2021; Chen et al., 2022; Gan et al., 2020; Jabeen et al., 2023; Raheem et al., 2021; Zheng et al., 2017). The process of pyrolysis is one of the best options (comparing different other thermochemical technologies) as it results formation and recovery of maximum quantity of biochar (and lesser quantities to bio-oil and syngas). In recent years, microwave-assisted carbonization (microwave pyrolysis), co-pyrolysis, plasma pyrolysis, and solar pyrolysis have also been studied to increase the efficiency of the process more energy efficient and to achieve the circular bioeconomy (Chen & Yang, 2023; Li et al., 2023; Walia et al., 2021). However, these advanced thermal treatment techniques are still in lab-scale largely.

Different kinds of reactor such as fixed-bed reactors with dry distillation system, or fluidized bed reactors for pyrolysis, gasification and torrefaction have been used to produce biochar (Mishra & Upadhyay, 2021). In addition, on-site pits or kilns and drums have also been used at small-scale for producing biochar employing the pyrolysis. However, these methods have low efficiency (Lohri et al., 2016). Keeping the critical importance of process parameters in consideration specialized manufacturing requirements and high-pressure resistant equipment are needed for carbonization (Devi et al., 2023). Irrespective of the methods used, while producing biochar from algal biomass, it is necessary to select pyrolysis methods and operation conditions (end temperature, retention time, heating rate, feedstock composition, heat flux) meticulously to achieve the expected purposes of biochar synthesis (Escalante et al., 2022).

Pyrolysis is one of the most efficient thermochemical processes to treat biomass at low to high temperature (300-900°C) in de-oxygenated/ anoxic environment (destructive distillation), which produces 35-40% mass yield of biochar (Bolan et al., 2022; Sirohi et al., 2023). Haris et al (2021) reported that slow heating rate promoted the high biochar yield during the slow pyrolysis. Type of algal species, their habitat and type of stress they adopted during their life-cycle also influence the biochar properties. López-Aguilar et al. (2022) studied the pyrolytic behavior of endemic microalgae consortium, *Spirulina* and a consortium comprising *Sargassum natans* and *S. fluitans* and found that different algal species liberate different volatile solids during the pyrolysis that significantly changes the composition of other by-products of pyrolysis. They also found variation in the properties of biochar. Additionally, during the life span of algae due to the assimilation of inorganic alkali minerals such as Zn, Fe, Ca, Mg, Mn etc. from their habitat, the produced biochar showed higher content of ash (Lee et al., 2020; Tiwari & Troy, 2015).

Microwave-assisted pyrolysis is considered as a recent development of fast pyrolysis process where microwaves radiation (200-600°C) is absorbed by biomass to get more efficient and uniform heat transfer that shorten the initiation heating time of pyrolysis reaction with less energy requirements. For plasma pyrolysis, fourth state of material (hot) plasma is used. The high energy of plasma and high reaction temperatures (900-2000°C) promote fast pyrolysis reactions, and produce more gas than char and oil (Fahmy et al., 2020). When concentrated solar energy is employed for biomass pyrolysis, the process is termed as solar pyrolysis. *Chlamydomonas reinhardtii* and *Spirulina platensis* microalgae were explored for the catalytic solar pyrolysis for increased the hydrocarbon formation (Andrade et al., 2020; Andrade et al., 2018).

Gasification process comprises partial oxidation of the biomass and is mainly used for the production of syngas (85%). It is further sub-classified as supercritical gasification conducted at 600–1000°C and conventional gasification conducted at 800–1000°C (Guo et al., 2022). In this process also, there is formation of biochar although in low quantities such as10-15%. Algal biomass has been extensively explored for various gasification processes, including supercritical water gasification and steam gasification (Duman et al., 2014; Guan et al., 2012; Mishra et al., 2023).

Torrefaction is another promising thermochemical technique which is used as a pretreatment process for the algal mass for removing volatile matter (before using it for pyrolysis) Torrefaction process is further classified as dry or wet torrefaction. In dry process, heating is done at 200-300ºC under a nitrogen atmosphere, while in wet process, temperature is 180-260ºC in the presence of water. There is variation in the time of residence in both the processes (Law et al., 2022; Yu et al., 2017). Due to high process pressure (ca. 2 t-10 MPa), there is formation of solid carbonized material (hydrochar) with low carbon (<60%) for fuel applications. During high temperature treatment, the char undergoes secondary reactions, leading to the decomposition of primary char into volatiles (gaseous form), which results in lower yield of biochar except, if biomass contains high amount of non-condensable mineral that may lead to relatively higher yield of biochar at high temperatures.

The pretreatment of algal biomass changes the physicochemical characteristics of the biochar; for instance, chemical or solvent treatment enhance the surface functionality of the produced biochar while, mechanical pretreatments such as grinding and milling lead to the formation of smaller size of the particle size, which show better adsorption efficiency for the removal of pollutants.

Table 1 summarizes the properties of algal biochar obtained from various source studied so far, which gives an idea about the impact of production process parameters and type of algal biomass on its characteristics. Table 2 presents the yield of biochar produced from different macroalgae and microalgae under different operating conditions.

2.1. Production of biochar from macroalgae

Macroalgae are multicellular, eukaryotic colored seaweeds of red, green and brown in color, belonging to *Rhodophyta, Chrorophyceae* and *Phaephyceae* families, having as high as 4000 – 6000, 700 – 7000 and 2000 – 5000 species, respectively (Lee et al., 2020). Several studies have reported the formation of biochar from different macroalgae. For example, macroalgae kelp and hijikia were pretreated with iron salt to produce magnetic biochar for heavy metal adsorption. The modification process extensively increased the surface properties of the biochar; however, no significant change in elemental composition was observed (Son et al., 2018). Water pretreatment of *Saccharina japonica* in varying ratios dramatically increased the specific surface property, i.e., area and reduced the amount of alkali minerals in produced biochar (Boakye et al., 2019). *Laminaria japonica* was electro-modified before slow pyrolysis to obtain biochar with surface modified for better phosphate adsorption (Jung et al., 2015).

There are many studies describing the catalytic pyrolysis of macroalgae such as *Cladophora glomerata, Gracilaria gracilis, Enteromorpha clathrata, Ulva prolifera, Pavlova, Cynobacteria, Arthrospira plantensis, Oscillatoria,* etc. However, these studies are not sufficient to sum up the outcome in a generalized form, and more research is needed in this field (Lee et al., 2020). Zeolite-based catalysts such as ZSM-5, HZSM-5, H-Beta, H-Y Meso-

MFI, HBEA, USY, SAPO5, SAPO11, MCM41, Al-MCM-48; metal-based and ceria-based catalytic such as Ce/ZSM-5, MgCe/ZSM-5, CeNi/ZSM-1; metal catalyst such as MgNi/ZSM-5 can be used for the catalytic pyrolysis of macroalgal biomass (Lee et al., 2020; Wang et al., 2018; Yang et al., 2016).

2.2. Production of biochar from microalgae

Chlorella sp*., Chlamydomonas* sp. JSC4*, Chaetocerous muelleri, Pavlova* sp*, Spirulina* sp, *Spirulina platensis, Dunaliella salina, Arthrospira platensis, Nannochloropsis* sp, etc are the generally explored microalgae to produce biochar. Li et al. (2023) co-pyrolyzed *Spirulina platensis* a N-rich microalgae at 800, 850 and 900 °C in molten salt (Na_2CO_3–K_2CO_3 and Li_2CO_3–Na_2CO_3–K_2CO_3) to produce carbon and reported high carbon yield with superior microstructure and surface area as high as 2009.26 m^2/g at around 900°C. Biochar derived from *Nannochloropsis oceanica* and *Chlorella* sp. were torrefied under the oxidative and non-oxidative conditions. The process parameters significantly changed the physicochemical properties of the produced biochar and also oxidative process shortened the reaction time with low biochar yield (Zhang et al., 2019). Various properties of the produced biochar such as pH, content of the ash and carbon increased exponentially with the increase of pyrolysis temperature.

Microalgal biomass contains high amount of moisture (≈86-90%), for which hydrothermal carbonization could be an effective process for (hydro/bio) char production. However, as mentioned earlier, the process parameters and choice of species change the properties of the biochar. *H. reticulatum (HR)* and *C. vulgari* was treated hydrothermally at 180 to 270°C with a 60 min retention time and increasing process temperature significantly lowered the biochar yield from 72 to 37% for *H. reticulatum* and 71 to 50% for *C. vulgari* (Chen et al., 2020).

The catalytic fast pyrolysis of microalgae assisted by microwave showed condensation and presence of some metals and nonmetals including Al, Zn, Mg, Mn, etc. and increase in temperature increased the metal accumulation (Borges et al., 2014; Hong et al., 2017). A mixed culture of *Chlorella* sp alone and with sewage sludge, co-pyrolyzed at 500 and 350°C resulted biochar in high yield (80-74%) that contained 24-30% ash (Park et al., 2018).

