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Review article

Lipid-extracted algae as a source of biomaterials for algae biorefineries

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ABSTRACT

The repertoire of novel biobased materials is continually expanding as they represent green alternatives to carbon-intensive fossil materials. Lipid-extracted algae (LEA) biomass is a promising feedstock for the production of a spectrum of biobased materials, such as hydrochar and biochar, electrodes in microbial fuel cells (MFCs), supercapacitors, biocomposites, biopolymers, activated carbon including N-doping, and biosorbents. By selecting appropriate process conditions, these renewable products can be designed to possess desirable properties and, at the same time, be more sustainable. Most importantly, we view LEA as a potentially significant additional source of revenue for algae biorefineries that can accelerate the commercial development of algae. The present study assesses the utilization of LEA for the production of biobased materials, their applications and sustainability profile, and future trends.

1. Introduction

Increasing concerns about carbon emissions from fossil fuels contributing to climate change continue to boost interest in sustainable materials from natural resources. Products manufactured from lignocellulosic and algal biomass have emerged as promising alternatives that can replace conventional petroleum-based products [1]. These resources can be processed to engineer a plethora of green and sustainable products, such as sorbents, fibers, composite materials, plastics, and catalysts [2]. In 2018, the market for biobased materials was worth $13.3 billion and is expected to grow at an impressive compound annual growth rate (CAGR) of 26% from 2019 to 2026 [3].

Among biobased resources, microalgae are being viewed as a potentially sustainable source of biofuels and bioproducts that can aid the transportation and manufacturing sectors, respectively, in lowering greenhouse gas emissions. Algae are fast-growing photosynthetic microorganisms that can be cultivated in saline or freshwater or even wastewater to produce biomass (cell mass) composed mainly of lipids (4–45%), proteins (6–71%), and carbohydrates (4–64%), whose intracellular concentration varies among algae species and depends on growth conditions [4,5]. Lipids, among the most valuable algal products, comprise mostly C14-C18 fatty acids destined for jet biofuel and biodiesel production, while omega-3 fatty acids, like the C18 alpha-linolenic acid (ALA), the C20 eicosapentaenoic acid (EPA), and the C22 docosahexaenoic acid (DHA), are excellent sources of nutraceuticals and dietary supplements [6]. The algal product market was $3.8 billion in 2017 and is forecast to grow by 2023 to $5.2 billion at a CAGR of 5.4% [7].

As a nascent technology, algae biorefineries are still not commercially feasible because their economics cannot be viable solely on the base of lipid production, as evidenced by the lack of commercial operations. Instead, an entire portfolio of value-added algal products will be needed to complement the lipids and make algae profitable. It is in that context that we consider lipid-extracted algae (LEA) biomass a promising source of biobased materials, which can potentially replace fossil-derived products and pave a path towards a cost-competitive and more sustainable algae biorefinery, as depicted in Fig. 1.

After rupturing the cells physically or chemically, lipids are extracted from algae using organic solvents, such as chloroform or hexane (Fig. 1). Lipid extraction follows either a dry or a wet route. The dry route uses conventional extraction methods, such as the Bligh & Dyer method and the Folch method, which have high extraction efficiency, but is energy-intensive due to the drying required prior to lipid extraction [5]. The wet route requires less energy in a biorefinery by avoiding the drying step, but needs a cell disruption step to increase lipid extraction yield. Thermochemical processes, such as hydrothermal liquefaction (HTL), look promising for lipid conversion to biocrude oil, which is further processed into biofuels [8]. HTL of microalgae is carried out using subcritical or supercritical water extraction with subcritical conditions reportedly being more effective [8]. It has several advantages compared

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to conventional lipid extraction methods, including high throughputs, high energy and separation efficiencies, and production of drop-in biofuels, making it a promising technology [5,9]. The main products of HTL are biocrude oil and water-soluble organics, which can be utilized as nutrients for microalgae cultivation [10]. However, it cannot be utilized if the primary target algal product is a high-value intracellular component, such as omega fatty acids, carotenoids or pigments.