3. Structure and characterization of biochar

Numerous inorganic elements, including K, Ca, and Mg, are abundant in biochar derived from algae. It also has a wide variety of functional groups with O and N in it (Zhang et al., 2024). It has been demonstrated that this kind of biochar increases the system's P and N bioavailability (Wang et al., 2020). However, with an energy yield of between 80 and 90% and a mass yield of between 70% and 80%, biochar derived from lignocellulosic materials has a great potential for energy recovery (Nanda et al., 2014). Trace elements (Fe, Co, Ni, Mo, Zn, Cu, and Mn) are abundant in the biochar synthesized from digestate wastes (Cai et al., 2023). Furthermore, algal biochar has a larger concentration of alkaline groups, which neutralize fatty acids to effectively reduce acidification (Du et al., 2023). Moreover, biochar derived from food waste shows a great potential for microorganism colonization (Zhang et al., 2024). As was previously indicated, a number of factors, such as the presence of common or trace elements, differences in functional groups, and electron transport efficiency, can be used to evaluate the performance of biochar. By increasing the availability of trace elements for supporting AD microorganisms, regulating the pH and alkalinity of the system, and promoting both direct interspecies electron transfer (DIET) and interspecies electron transfer (IET), these parameters play a significant role in strengthening the performance of AD. Several properties of the biochar such as surface properties including area and porosity and functional groups, capacity to exchange cations, electric conductivity (EC), redox characteristics, pH, etc are significant for the determining the end-applications in biological methanation or other processes (Mishra et al., 2021; Chiappero et al., 2020)

3.1 Specific surface area (SSA)

The specific surface area is an important characteristic of the biochar which determines its efficiency to remove the pollutants by adsorption (Anerao et al., 2022a, b). Algal biochar has been reported to have a low SSA which can be enhanced if pyrolysis is carried out at higher temperature. It is also important to note that in contrast to the biochar derived from lignocellulosic materials wherein the biochar retains its structure of the feedstock before pyrolysis, algal biochars have an irregular and compact structure as opposed to their feedstock (Yu et al., 2017). Sethupathi et al. (2017) used a specially built biogas reactor to study the removal of carbon dioxide (CO_2) and hydrogen sulfide (H_2S) by biochar, which showed higher removal efficiency of CO_2 compared to H_2S. Creamer et al. (2014) evaluated the adsorptive removal of CO_2 by biochar, which clearly showed the role of high SSA and nitrogen containing functional groups. There are several other studies on the removal of CO_2, establishing the significance of size of the pore of the biochar (which should be in the range of 0.5–0.8 nm), higher SSA, and the contents of alkali and alkaline earth metals (Abhishek et al. 2022; Bolan et al. 2022).

3.2 Porosity

The pore size of the biochar is an important component in identifying the likely connections with the microorganisms responsible for biological methanation. Owing to its unique oxygen containing functional groups and porous structure, algal biochar has excellent electron transport properties and a higher storage capacity. The cytochrome and ferredoxin involved in the synthesis of Fe (II) are important components in electron transport, and this feature speeds up the reduction of Fe (III) to Fe (II) (Wang et al., 2020). It is important to note that the majority of microbes involved in DIET, including species of *Geobacter*, *Sphaerochaeta*, and *Sporanaerobacter*, depend on exchangeable (bioavailable) iron and sulfur in order to complete the extracellular respiration process (Li et al., 2020). In addition, porous biochar promotes the production of biofilm, which protects the precisely involved microorganisms in selective enrichment during the biological methanation process impacted by the stress caused by the production of acids (Luo et al., 2015). In the anaerobic digesters supplemented with biochar, a number of bacterial species selectively get enriched and enhanced. Several studies have identified *Methanolinea*, *Methanosaeta*, *Methanobacterium*, and *Methanosarcina* sp. among the archaea in an AD reactor supplemented with biochar (Xu et al., 2018, Zhang et al., 2019). Lü et al. (2016) studied the spatial distribution of methanogenic microbes in the biochar pores, based on the morphology. *Methanobacterium*, which has a larger shape and size remained inside the pores; however, *Methanosaeta*, which has a smaller shape and size was found inside and outside of the pores (Lü et al., 2016; Kumar et al., 2021). The generation of methane (CH_4) during AD may be boosted by these widely dispersed and enhanced microbial communities in biochar pores (Luz et al., 2018).

3.3 pH

The conductivity of biochar is significantly impacted by the pH, which further influences the microbial interaction in anaerobic reactor (Yin et al., 2019). During the process of pyrolysis, due to the increase in the temperature, there is increase in the content of ash and the function groups of acidic nature disappear (being volatile in nature), resulting change of the pH towards alkalinity (Ren et al., 2020; Yin et al., 2019). In addition, the redox nature of biochar enables it to act as donor or receiver of electrons (Yuan et al., 2017) and the existence of species that can accept and provide electrons, such as poly-condensed aromatics, quinones, and phenolic groups (Klüpfel et al., 2014; Yuan et al., 2017). Biochar promotes the microbial activity to generate methane and also helps in developing adaptation to shock loadings by increasing the alkalinity of AD (Li et al., 2017). Biochar may efficiently facilitate the methanogenesis phase in an acidic (pH 1.0–5.3) environment, which improves its working efficiency under higher solid loadings (Ren et al., 2020). A continuous anaerobic digester, supplemented with biochar may work well under lower hydraulic retention time and high solid loadings.

3.4 Cation exchange capacity (CEC)

It is known that the buffering capacity of biochar is due to the CEC, which supports balanced microbial growth. The presence of free ammonia or ammonium ions affects the working of anaerobic digester. Free ammoniacal nitrogen harmfully impacts the methane-producing microbes and this inhibition is concentration dependent (Rajagopal et al., 2013; Ho and Ho, 2012, Poirier et al., 2017). Biochar with high CEC can overcome this inhibition and improve microbial activity to produce biogas in different systems involving sewage sludge, food waste, etc. (Mumme et al. 2014, Shen et al. 2017, Su et al. 2019, Lü et al. 2016). Shen et al. (2017) promoted the beneficial use of biochar in SS AD, and Su et al. (2019) asserted that the NH_3-N up to 1500 mg/L could be alleviated by biochar addition in food waste AD operation (Ciccoli et al., 2018). Similarly, Lü et al. (2016) reported that high NH_4^+ stress (up to 7 g-N/ L) in an AD could be overcome by biochar addition. The involved mechanisms were believed to include: surface functional groups, CEC (Shen et al., 2017), microbe immobilization (Lü et al., 2016; Su et al., 2019) and advancement of DIET (Lü et al, 2016). Thus, AD may achieve NH_3 mitigation through indirect pathways (via microbe immobilization and DIET) and/or direct adsorption effects (depending on surface functionality, CEC, etc.) depending on the operating conditions of AD (e.g., temperature and pH), substrate, and biochar (Tang et al., 2020). Overall, collective attributes of biochar such as CEC, surface functional groups, and advancement of DIET have been considered as the possible mechanisms for this phenomenon.

3.5 Surface function groups and redox properties

The surface of biochar may contain different kinds of function groups such as hydroxyl, carboxyl and amine functional groups among others, which determine its specific agricultural or environmental applications (Kumar et al., 2020a, b, c). Kizito et al., (2015, 2016) and Yin et al., (2017) also reported similar behavior in their studies on ammonia removal and other contaminants. Extremely high efficiencies of 84 and 98% were achieved by Sahota et al. (2018) and Kanjanarong et al. (2017), respectively who employed biochar with different function groups on its surface. Furthermore, it has been demonstrated that the biochar derived from algal biomass improves the anaerobic fermentation process to produce short-chain fatty acids. Additionally, the amount of biochar altered the acetate concentration (Zhang et al., 2024). In order to provide more macromolecular organic substrates for the synthesis of short chain fatty acids, the algae-based biochar may break the algae cells. Further, microbes can attach to and grow on the surface of biochar because to its abundance of hydrophilic functional groups, and the material's conductive characteristics facilitate electron transmission throughout the system (Duan et al., 2019).

Redox characteristics of biochar is yet another important attribute which significantly influences the biological methanogenesis (Wang et al., 2019). Functional groups of biochar present on the surface along with free radicals and metals and metal oxides impact the redox characteristics of biochar (Kumar et al., 2021). For example, quinoid C=O groups are attributed for its electron-accepting capacity (EAC) and the phenolic C-OH groups (as the essential functional groups provide it electron-donating properties (Klüpfel et al., 2014), which jointly determine the electron exchange capacity of biochar. A strong oxidation process that can induce changes in the functional groups can improve the surface properties of biochar (Kumar et al., 2020b, c). However, the process should be capable of inducing new functionalities and must not lead to the transformation of available functional groups to redox inactive COOH functional groups or its removal as $CO_{2.}$ Joseph et al. (2015) reported that carbon-centered aryl radicals (carbon-centered) and semi-quinoid free radicals affect redox property of biochar.

Some metal oxides such as iron and magazine, considered as redox active metals oxides, are usually present in naturally occurring biomass, including algal biomass. These could occur in various oxidation state, working as electron donors and acceptors with regard to the inorganic components of biochar (Dieguez-Alonso et al., 2019). Supplementation of biochar enhanced the DIET during the entire course of anaerobic process. Improved DIET promotion has been shown by the solid biochar with its soluble fraction than by the soluble portion of biochar alone. Still, there are not many studies to support the theory conclusively that biochar redox helps in AD processes, requiring further studies to fulfill this gap. They have investigated the influence of biochar on anaerobic digestion (AD), pinpointing the enhanced performance and microbial interactions. Feng et al. (2024) examined that magnetic biochar derived from waste enhanced the methane yield meaningfully by increasing the protein hydrolysis and enabling direct interspecies electron transfer (DIET), vital for acetoclastic methanogenesis They synthesized the magnetic biochar displayed highest electron accepting capacity (EAC) and electron donating capacity (EDC) values of 76.04 μmol e^{-} g^{-1} and 30.34 μmol $e^{-}g^{-1.}$ They analyzed that MFeBC had the strongest electron capacity, potentially playing an important role in accelerating electron transfer between bacteria and archaea during the AD process due to the presence of Fe^{3+} and abundant oxygen-containing functional groups. Ramírez et al. (2024) demonstrated that biochar improved the AD of untreated sewage sludge with MSW under mesophilic conditions, resulting in enhanced methane production and reduced volatile fatty acids (Ramírez et al., 2024). In another study, Ding et al. (2024) analyzed that biochar modulated microbial community structure, enhancing the stability and degradation efficiency of AD system (Ding et al., 2024). In addition, Gao et al. (2024) described the role of biochar in enhancing biomethane via quorum sensing-mediated inter-microbial communication, endorsing extracellular electron transfer (Gao et al., 2024). Further, DIET mechanism was explained in next section.

3.6 Electrical conductivity (EC)

EC has been attributed an important role in the syntrophic activities performed out by the microorganisms (Kumar et al., 2021, Wang et al 2019). Despite having a lower EC than granular activated carbon (GAC), biochar showed the potential to result DIET. EC could be as high as of 0.2-36.7 mS cm^{-1} in some microbial species obtained from the anaerobic digester due to DIET (Barua and Dhar, 2017). Martins et al. (2018) hypothesized that conductive materials such as humic compounds (which are conductive in nature) might act as electron transporters as electrons donors and receivers to speed up the DIET. A comparative study on the biological methanogenesis of food waste was conducted by Viggi et al. (2017) using silica sand and biochar, which clearly showed the superiority of latter due to the EC.

4. Applications of biochar in anaerobic digestion

AD is gaining increasing attention globally as a promising and sustainable process for sustainable use of organic waste to generate biogas and fertilizers (Ovi et al., 2022). AD process involves the biochemical decomposition of biodegradable substances (organic nature) such as crop residues, animal dung, etc. in a digester under the absence of oxygen (Paritosh et al., 2021; Sarangi et al., 2022).

While AD is being used globally the process still largely faces several issues related to low methane yield, process instability due to pH fluctuation and ammonia formation, formation of hydrogen sulfide (H_2S), inadequate buffer capacity and low digestibility at normal conditions. However, some of these problems can be tackled by the supplementation of certain additives, e.g., biochar (Singh et al., 2022), macro- and micro-nutrients, including phosphorus, nitrogen, sulphur, iron, nickel, molybdenum, cobalt, selenium, etc. and fly ash from incineration and nano-materials (Romero-Güiza et al., 2016). Among these, supplementation of biochar shows promising influence on the process, resulting improved production of biogas as well as helps in stabilizing the bioprocess (Chiappero et al., 2020). However, as the characteristic of biochar depends upon from the feedstock used for its production, its impact on the process and biogas formation may also differ. Figure 1 shows the application of biochar action in AD and its mechanism.

Salehiyoun et al. (2022) studied the AD of high organic municipal solid waste (MSW) with 15% garden waste under the action of biochar which helped to enhance the bio-CH_4 yield up to 36.6%. It was also reported that higher doses of biochar (100g/L) were not that much significant for methane yield enhancement; rather, it inhibited the volatile free acids (VFA) produced in AD.

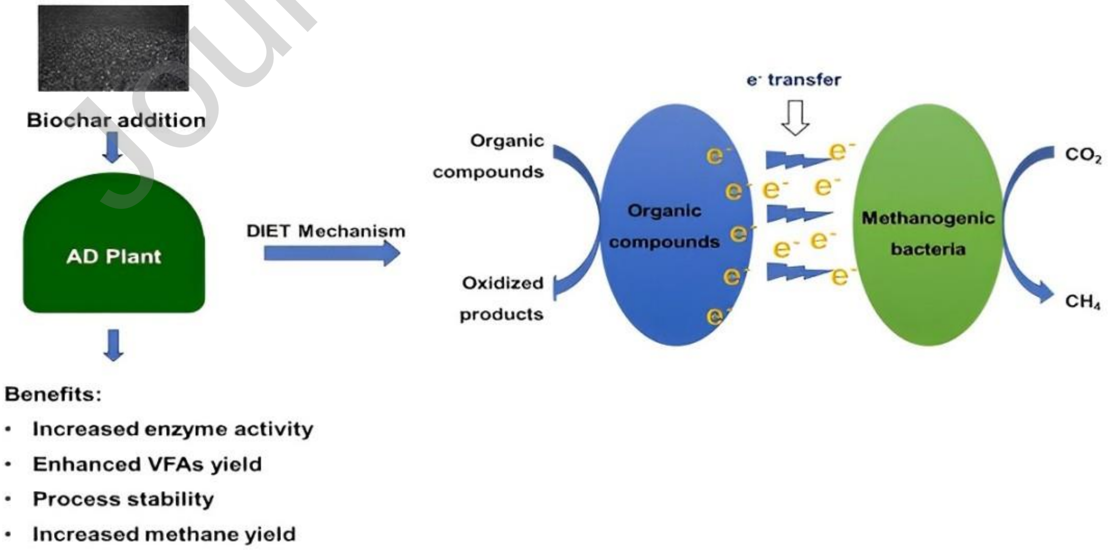

Figure 1. Effect of supplementation of biochar on AD process

Madrigal et al. (2022) evaluated the production of biogas from cheese whey production industries and analyzed the effect of biochar dosing (0-2g/substrate (g/vs) on bio-CH_4 production as well as process stability. Results showed increased biogas yield (from about 163 mL to 358 mL methane per gram volatile solids and reduction in the formation of volatile fatty acids. These results were attributed to the properties such as presence of pores and high surface area of biochar. Furthermore, Huang et al. (2023) studied the AD of pig manure and corn straw to produce biogas and evaluated the influence of supplementation of biochar on the yield of biogas. Results showed higher bio-CH_4 production. In order to study the effect of source of biochar on biogas production, they used biochar produced from various sources such as digestate and crop residues of coconut and corn) and reported the biochar produced from digestate as the best among all, which led the formation of highest quantity of methane. It effectively stabilized the fatty acids, enhanced substrate breakdown, and helped maintain minimal levels of NH_4-N, thus controlled the presence of free NH_3 in the medium. Thus, the inclusion of biochar enriches bacterial activity, creating an optimal environment for methanogenesis, ultimately leading to increased biogas yield (Duan et al., 2023; Zhang et al., 2023). Apart from biochar produced from sludge and lignocellulosic biomass, algal biochar has several significant properties which showed that algal biochar can be employed in the AD plants for enhanced the biogas yield as well as may improve the process stability. However, the usage of algal biochar in AD is still in the initial phase of research, there are very limited literature found on the application of algal biochar in AD. There are some distinctions between biochar prepared from algal sources and other precursors lies primarily in the unique properties and applications of algal biochar. Algae-based biochar contains high nitrogen content due to the protein-rich nature of algae, which increases its catalytic activity and adsorption capacity for pollutants. Tan et al. (2023) analyzed the algae-based biochar has superior direct electron transfer/exchange competences and is effective in degrading organic and inorganic pollutants in wastewater (Tan et al., 2023). Similarly, González-Hourcade et al. (2022) stressed the sustainable preparation of nitrogen-doped biochar from microalgae, which showed significant efficiency in eliminating pollutants from aqueous media (González-Hourcade et al., 2022). Alazaiza et al. (2023) discussed the high specific surface area and rapid electron transport of algal biochar, making it suitable for applications like AD catalyst, CO_2 adsorbents and supercapacitors (Alazaiza et al., 2023). Moreover, Hidalgo et al. (2023) described that algal biochar can be converted into carbon nanotubes, offering assorted applications due to its graphitic structure (Hidalgo et al., 2023). Table 3 shows the impact of different feedstocks biochar and algal biochar on biomethane yield enhancement from different organic biodegradable waste.