The residual biomass after lipid extraction, termed LEA or defatted algae, can be generated in significant quantities given that it accounts for approximately three times the mass of the extracted lipids [11]. LEA mainly consists of carbohydrates, proteins, and inorganic elements (ash), as depicted in Table 1, and can be converted to biofuels and bioenergy (biogas), animal feed, human health products, and biomaterials [12–14]. In some applications, such as food, feed, and nutraceuticals, LEA will need to be first purified before use, since lipid extraction utilizes solvent (e.g. chloroform or hexane) [15]. A recent review summarized LEA application in bioenergy, animal feed, bioethanol, and human health products [6]. The present study focuses on LEA conversion to value-added biomaterials and critically examines their manufacturing, applications, and sustainability for future commercial deployment as part of the portfolio of products manufactured by algae biorefineries.

2. Biomaterials from lipid-extracted algae (LEA)

LEA biomass, a byproduct of algal lipid extraction, is a renewable source for synthesis of a spectrum of materials, including hydrochar and biochar, electrodes for microbial fuel cells (MFC), supercapacitors, biocomposites, biopolymers, activated carbon, N-doped materials, and biosorbents (Fig. 2). Depending on the conditions of LEA processing, these renewable products can be tailored to possess a wide range of desirable properties similar to those of their non-renewable counterparts and simultaneously achieve low cost, high performance, and sustainability, as detailed in Table 2.

2.1. Biosorbents and activated carbon

The build-up of toxic and carcinogenic metals and metalloids in both aquatic and terrestrial ecosystems has been causing global health problems. The conventional methods employed for removing these pollutants, such as coagulation, precipitation, reverse osmosis, and ion exchange, tend to be costly or inefficient and generate toxic sludge creating a need for development of natural biosorbent materials [38]. Biosorbents have the advantage of possessing on their surface diverse and abundant polar functional groups, such as hydroxyl, carboxyl, phosphate, and sulfate, making them highly efficient, sustainable, and cost effective [23]. LEA-based biosorbents without modification are reported to achieve high metal removal and sorption efficiencies, while generating minimum secondary effluent pollution [38,39]. After use, the LEA biomaterial can be disposed of in landfills with a low environmental impact or can even be converted further to biochar [40]. By thermally converting LEA to biochar, as detailed later, the density of functional groups present on the particle surface increases, thereby making the material a more efficient adsorbent for heavy metal mitigation in wastewater treatment.

A related LEA application is activated carbon, a material with high surface area (900–3000 m^2/g) that is utilized in drinking water purification [41], wastewater treatment [41], metal recovery [42], food industry [43], landfill gas emission purification [44], and other applications. Activated carbon can be produced from renewable resources, such as lignocellulosic biomass and algae, through hydrothermal processing followed by an activation step [45]. Indeed, LEA was successfully converted to activated carbon through a two-step process, carbonization and activation, with a surface area of 840 m^2/g comparable to commercial activated carbon with a surface area of 500–1500 m^2/g [24]. Both LEA and activated carbon can be used in wastewater treatment, drinking water purification, and landfill gas purification.

In order to improve the physicochemical properties of carbon materials, the number of active sites for ion adsorption is increased by introducing nitrogen (N) to the carbon surface [46]. Utilization of glucose for the preparation of carbon materials has been reported to increase nitrogen retention [26]. N-doped activated carbon from algae has been used for CO_2 capture in gaseous streams [25,26,47]. In the latter studies, the micropores of N-doped porous carbon had high specific volume, which resulted in high CO_2 adsorption performance [25]. Activated carbon with nitrogen modification demonstrates good