4.1. Biomethane yield and process stability

Biomethane yield and process stability are the prominent parameters which are mutually dependent. The stability of the process is mainly impacted by the production of ammonia and organic acids, resulting from the substances which are rich in nitrogen as these hinder the activity of microorganisms, causing the low CH_4 yield (Quintana-Najera et al., 2022). Ovi et al. (2022) studied the effect of biochar obtained from rice husk and palm tree waste on the AD of food waste together with sludge at mesophilic conditions. The addition of biochar helped in the formation of increased quantities of volatile fatty acids, leading to enhanced yield of methane and improved reduction of COD removal. The reduction of NH_4-N and VFA helped to in stabilizing the digester.

Biochar enhances the exchange of electrons between the bacteria and methanogenic microbes of electrotrophic nature. It induces the process of denitrification process for stabilizing the NH_4-N quantity by *Epsilonproteobacteria* (Pan et al., 2019). In this regard, several studies have been performed to modify the surface properties of biochar. For example, iron based modified was used by Che et al., (2022) for wastewater treatment who found much improved process performance and higher bio-CH_4. In order to study the process performance and stability, Wang et al. (2020) evaluated the influence of biochar obtained from Douglas fir biochar on bio-methanation at different temperature and also studied the microbial dynamics in the digester. Result showed enhanced biogas production (11% increase at 37ºC and 98% increase at 25ºC), in comparison to process when no biochar was added. The surface characteristics of biochar, specifically the presence of pores and increased area of surface were considered as the reasons which led to these results. It is known that these properties of biochar helps in improved growth and activities of the microbes in acidogenesis and methanogenesis during the methanogenesis (Zhang et al., 2023). Zhang et al. (2020) investigated the effect of algal biochar on mesophilic and thermophilic Co-AD of 75% algal biomass and 25% food waste in semi-continuous mode in which they achieved the 12%-54% increment in biomethane yield (275.8–394.6 mL/gVS) than controls. Moreover, the impact of microalgae and macroalgae based hydrochar were employed by Wang et al. (2020) in the AD of seed sludge and hydrolysate from HTC of algae. They found that both types of hydrochar enhanced the methane yield by 36% and 31.4% owing to promotion of *Methanothrix* (genus of methanogenic archaea) relative abundance. This increase in methane yield showed that algal based biochar and hydrochar have potential to enhance the methane yield as well as stabilize the AD process.

4.2 Buffer capacity and microbial activity

The performance of anaerobic process, especially its stability is influence by various factors, such as the pH, which is a key factor, which should be in a buffering zone. AD system primarily relies on the pH level or buffer capacity. When the pH decreases, it notably reduces microbial activity and vice versa (Chen et al., 2023). A substrate with high digestibility and a low C/N ratio can increase the acidification process in the digester. The accumulation of acids in AD process decreases the activity of microbes, leading to low bio-CH_4 yield (Zhang et al., 2023). As stated above, biochar is alkaline in nature owing to its chemical composition, i.e., content of ash, which are of inorganic nature compounds) and devolatilization of acidic substances during the pyrolysis process (Kainthola et al., 2022; Singh et al., 2023). To analyze the influence of biochar on the buffering in an anaerobic digester, Sun et al. (2022) investigated the dosing of biochar and found increased growth of methanogens, which directly utilized the mono-carbon, acetic acid, and hydrogen/carbon dioxide as substrates. Biochar efficiently boosted the *Coriobacteriia* for higher bio-CH_4 yield. The abundance of *Cloacimonadia* may transform into amino acids and alcohols, resulting the production of VFAs (Ni et al., 2020). However, authors found that biochar dosing lessened the *Cloacimonadia* growth by increasing the buffering capacity of AD system. In another study, it was reported that the toxic compounds, mainly VFA and NH_4-N were adsorbed on biochar owing to higher buffering capacity of biochar (Cai et al., 2023). It was found that ammonia inhibition could be major parameter to transform the aceto-clastic methanogen to hydrogenotrophic methanogen in methanogenesis stage. Li et al. (2017) found that the supplementation of biochar supported the microbial colonization and promoted the growth of microorganisms, which resulted enhanced bio-CH_4. Verma et al. (2023) also observed increase in fungal dynamics with addition of 15% biochar of the total biomass during food waste composting. In respect of usage of algal biochar, the oxidation of algal biochar with H_2O_2 boosted acetoclastic methanogenesis, while also potentially aiding hydrogenotrophic methanogenesis through enhanced electron transfer activity. The H_2O_2 treatment significantly increased specific functional groups like phenolic and lactonic groups on the biochar by 1.2 and 5.1 times respectively, compared to untreated biochar. Moreover, the redox capacity of the biochar, particularly its electron-donating ability, surged by 64.9% post-H_2O_2 oxidation. This enhancement contributed to improved electron transfer activity, thereby fostering methanogenesis (Jiang et al. 2022). Therefore, it is required to further study the influence of biochar on microbial dynamics community and their growth in the digester, which would provide the information about the microorganisms present in the AD systems.

5. Mechanism of action

To improve the AD performance, biochar is thought to have several properties such an agent leading to the buffering of the medium, a habitat for the microbes, a substance to absorb and remove pollutant, a donor and acceptor for the DIET, etc (Alazaiza et al., 2023; Mishra et al., 2021; Chiappero et al., 2020). The main reasons for enhanced AD efficacy due to biochar is generally believed due to reduced microbial metabolic inhibitions, enhanced interspecies electron transfer efficiency, and overcoming the toxicant inhibitions (Ren et al., 2020; Yin et al., 2019; Luz et al., 2018). The possible mechanisms associated with the biochar, which foster the performance of AD are detailed below and schematically represented in Figure 2.

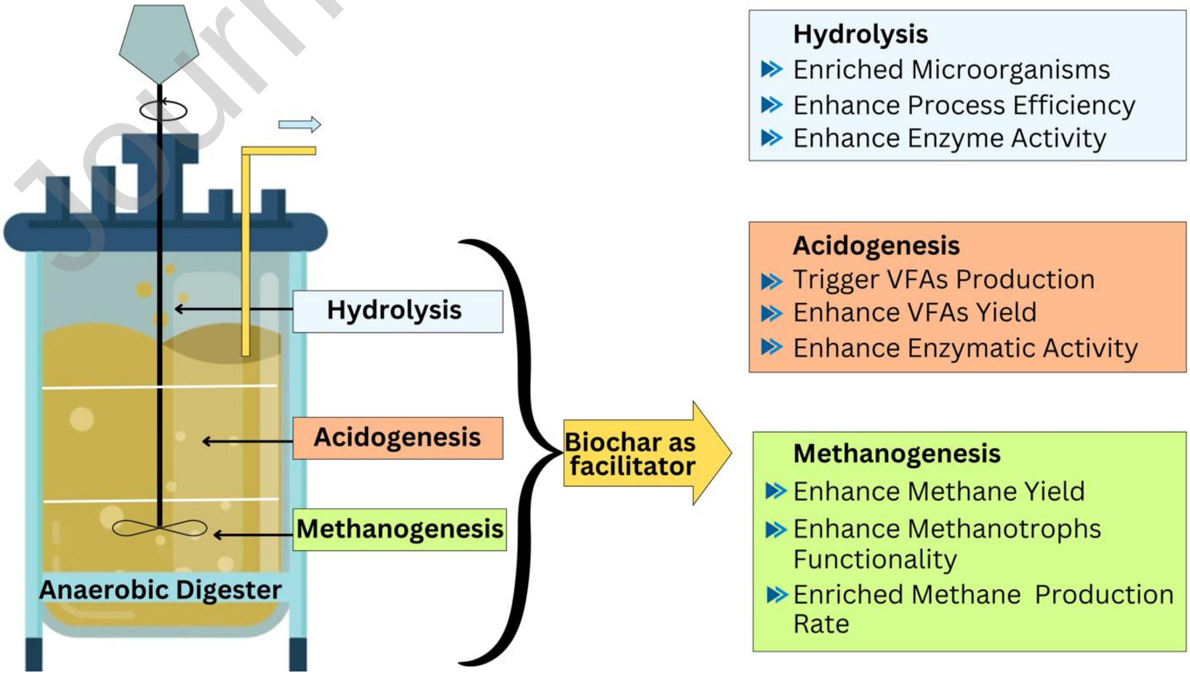

Figure 2. Potential mechanisms involved in improving the performance of AD by biochar

5.1 Buffering of the pH

There are several factors which limit the effectiveness of the AD process, which includes low pH, which may stop the activity of the microorganisms that produce methane. The metabolic pathways of AD systems, notably during methanogenesis, may be significantly affected by the VFAs as inhibitors (Wang et al., 2019). Because of the quick formation of volatile fatty acids, when the loading rate of organics with readily acidifying substrates, the pH is brought down. The recovery of an AD reactor from high VFA concentrations often takes a long period (Ren et al., 2020). Biochar demonstrated a significant buffer capacity that could efficiently neutralize the produced VFAs and stop the quick pH lowering (Li et al., 2018). Shen et al. (2015) reported that the use of biochar (hydrochar) helped in the formation of an environment where methanogens could convert the VFAs to CH_4. This was due to the presence of specific functional groups on the surface of hydrochar, which helped in creating buffering of the medium around pH 7.5-8.0. Wang et al. (2018a) also showed the relevance of buffering property of biochar in their work AD of food waste together with sewage sludge (dewatered). The supplementation of biochar led to the maintenance and stabilization of pH of the medium in the digester. In a two-phase AD, Sunyoto et al. (2015) demonstrated that biochar helped in providing the conditions that stabilized the pH during AD. Similar findings were reported by Jang et al., (2018) in the AD of diary manure, which found that biochar's high nutritional content and propensity for alkalinity significantly increased methane production. In another study, where algal biochar was employed on the AD of algal biomass and food waste, they maintained the pH around 7-7.5 however, during the process pH of process lies in between of

6.5-8.6 which showed that formation of the Thus, it could be determined that biochar has a considerable potential for reducing the impacts of acidification brought on by the accumulation of VFAs, and it also encourages microbial development and capacity to adopt to solid loading shocks as well as helps in acidogenesis (Tang et al., 2020; Lü et al 2016). However, there are several aspects such as the primary mechanisms and parameters which influence of increased formation and accumulation of volatile fatty acids are not well established (Wang et al., 2017). Hence, the hypothesis that biochar provides buffering properties in the digestate in anaerobic reactor is not conclusive. The probable reasons for this uncertainty seemingly are the facts that there is variation in the properties of biochar derived from different feedstock which have varying compositions and the conditions of their production.

5.2 Inhibitors adsorption

One of the primary methods for increasing the AD with biochar is adsorption. The adsorption of inhibitors performed by the biochar is due to its π-π – interaction (Tang et al., 2020). Kanjanarong et al. (2017) showed that COOH and OH radical groups are important groups for the adsorption. Tang et al. (2020) reported that biochar's pores could absorbed different kinds of organic and inorganic contaminates. Tan et al. (2015) evaluated different properties of biochar (hydrochar) which influence its properties for the adsorption and found that the functional groups had higher significance the shape of the pores for adsorption. However, overall, there are conflicting findings about the adsorption capacity of biochar, which necessitates to conduct thorough studies to evaluate these physiochemical or other features to drawn a clear conclusion.

Shanmugam et al. (2018) explored the adsorption properties of biochar, specially focusing on the adsorption of volatile fatty acids, which was affected by the acids and led to increased production of methane in the digester. Cheng et al. (2018) also reported that biochar adsorption significantly improved short-term AD performance by reducing the VFAs inhibition. However, according to Wang et al. (2018a) the amount of adsorption of ammonical nitrogen increased due to higher surface area of hydrochar. Reza et al. (2015) demonstrated that the removal of ammonical nitrogen was higher (about one-third) and that this was proportional to the surface area of hydrochar. Lü et al. (2016) reported that biochar had little to no impact on the concentration of VFAs, which showed that biochar's adsorption ability had no effect on the inhibition of ammonia and VFAs.

From the above, it appeared that the increase of AD was not caused by the acids or ammonia adsorption. However, in their investigation, just one biochar synthesis process and raw material were examined. The biochar feedstock, particle sizes, and thermochemical process variables all affect how biochar adsorbs substances (Anerao et al., 2022a, b; Mishra et al., 2021). There are numerous other chemical and inorganic inhibitors that may suppress AD in addition to ammonia and acid inhibition. Therefore, using biochar can also make it easier to get rid of the AD inhibitors such nonylphenol, phenols, and heavy metals (Kumar et al., 2023a, b; Abhishek et al., 2023).

5.3 Functional microbial colonization and enrichment

Several studies conducted on functional microbial colonization and enrichment have shown the usefulness of biochar in improved microbial dynamics in the digester, leading to enhanced production of biogas (Su et al., 2019; Li et al., 2018). Biochar increases the release of extracellular polymeric substances, which are critical intermediates, offering support for the attachment of microbes on the surfaces during the formation of biofilm (Tang et al., 2020). Thus, the supplementation of biochar helps in microbial attachment, resulting in a quick formation of granular sludge, and then supports the methanogenic microbes in AD.

Several studies, including that of Wang et al. (2019) support the idea that biochar serves as an efficient transporter that dramatically improves the microbial abundance in AD. The *Methanosaetaceae* formed a biological-based relationship and preferred to adhere to biochar, which could shorten the lag phase time (Indren et al., 2020). These findings were in line with the study that found that supplementing *Methanosarcinales* with biochar helped bioaugmentation of methanogens (Lü et al., 2016). Wang et al. (2018b) found that hydrochar was more beneficial for the attachment of methane producing microbes at higher dosage. Similar findings were reported by Ren et al., (2020) for hydrochar enriched *Methanosaeta*, a strong methanogenic microbe. As a result, the immobilization of methanogens by the addition of hydrochar may facilitate the formation of CH_4 from VFAs (Xu et al., 2018). Additionally, biochar increased the output of VFAs by promoting the formation of biofilms during the early stages of AD (Yin et al., 2019). This result provided more evidence that biochar possessed the ability to improve the AD through functional microbial enrichment. Curiously, both HC-C and HC-L exhibited similar potential pathways in augmenting AD, which involved fostering sludge granulation, boosting the relative abundance of Methanothrix and enhancing key enzyme activities. Additionally, they facilitated potential direct exchange of electrons between methanogens and organic-degrading bacteria (Wang et al. 2020).

Biochar's morphological qualities have a significant impact on the variety of impacts it has on the enrichment of microbial communities. Biochar has also various macro, meso and micro pores that vary in size from 1 to 40 mm (Tang et al., 2020). Therefore, biochar's micro-/macropores might hold varying number of methanogenic cells (Lü, et al., 2016). It is assumed that the proper biochar pore size is essential for biofilm development and granulation (Zhang et al., 2017).

Biochar may enrich *Methanosaeta* sp, which have a pioneering role in the beginning stages of methanogenesis (Lü, et al., 2016). The acids that diffuse in the biochar pores could then be utilized by *Methanosaeta* sp, which are affinitive to biochar-associated regions to complete the acid degradation process by *Methanosarcina* sp (Lü, et al., 2013). The shape of microorganisms is associated with the methanogen accessibility to biochar pores (Lü, et al., 2016). *Methanosaeta* sp and *Methanosarcina* sp colonize the outermost layer of biochar, whereas minor *Methanoculleus* sp colonize its innermost porous region.

The selective enrichment of microorganisms may potentially be aided by biochar's conductive property. Biochar can function as a receiver of electron in respiratory activity and growth of the microbes; hence this may be a characteristic of biochar in general (Yu et al. 2016), Hence, biochar enhances the syntrophic metabolic interaction between the bacterial and archaeal populations and enriches the electro-active microbial consortia, both of which enhance the AD performance (Martínez et al., 2018). Wang et al. (2018c) also reported this type of enrichment on the syntrophic bacteria (*Anaerolineaceae* sp and *Methanosaeta* sp), which helped in the formation of methane in a digester using food waste and activated sludge (dewatered). This may be because of the selective cooperation between various microbial population involved in DIET (Li et al., 2018). Adding biochar to anaerobic fermentation systems altered the microbial community, reducing species richness and diversity. *Firmicutes, Bacteroidetes*, and *Proteobacteria* remained dominant, but their relative abundances shifted. Acid-consuming *Proteobacteria* decreased, while SCFAs-generating *Firmicutes* and *Bacteroidetes* increased. Orders such as *Clostridiales* and *Bacteroidales* were most abundant, with *Clostridiales* notably increasing with biochar addition. This shift favored the accumulation of SCFAs, particularly propionate and acetate, facilitated by *Bacteroidales*. Conversely, acetate-consuming *Erysipelotrichales* decreased significantly. Acidogenic genera like *Proteiniclasticum* and *Bacteroides* thrived with biochar, indicating a beneficial impact on SCFA accumulation (Duan, et al. 2019).

However, it is important to realize the challenges associated with this before drawing the inferences on how biochar conductivity affects the microbial richness during the AD. Cheng et al. (2018) observed that methane generation during swine wastewater AD was only weakly connected to the conductivity of biochar. According to Sunyoto et al. (2017), biochar helps in supporting the growth and activity of the microbial population, leading to the degradation of organic matter, and, therefore, encourage the formation of methanogenic biofilms during the AD. Overall, these findings clearly established that the effect of biochar on microbial dynamics in an anaerobic digester under certain circumstances could mostly be explained by other features (nutrient levels, adsorption, pH, surface morphologies) as opposed to the conductivity. Therefore, further studies are needed to establish a more coherent link between biochar application in AD and its role in enrichment and colonization of potential microbial communities.