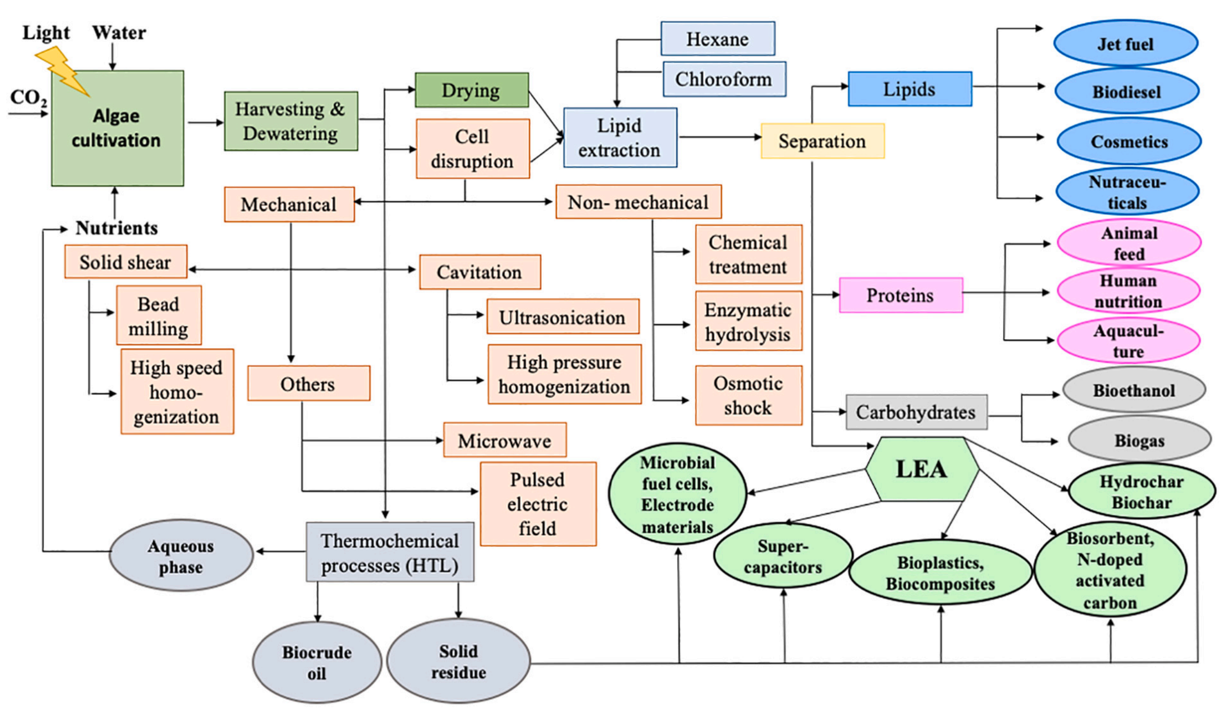

Fig. 1. Block diagram of the envisioned algae biorefinery that incorporates conversion of lipid-extracted algae (LEA) to biomaterials [4,5].

Table 1
Composition of LEA calculated[a] for various algae strains on a dry weight basis.

LEA composition (g/100 g DW)	*Chlorella vulgaris*	*Chlorella sorokiniana*	*Scenedesmus* sp.	*Nannochloris bacillaris*	*Tetracystis* sp.
Carbohydrates	8.2	21.5	36.8	62.7	61.5
Proteins	78.9	71.1	48.3	33.3	34.6
Ash	12.9	7.5	14.9	4.0	3.8
Reference	[14]	[16]	[16]	[14]	[14]

[a] For each strain the calculations involved subtracting the lipid content from the reported algal biomass composition and recalculating the content on a lipid-free basis.