5.4 Promoting direct interspecies electron transfer (DIET)

In the course of anaerobic biodegradation, DIET is a prominent electron transfer system, which is thermodynamically more advantageous pathway than other transfer systems such as interspecies hydrogen or formate (Tang et al., 2020) (Figure 3). Using hydrochar material as an electron route between syntrophic partners is typically the foundation of DIET. Thus, the key elements to methanogenic improvement by DIET were successively identified as major characteristics related to electron exchange, such as conductivity (Jiang et al., 2021), redox property or electron-donating capacity (Viggi et al., 2017, Wang et al., 2020), and surface functional groups (Ren et al., 2020). Otherwise, some investigators thought that the main goal of methanogenic improvement should be the generation of the DIET-based syntrophic metabolism. For example, Li et al. (2020) and Zhao et al. (2020) have both observed a discernible increase in the abundance of *Methanosarcina* or *Methanosaeta* sp. following the initial feeding of ethanol into the anaerobic digesters. This observation also validates the implementation of a DIET-based strategy for methanogenic improvement during AD. It was also suggested that improving microbial interspecies interactions would benefit from the microbial aggregation of several functional microorganisms (Zhang et al., 2021).

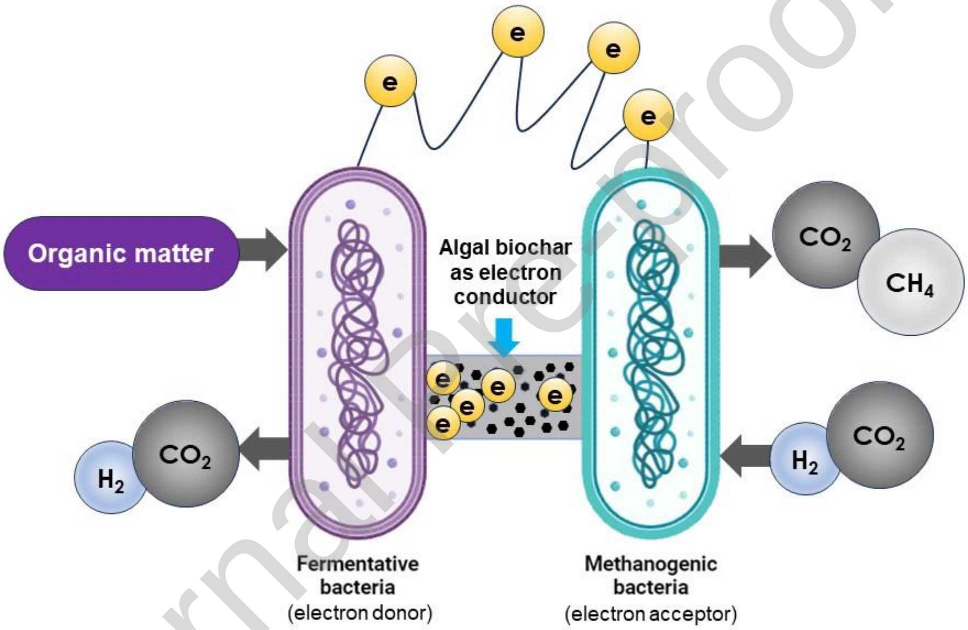

Figure 3. DIET mechanism in biochar-assisted anaerobic digestion

The addition of biochar can improve the dynamics of DIET between methane-producing population and their syntrophic population. For example, *Methanosarcina barkeri* and *Geobacter metallireducens* showed this relationship and led an increase in the capture of electron (77 to 86%) (Barua and Dhar 2017), An analysis of electron stoichiometry by Yu et al. (2016) found that biochar helped in recovering more than 58% of electrons, which were lost during acetate oxidation by *Anaerolineaceae* sp and *Methanosaeta* sp. According to Ren et al. (2020), the AD of glucose was increased by the supplementation of hydrochar increased due to the presence of functional groups on the surface, which contained oxygen. Redox active substances such phenazines and quinones induced electron transport in biochar, which in turn speed up the DIET and enhanced CH_4 production (Shanmugam et al., 2018). According to a study by Zhuang et al. (2018), biochar increased the conductivity and electron transport system in the AD of coal gasification wastewater by 1.9 times and 80.2%, respectively.

It has been shown that during the butyrate AD, biochar promotes the syntrophic breakdown of volatile fatty acids (Wang et al., 2018b). Li et al. (2018) observed that biochar increased electron exchange between bacterial and methanogenic population related to biochar considerably by employing syntrophic oxidation of butyrate and acetate, which was assumed to be caused by the DIET. Furthermore, by promoting hydrogenotrophic methanogens and replacing exo-electrogen, biochar may aid a DIET (Zhang et al., 2017).

In AD process, the conductive materials such as biochar, iron oxides, AC, etc may increase the DIET between the methanogenic and volatile fatty acids degrading population (Mishra et al., 2021). Rotaru et al. (2014a) found that carbon-based materials can act similarly by replacing outer surface cytochromes and/or pili. Because of its broad range of electrical conductivity, biochar increases the AD process by DIET between *Geobacter metallireducens* and *Methanosarcina barkeri* (Chen et al., 2014). *Methanosarcinales* sp. may utilize the conductive surface of charcoal to absorb electrons and produce CH_4 while being distant from acetate (Lü et al., 2016). This study demonstrated that biochar-induced DIET increased *Methanosarcinales* sp affinity for biochar and enhanced their capacity to fend off the inhibitors.

A DIET was observed between *Methanosaeta* sp and its syntrophic bacteria. With the addition of biochar, *Methanosaeta* sp can directly exchange electrons with the bacteria that produce bioelectricity (Rotaru et al., 2014b). Biochar improved the DIET by increasing the concentration of *Methanosaeta* sp and *Geobacter* sp., two possible syntrophic metabolic partners, during the AD of synthetic wastewater (Wang et al., 2018b). Overall, these findings strongly suggest that biochar has a large potential to strengthen the AD based on the DIET by altering the primary microbial metabolic pathways. In addition, it was discovered that the DIET's function changed depending on the operating parameters, such as temperature (Lin et al., 2018), mixing speed (Kariyama et al., 2018), and ammonium content (Yan et al., 2020). Furthermore, Ren et al. (2020) reported that no discernible differences were seen in the lower OLR operations with or without hydrochar, despite the fact that the addition of sludge hydrochar was shown to improve methanogenesis through DIET at the higher OLR operations after the reactors were started with different initial OLR in batch operations. To the best of our knowledge, DIET was acknowledged as a syntrophic methane generation method that is more efficient, particularly when there is a significant level of organic loading (Jiang et al., 2021). Though little is known about how these two OLR regulation approaches affect methanogenesis during AD, it should be noted that variations in inoculation ratios and substrate concentrations may cause an initial change in OLR during batch operations. Furthermore, in batch operations, varying inoculation ratios would alter the microbial community and metabolic pathways in addition to the OLR variations (Lü et al., 2016). Even though this process has not yet been thoroughly studied, it may be hypothesized that the hydrochar-based enhancement for methanogenesis may be impacted by the metabolic alterations under various inoculation ratios (Jiang et al., 2021).

Furthermore, there are several studies on biochar produced from biomass and its application in improving the performance of AD, however, very few literatures were found on algal biochar in AD which showed significant results in terms of high methane yield, proper process stability and microbial community analysis, which needs consideration in future studies.

6. Life cycle assessment of algal biochar integration in the AD process

The environmental consequences of the algal biochar production process and integration with AD processes can be well understood through life cycle assessment of the system. Four steps make up life cycle evaluation, according to ISO 14040 and ISO 14044. These include: (i) defining the goal and scope, (ii) the life cycle inventory analysis, (iii) environmental impact assessment and (iv) life cycle interpretation. The typical goals suggested in literatures defining the different functional units of the system include inlet biomass feedstock, quantity of products after process completion (bioenergy and biochar). Apart from this, the system boundary in terms of different phases such as the carbon emissions, transportation of biomass, pyrolysis, transportation of products obtained and the end-use of the products, all affect the environmental impact calculation. During the life cycle inventory analysis for the system, the requirements for raw materials, energy input, air emissions, production of wastewater, creation of solid waste, and emissions to land, energy consumption of equipment have been usually considered (Osman et al., 2023). The environmental impact analysis of pyrolysis process has suggested that the environmental damage caused by the process can be minimized by using materials deemed as ‘waste’ resulting in more environmentally friendly energy production as opposed to the degradation of land and water usage caused by the cultivation of energy crops. In this regard the production of microalgae seems promising. Further, biorefining of the pyrolysis products including bio-oil and biochar can lead to more sustainable recovery of chemicals and materials. To cite an example, a study by Jiang et al. (2021) reported that the production of nitrogen-doped biochar aerogel-based electrode using

Entermorpha prolifera (an algae in the family *Ulvaceae*) had a life cycle global warming potential 53.1−68.1% lower than the electrode generated from using carbon aerogel-based materials. In another investigation, Wang et al. (2023) reported that *Enteromorpha* based adsorbent preparation through pyrolysis at 500°C had lower environmental impact than *Chlorella vulgaris* and a mixture of both the microalgae in the ratio 2:8. It can be inferred from this study that although microalgal biochar processes can have lower environmental impact values, the choice of microalgae is also crucial.