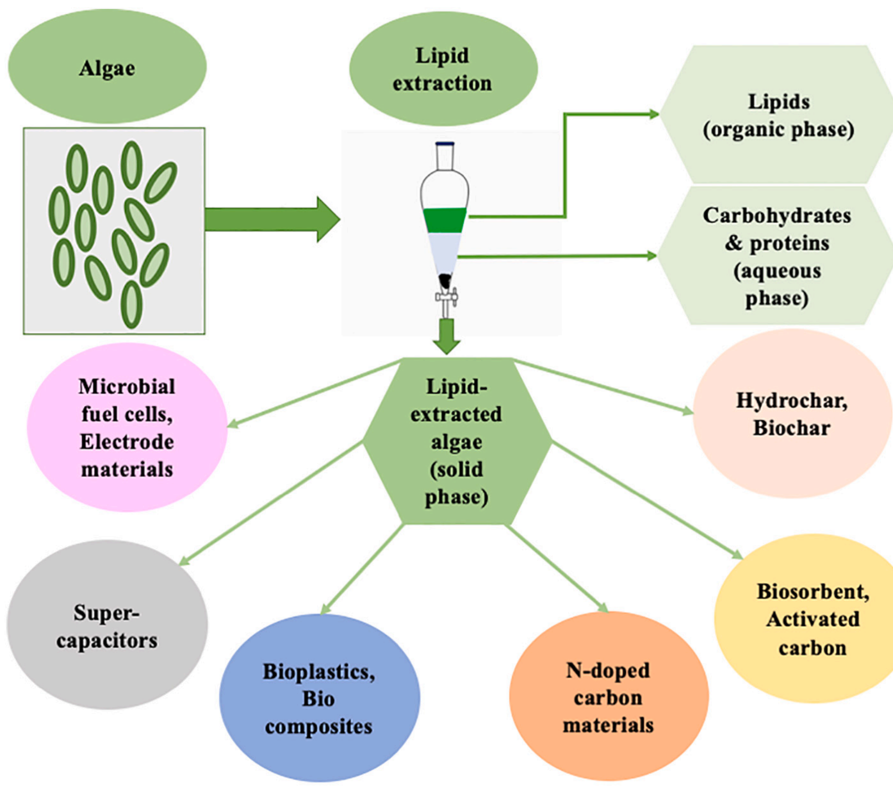

Fig. 2. Biomaterials from lipid-extracted algae (LEA).

reusability and high selectivity [47]. Additionally, N-doped porous carbon has been utilized for separation of light hydrocarbons and gas purification [27,28]. As a result, algae-based N-doped activated carbon is a promising adsorbent for industrial separations, such as of C3/C1/C2 compounds and of C_2H_6/CH_4, CO_2/CH_4, and CO_2/H_2. Overall, activated carbon represented a sizeable market of $2.9 billion in 2019 that is projected to reach $4.0 billion by 2027 [48]. Hence, in our opinion, N-doped activated carbon constitutes an attractive LEA application that can be scaled up to mitigate global warming potentially displacing activated carbon from fossil sources. Naturally, the higher efficiency of activated carbon that stems from the larger number of functional groups present on its surface comes with a higher production cost, as it involves more intensive processing of LEA, thus there is a tradeoff between cost and efficiency.

2.2. Hydrochar and biochar

Hydrochar and biochar are carbon-rich solid materials commonly produced by thermochemically processing algal or cellulosic biomass. They find use in various applications, such as soil amendment, solid fuels, capacitors, low cost adsorbents, wastewater treatment, and carbon sequestration [49,50]. Hydrochar is produced in a wet (aqueous) environment under moderate temperature (180–350 °C) and pressure (2–10 MPa), whereas biochar is produced in a dry environment (moisture below 10%) under more energy-intensive conditions at temperatures up to 600 °C [51]. Hydrochar and biochar produced from LEA have been utilized as solid fuel, microwave absorber, soil amendment in crop production, and carbon sequestration (Table 2). LEA from *Chlorella vulgaris* was converted to hydrochar through hydrothermal carbonization (HTC) and was successfully utilized as a solid fuel for waste disposal and energy recovery [15]. Interestingly, LEA-based hydrochar is produced under milder conditions than from lignocellulosic feedstocks, such as sugarcane bagasse and pine wood [16]. Using milder conditions significantly reduces the use of energy and hence the cost of the process, while at the same time increasing the sustainability footprint of LEA-based products and their prospects for commercialization.

Biochar is produced using either conventional slow pyrolysis or microwave-assisted pyrolysis that requires higher temperatures (up to 600 °C) than HTC [52]. Biochar produced from LEA of marine *Chlorella* sp. was utilized as a microwave absorber for the pyrolysis of the algal residue for bio-oil production [17]. Microwave absorbers are materials that convert microwave energy to heat for treatment of biomass. Biochar is a promising microwave absorbent thanks to its high ash content (56%) that helps optimize production of bio-oil by reducing heating time and increasing bio-oil yields up to 46% [17]. Biochar produced from LEA was also used as soil amendment to enhance crop productivity and for

Table 2
Sources, process conditions, and applications for LEA-based products.

Biobased material	LEA source	Conversion process conditions	Application	Product properties	Reference
Hydrochar	*Chlorella vulgaris*	Hydrothermal carbonization under anaerobic conditions at 180–220 °C for 30 min	Solid fuel production and waste disposal	High heating value, stable combustion characteristics at high temperatures & low sulfur and ash contents	[15]
	Spirulina maxima	Hydrothermal carbonization at 175 °C for 30 min	N.R.	Energy-dense hydrochar	[16]
Biochar	*Chlorella* sp.	Slow pyrolysis in N_2 environment at 450 °C for 60 min	Microwave absorber for bio-oil production	Surface area of 266 m^2/g and high ash content (56%) good for microwave absorbent	[17]
	C. vulgaris	Fast pyrolysis using fluidized bed reactor at 500 °C	Soil amendment for enhancing crop productivity	High concentrations of trace elements N, P, K, Ca, and Mg	[18]
		Pyrolysis up to 500 °C for 30 min under continuous nitrogen gas flow	Carbon sequestration	Presence of functional groups and irregular porous structure	[19]
	Cladophora glomerata	Hydrothermal liquefaction at 350 °C for 15 min	Wastewater treatment, low-cost efficient adsorbents	Oxygen-containing acidic functional groups on surface suitable for adsorption	[20]
		Pyrolysis at 300–450 °C under N_2 flow	N.R.	Total pore area of 20 m^2 g^{-1} and small pores with functional surface groups. Removal efficiency of 89.9%- 93.7%	[21]
Biosorbent	*Chlorella* sp., *Chlamydomonas* sp. and *Coelastrum* sp.	Flasks with Cd solutions shaking at 100 rpm, 30 °C & pH 7.5	Cadmium removal	Functional hydroxyl, carboxyl, amino, and amine groups	[22]
	Scenedesmus sp.	Sorption experiments performed using aqueous dye solutions of Acid Blue 161	Dye removal from industrial wastewater	Surface area of 3.47 m^2/g, irregular surface roughness with cavities, functional groups on surface	[23]
Activated carbon	*C. vulgaris*	Carbonization- activation under flowing N_2 and CO_2	N.R.	Nitrogen content of 3.6–9.6 wt% and 54.6–68.4 wt%	[24]
	Chlorococcum sp.	Hydrothermal carbonization coupled with KOH activation or NH_3 modification	CO_2 capture at low cost	High CO_2 uptake of 4.03 mmol g^{-1} at 25 °C and 6.68 mmol g^{-1} at 0 °C	[25]
N-doped carbon	*Spirulina platensis*	Hydrothermal co-carbonization of microalgae and glucose, followed by activation with potassium hydroxide	CO_2 capture	Adsorbents with high CO_2 capture capacity, among the highest for porous materials, up to 7.4 mmol g^{-1} at 0 °C	[26]
	Nannochloropsis. salina	Carbonization process at 600–800 °C for 1 h under N_2 atmosphere. Chemical activation with HCl	Separation of light hydrocarbons	Materials exhibited outstanding adsorption capacity with excellent separation selectivity of C3/C1, C2/C1, and C3/C2 at 25 °C and 1.0 bar	[27]
	Nannochloropsis salina	Hydrothermal carbonization at 200 °C and chemical activation with KOH at 600 °C	Separation of C_2H_6/CH_4, CO_2/CH_4, and CO_2/H_2	High selectivity for separating C_2H_6/CH_4, CO_2/CH_4, and CO_2/H_2 gas mixtures	[28]
Bioplastic	*Hydrodictyon reticulum*	Production of lactic acid via fermentation and polymerization to polylactic acid (PLA)	PLA manufacturing	N.R.	[29]
Fibers	*Botryococcus braunnii*	LEA proteins and PEO mixed at pH 7 and pH 12 at 25 °C for 12 h in water, NaOH (1%) or acetic acid	Fibers	FTIR revealed changes in the secondary structure of LEA proteins that enhance physical chain entanglement in the polymer solution	[30]
Bio composite	*Nannochloropsis salina*	LEA mixed with water at 400 rpm for 5 min, followed by ultrasonic cleaner for 15 min. PVA added to the suspension and stirred at 400 rpm for 5 min	Filler in biocomposite fabrication with polyvinyl alcohol for 3D printing	Improved thermal stability, but reduced tensile strength and elongation at break. Addition of PD as plasticizer significantly enhanced properties	[31]
	Nannochloropsis gaditana	LEA and polybutylene adipate-*co*-terephthalate extrusion at 140 °C for 2 min at 100 rpm and injection molding at 30 °C	Biocomposite production for agricultural films	Plasticization improved tensile modulus and elongation	[32]
Anode material	*Chlorella* sp.	LEA dispersed in 0.05 M $SnCl_2$ and autoclaved at 195 °C for 12 h. Then heated at 500 °C for 1 h and at 800 °C for 1 h under 5% H_2–95% Ar	Nano/micro hierarchical Sn/C anode materials for lithium-ion batteries.	Uniform elemental distribution and higher surface area compared with the non-extracted Sn/C	[33]
	Nephroselmis sp. KGE8	α-Fe_2O_3 and N- doped carbon composites were synthesized using one-pot spray pyrolysis	N-doped carbon with α-Fe_2O_3 for lithium-ion batteries	Stable carbon materials with excellent cycling performance. High discharge capacity	[34]
	C. vulgaris	Anodic bacterial community acclimatized with LEA by mixing pretreated cow manure with LEA, followed by anaerobic incubation at 30 °C for a week	Electron donor anode substrate in microbial fuel cells	Power density of 2.7 W m^{-3} and electrical energy of 0.1 kWh m^{-3}	[35]
Supercapacitor	*Nanochloropsis salina*	Production of porous carbon and CoO composite electrodes	Electrode material for electric double layer capacitors	Electrochemical measurements revealed that micropores and mesopores significantly contributed to the capacitance in the carbon electrodes.	[36]
	Enteromorpha prolifera	HTC followed by mild activation with KOH	Electrodes for supercapacitors	Excellent electrochemical properties, such as high specific capacitance	[37]