7. Research needs and circular economy perspectives

Biochar can be used as an inexpensive carbon source, with potential ecological benefits and has diverse applications. Even though recent works on the production and use of biochar from the microalgae and macroalga have proceeded well, there are several research gaps that must be filled in order for its effective applications at large scale. For instance, the feedstock variability (affecting biochar compositions), manufacturing conditions, and activation parameters have a major influence on the properties of the resulting algal biochar. In such circumstances, categories of feedstock compositions may be created based on intended applications to generate the biochar with desirable characteristics. Further, more attention is needed to develop the effective activation methods and to enhance the existing approaches. For this, by combining the benefits of comparable strategies to create integrated activation methods should be explored to provide a more viable option for boosting the activation output.

To determine the possible benefits and drawbacks of certain algal biochar applications, a life-cycle study is necessary. However, it is known that the optimal conditions for the production of biochar are not similar or identical, hence, the criteria must be tailored to individual applications based on the end-products or end-applications. For example, higher temperatures are required for carbonization for biochar formation in microbial fuel cells. In comparison, a carbonization temperature of 400-600°C is ideal for bio-oil processing. As a result of the life-cycle analysis of bio-based products (biochar, bio-oil and syngas), efforts should be made to decrease the environmental effect and expenses. In addition to this, as is known, the cost of producing algal biochar and using it as a sorbent to remove pollutants is determined by a variety of factors. These parameters include feedstock type and availability, its method of preparation, conditions of pyrolysis process, modification of biochar properties, regeneration of biochar for its multiple times usage, etc. Thus, one key issue for future biochar usage optimization is reducing the amount of chemicals necessary for activating biochar, which involves improving the biochar: modifying agent ratio, and thus lowering the manufacturing costs. Furthermore, the use of strong oxidants for the modifying the properties of biochar during the production of tailored biochar could bring environmental contamination risks. As a solution, weak organic acids such as tartaric, acetic, and citric acid could be employed in the manufacture of tailored algal biochars, resulting in a cleaner and more efficient process.

Thus, more studies are needed for producing biochar with specific properties and for specific end-use, employing no-so-harsh chemicals. The process should offer economic and environmental sustainability. Extensive research is needed on various aspects of macroalgal and microalgal biochar such as feedstock selection and variability, production optimization with less or no formation of other products (bio-oil and syngas), less harsh conditions for the production, properties of biochar, including development via heterogenous and homogenous catalysis for developing desired properties, development of structurally improved and bioengineered biochar. Development and application of macroalgal and microalgal bioengineered biochar for agricultural and environmental processes, together with their use in the degradation of organic pollutant will lead to realize zero-waste and help in attaining circular economy in the future. Further, the life cycle assessment of algal biochar integrated

AD systems should take into consideration the biorefinery products of pyrolysis for lower environmental impact.

8. Conclusions

Currently, a great attention is being given towards producing carbon neutral and carbon negative energy, as well as diverse bio-products, while safeguarding the environment and lowering the GHG emissions. Effectively recycling the products and byproducts created within an integrated biochar production system, as well as the CO_2 generated in the process can serve as a feed to grow macroalgae and microalgae, with the goal of creating a zero direct GHG emissions algal biorefinery. The most logical and practical strategy to develop an efficient algal biochar-based circular economy would be to decentralize its production from the local feedstock sources. Such systems would benefit from more homogenous feedstock qualities, as well as the ability to specify and tailor the requisite final product attributes based on local uses, while minimizing environmental effect.

Conflict of interest

The authors declare that they have no conflict of interest.

Data availability statement

Data used in this article have been taken from literature sources which have been duly cited within the article. No additional source of data has been used.

Authors contribution

Ranjna Sirohi, Manish Kumar, V. Vivekanand: Conceptualization, literature review, writing original and revised manuscript; Amita Shakya, Ayon Tarafdar, Rickwinder Singh, Ankush D.

Sawarkar: Literature review, writing original draft; Anh Tuan Hoang: Review and editing; Ashok Pandey: Conceptualization, review and editing

Table 1. Properties of biochar produced from various micro/macro algal biomasses

Macro/ Microalgal-based biochars	**Type of thermochemical treatment**	**Thermochemical treatment conditions**	**Moisture content**	**Volatile matter**	**Fixed carbon**	**Ash content**	**C**	**H**	**N**	**O**	**pH**	**Surface area (m^2/g)**	**Reference**
Sargassum sp.	Pyrolysis	400°C	NA	NA	NA	NA	51.28	3.05	1.38	41.82	NA	NA	Farobie et al., 2022
		500°C	NA	NA	NA	NA	52.58	2.99	1.32	40.65	NA	NA	
		600°C	NA	NA	NA	NA	54.01	2.89	1.24	39.48	NA	NA	
Chlorella vulgaris ESP-31	Wet torrefaction (microwave-assisted heating)	170 °C, RT: 10min	1.76	77.88	15.64	4.72	57.4	8.6	3.8	30.0	NA	NA	Yu et al., 2020
Chlorella sp. GD		170 °C; RT: 5min	5.27	71.36	17.89	5.50	54.8	8.1	10.9	26.2	3.77	2.66	
Spirulina sp.	Pyrolysis (Fixed bed)	750 °C; RT: 120 min	NA	19.6	70.0	10.4	66.6	1.3	9.4	12.3	8.30	2.63	Choi et al., 2020
Chlorella sp. Cha-01	Pyrolysis	600°C for 30 min with N_2 purge	NA	NA	NA	17.48	59.69	1.67	6.38	10.86	NA	6.163	Zheng et al., 2017
Chlamydomonas sp. Tai-03			NA	NA	NA	8.13	79.54	2.35	6.93	6.60	NA	6.163	
Coelastrum sp. Pte-15			NA	NA	NA	15.26	64.405	1.78	5.06	8.55	NA	2.122	
Spirulina	Pyrolysis	400°C	NA	14.0%	44.5	41.5	69.2	NA	NA	18.4	NA	NA	Hong et

	(Microwave-enhanced)	550°C		16.3%	45.7	38.0	61.7			19.6			al., 2017
		700°C		11.4%	47.6	41.0	50.7			24.8			
Chlorella		400°C		26.9%	40.5	32.6	58.6			14.5			
		550°C		27.2%	42.0	30.8	56.1			17.7			
		700°C		13.0%	61.3	25.7	38.9			12.8			
Porphyra		400°C		25.5%	50.7	23.8	70.6			8.4			
		550°C		26.2%	49.1	24.7	51.8			16.2			
		700°C		21.4%	51.6	27.0	65.4			8.4			
Scenedesmus dimorphus	Pyrolysis (fixed bed reactor)	500 ◦C	0.06	4.3	52.4	43.3	50.2	8.0	6.0	35.8	7.96	123	Bordoloi et al., 2017
Anthrospira platensis	Pyrolysis (fixed bed reactor)	500 ◦C; RT: 20 min		28.0	42.0	29.5	51.0	2.5	7.7	18.0	NA	NA	Conti et al., 2016
Tetraselmis sp.	Catalytic pyrolysis	500°C; RT: 60 min; HR: 100°C/min	NA	NA	NA	NA	49.84-48.14	1.55-1.77	4.25-3.57	47.54-45.96	NA	NA	Aysu et al., 2016
Isochrysis sp			NA	NA	NA	NA	43.52-41.38	1.50-1.39	3.72-3.58	53.57-51.31	NA	NA	
Chlorella sp.	Microwave assisted catalytic fast pyrolysis	450-550°C	NA	NA	NA	NA	49.70	4.79	11.07	33.44	NA	NA	Borges et al., 2014
Nannochloropsis			NA	NA	NA	NA	34.21	2.62	5.38	56.79	NA	NA	
T. chui	Pyrolysis	500°C; 10°C/min; RT	6.2	32.6	30.9	30.3	57.8	2.8	5.5	33.6	12	19.03	Grierson et

		20 min; He gas											al., 2011
Macroalgae	Pyrolysis	450°C; RT: 2h	NA	38.15	39.51	22.34	41.08	3.01	2.10	31.13		12.03	Fazal et al., 2021
		550°C; RT: 2h	NA	31.03	43.92	25.05	46.81	1.65	1.40	24.88		25	
		650°C; RT: 2h	NA	27.53	45.74	26.74	51.25	0.94	1.02	20.04		55.3	
Kelp	Pyrolysis	500°C with N_2 gas flow, HR: 7 °C/min	NA	NA	NA	NA	62.31	2.12	2.68	31.26		0.39	Son et al., 2018

Table 2. Operating conditions of micro/macro algal biomass thermal treatment with product yield

Name of algae	**Process**	**Temperature (°C)**	**Yield of biochar/ hydrochar (%wt)**	**Retention time**	**Other products**	**References**
Chlorella vulgaris	Hydrothermal carbonization	180 – 220	78 – 82	15-60 min	NA	Jabeen et al., 2023
Sargassum sp. (Macroalgae)	Pyrolysis	400	> 80 ≈70 ≈50	10 min 30 min 50 min	NA NA NA	Farobie et al., 2022
		500	> 75 ≈50 ≈40	10 min 30 min 50 min	NA NA NA	
		600	≈70 < 50 ≈30	10 min 30 min 50 min	NA NA NA	
Chlorella sp.	Pyrolysis	500 and 350	25.1	30 min	NA	Bolognesi et al., 2021
Macroalgae	Slow Pyrolysis	450 550 650	61 65 68	120 min	NA NA NA	Fazal et al., 2021
Chlorella vulgaris (High-ash low-lipid)	Hydrothermal Carbonization	180–250	26.3–41.9	0.5–4.0 h	NA	Khoo et al., 2020