N.R.: not reported.

carbon sequestration [18,19]. Furthermore, it was successfully utilized in wastewater treatment as low-cost adsorbent material for heavy metal removal with high efficiency [20,21]. The production cost of various biochar/hydrochar products ranges between $0.20 and $0.50 per kg, compared to commercial adsorbents, such as ion-exchange resins, that cost up to $150 per kg [53]. We believe that biochar and hydrochar can potentially replace synthetic adsorbents in remediation by providing a competitive cost.

2.3. Bioplastics and biocomposites

In the past decade, plastic waste pollution has become a global challenge necessitating the need for biodegradable and sustainable plastic products, since recycling of plastics is not a sufficient solution per se. Renewable and biodegradable plastics, such as polylactic acid (PLA), polybutylene succinate, and polyhydroxybutyrate, can be produced from various renewable resources, such as sugarcane, corn, woodchips, and algae [54–57]. LEA can potentially serve as a more sustainable feedstock, since algae do not compete with food [56]. Carbohydrates, a major component of LEA (Table 1), can be converted through fermentation to lactic acid, which is then polymerized to PLA [29,57]. Additionally, proteins extracted from LEA can be used for plastic fiber manufacturing, when combined with polyethylene oxide (PEO) to generate electrospun protein concentrate fibers, as PEO and proteins from LEA are compatible with each other [30].

There has been great interest in the development of biocomposites due to their important attributes, such as cost effectiveness, renewability, and biodegradability, that can serve well a variety of industrial applications in the automobile, aerospace, and construction fields [58]. LEA was used as a filler in biocomposite fabrication with polyvinyl alcohol (PVA), which improved the thermal stability of the PVA matrix, although it lowered tensile strength requiring addition of poly-diallyldimethylammonium chloride (PD) as plasticizer [31]. The PVA-LEA-PD biocomposites are promising materials for 3D printing. Moreover, biocomposites are produced by extrusion and injection molding that combines LEA and polybutylene adipate-*co*-terephthalate (PBAT) for agricultural films, which biodegrade after prolonged contact with soil [32].

In the last few years, algal carbohydrates have attracted interest as a feedstock for bioplastic production by various industries, including shoe and clothing companies, but commercialization is still years away. Significantly more research is clearly needed to fine tune the properties and cost of algae-based bioplastics before they can attract the attention of investors.