Nannochloropsis Oceanica	Oxidative torrefaction	200-300	96.42 - 49.59	15-60 min	NA	Zhang et al., 2019
Chlorella sp.			93.26-50.12		NA	
H. reticulatum (HR)	Hydrothermal Carbonization	150-270	72-32	60 min	NA	Park et al., 2018
C. vulgari			71-50		NA	
Chlorella vulgaris	Oxidative torrefaction	200	41.08	30 min	NA	Phusunti et al., 2018
Arthrospira platensis	Hydrothermal carbonization	190–210	21.6–36.7	2–3 h	NA	Yao et al., 2016
Tetraselmis sp.	Catalytic pyrolysis	500	79-82	60 min	Liquid yield: 23-25%	Aysu et al., 2016
Chlorella pyrenoidosa	Catalytic hydropyrolysis	150 – 450; RT:; Applied Pressure (MPa): H_2 (1 atm – 8)	12.3 – 74.0	5 – 12 min	NA	Chang et al., 2015
Algae Meal	Microwave-Assisted Pyrolysis	750; HR: 5°C/min; 100 of N_2	27.83	60 min	Liquid yield: 35.02%; Gas yield: 37.15	Ferrera-Lorenzo et al., 2014
Chlamydomonas reinhardtii	Pyrolysis (fixed bed reactor)	350	44	20 min		Torri et al., 2011
Undaria pinnatifida, *Laminaria japonica*, *Porphyra tenera* (Macroalgae)	Slow pyrolysis	300-600	40-60	60 min	Liquid yield: 22 – 40%; Gas yield: 15 – 25%	Bae et al., 2011
Scenedesmus almeriensis	Pyrolysis	400; He as purge gas	44	30 min	Liquid yield: 41%; Gas yield: 14.5%	Beneroso et al., 2013
		800; He as purge gas	31		Liquid yield:	

					48.2%; Gas yield: 20.7%	
Gracilaria	Microwave assisted pyrolysis	100 – 300	32.2 – 71.0	NA	NA	Budarin et al., 2011
Chlamydomonas reinhardtii	Hydrothermal carbonization	200; Pressure: <2 MPa	25.3–45.7	< 60 min	NA	Heilmann et al., 2010

Table 3. The impact of addition of biochar on biomethane yield enhancement from different organic biodegradable waste

Reference	**Feedstock**	**Experiment**	**Biochar feedstock**	**Biochar Dosing**	**Enhanced biomethane**
Zhang et al., 2023	Food waste & waste activated sludge	Mesophilic (35-37 °C) thermophilic (55 °C)	Kitchen waste	15 g/L	10.92%
Duan et al., 2023	Waste activated sludge	Biochar at 516 ◦C mesophilic for AD	Digested sludge	15 g/L	50 %,
Batta et al., 2023	Bio-oil	Mesophilic	Digestate derived biochar and activated carbon	10 g/L	83%
Di et al., 2023	Chicken manure	Mesophilic	Nano-Fe_3O_4 modified biochar	15 % nano-Fe_3O_4 biochar	140.20%
Liu et al., 2023	Cow manure	Biochar produced at 600 °C and mesophilic	Potato, Rape seed and wheat straw	5% of all biochar	35.45%–52.66%
Ruan et al., 2023	Pigment sludge	Plexiglass reactor at Mesophilic	Reed straw	3 % biochar & modified biochar	37.20%
Liu et al., 2022	Sewage sludge and food waste	Thermophilic	Biogas residue	8.0 g/L	39.35%
Wang et al., 2023	Food Waste	Biochar supported nano zero-valent iron and mesophilic	Sugarcane bagasse	0.60, 1.01 and 1.41	31.4% and 24.8%

Zhang et al., 2022	Livestock manure	Effect of sulfamethazine on manure AD mediated by biochar	Corn stalks	5 g/L	27.41%
Collins et al., 2023	Chicken litter	Coupling a biochar-packed anaerobic filter (AF) to a batch leach bed reactor (LBR)	Wood or agricultural residues	1g/L	10%
Zhu et al., 2022	Food waste	Mesophilic	Fermented sludge and wheat straw	0, 10 g/L of SS600 and 10 g/L of SS1000	86.3% and 64.9%
Salehiyoun et al., 2022	Municipal solid wastes	Mesophilic 38 ^{o}C	Gasification of wood pellets at 700 ^{o}C	30 g/ L	Up to 36.6%
Başar et al., 2022	Switchgrass	Response surface method at optimum pretreatment (200 ◦C/min RT)	Pine, spruce, and cedar woods at 450–550 ◦C	2, 9, 16 g/g VS	256.9 ml CH_4/g (VS)
Madrigal et al., 2022 Al.	Cheese whey	Mesophilic	Bovine manure biochar	2 g/mol	58.40%
Ovi et al., 2022	Food waste/sludge	Mesophilic	Rice husk and palm tree	5, 10, and 15 g/L	36.5%, 19.25%, 19.15%
Jiang et al. 2022	Glucose (5 g/L), Sodium bicarbonate (4 g/L), Ammonium chloride (0.35 g/L),	Mesophilic	Algal biochar and H_2O_2-oxidized algal biochar	10 g/L	58.7%
Liu et al., 2022	Sewage sludge and food waste	Thermophilic	Residue biochar, or coconut shell, or corn stalk biochar	7.5-15.0 g/L	46.10%
Che et al., 2022	Synthetic salty organic wastewater	Mesophilic	Iron-based biochar derived from waste-activated sludge	10 g/L	75.40%

Lee et al., 2022	Food waste	Thermophilic	Sludge	1 g/L	20–35%
Jiang et al. 2021	Sludge	Mesophilic	Algae biochar	10 g/L	12.2- 17.5%
Zhang et al., 2020	Algal and Food waste	Mesophilic and Thermophilic	Algal biochar	15 g/L	12–54%
Wang et al. 2020	Seed sludge & *Laminaria* HTC liquid fraction	Mesophilic	Microalgae and Macroalgae-based hydrochar	Hydrochar: seed sludge (0.25:1, 0.5:1, 1:1, and 2:1)	31.4-36%

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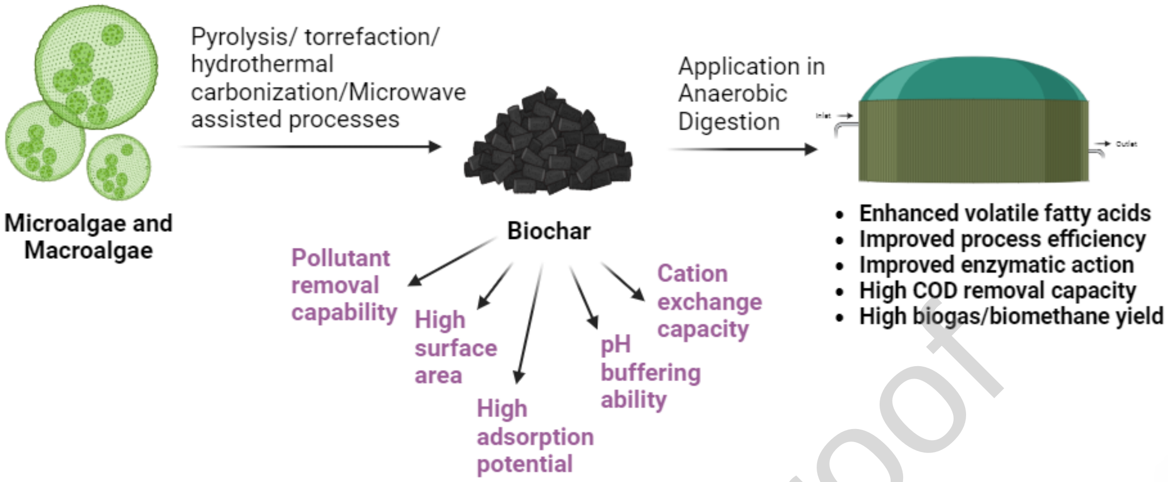
Graphical abstract



Conflict of interest

The authors declare that they have no conflict of interest.

Statement

We declare that all the authors have seen the manuscript and have agreed to its submission to ETI and that this is the original article prepared by the authors. We also declare that we The authors declare that they have no conflict of interest.

Highlights

- Structural, functional and electrical characteristics of algal biochar have been discussed
- Algal biochar enhances methane production during AD through increased methanogenic activity
- Algal biochar increases DIET due to higher electrical conductivity
- Modification of algal biochar using organic acids may be more economic