2.4. Microbial fuel cells, electrode materials and supercapacitors

Microbial fuel cells (MFCs) are bioelectrochemical systems that produce electricity from chemical energy using microorganisms as catalysts in a bioanode and/or a biocathode [59]. They are considered a clean energy producer, since they do not generate any waste and have a negligible carbon footprint. MFCs have found use in wastewater treatment, heavy metal removal, and CO_2 sequestration [60]. Algae used in MFC manufacturing are usually cultivated in the cathode chamber by utilizing sunlight, captured atmospheric CO_2, and industrial wastewater as source of nutrients and water [61]. In a recent study, LEA was successfully utilized as anode substrate, whereas *C. vulgaris* was cultivated on the cathode [35]. More specifically, LEA served as electron donor that reduced costs by eliminating the need for an external electron donor substrate [35]. Although whole algae have been extensively researched for utilization in MFC [62], more research is still needed for LEA incorporation to reap the benefit of lowering MFC production costs.

LEA biomass has also been utilized in the production of either nano and micro Sn/C anode materials or porous N-doped carbon for lithium ion batteries commonly used in electronic applications, such as energy storage, automobiles, computers, and cell phones [63]. The morphological and chemical features of LEA reportedly make it suitable for high energy anode materials as it contains functional groups, such as hydroxyl and amino groups, while its uniform spherical particle shape facilitates the manufacture of anodes [33]. Moreover, N-doped carbon supported with α-Fe_2O_3 was stable with excellent cycling performance [34]. Production of these biomaterials from LEA is reported to be more cost-effective and environmentally friendly, while their electrochemical performance is strong [33].

Supercapacitors represent another promising potential market for LEA, as they deliver high-power density, fast charge/discharge rates, and long-life cycles [36]. Nanoporous algae-based activated carbon composites of CoO were synthesized as electrode materials with better performance compared to pure CoO electrodes [36]. The pores present on the surface of algal activated carbon enhanced the electrochemical performance of the matrix. Activated carbon and N-doped activated carbon derived from algae through chemical activation with KOH were reported to be suitable materials for supercapacitors that can surpass the performance of commercial supercapacitor materials [37,64,65]. Hence, LEA-based supercapacitors have the potential to serve as a renewable alternative to current supercapacitors.

3. Conclusions

In order for algal biofuels and bioproducts to become more cost-competitive with fossil ones while offering sustainability advantages, LEA needs to be monetized. LEA-based biomaterials have the potential to enhance the overall economics of the algae industry by generating additional revenue from coproducts that supplement the value of the primary algal products, such as biodiesel, jet fuel, cosmetics, and nutraceuticals. The present study illustrates the potential of LEA to be converted into a range of promising value-added materials, particularly biosorbents, N-doped activated carbon, hydrochar, biochar, bioplastics, microbial fuel cell electrodes and supercapacitors. Overall, as demand for sustainable products increases, LEA can serve as a low-cost feedstock that fosters sustainability within the green bioeconomy of the future with applications in a wide range of sectors, including energy, plastics, remediation, and composite materials.

4. Future perspectives

Although clearly LEA can be utilized in a variety of applications, there is still a lack of technoeconomic analysis and life-cycle assessment for algae operations integrated with LEA conversion to value-added products, so further efforts are warrantied in that direction. Moreover, the application fields of LEA can be further expanded by exploring its use in biosensors, tissue engineering, drug delivery, packaging materials, and construction materials. In our opinion, low cost adsorbents represent a mature application for LEA. Carbon materials are commonly utilized as adsorbents for remediation of metals/heavy metals, pesticides, antibiotics, and organic compounds from water and soil. Hence biochar, modified hydrochar, and activated carbon from LEA can be employed in hazardous waste treatment, such as landfill leachate that contains heavy metals, and in the removal of nitrogen and phosphorus that promote eutrophication. As hydrochar does not decompose at low pH values below 4 [66], we believe that hydrochar or modified hydrochar should be assessed for metal remediation of acid mine drainage, which is the outflow of acidic water from metal and coal mines [67]. Finally, N-doped algal activated carbon could be used for treatment of *per*- and polyfluoroalkyl substances (PFASs) in aqueous phases [68]. By integrating production of LEA biomaterials into the infrastructure of algae biorefineries, there are opportunities to reduce overall production costs and enhance the sustainability of algae technologies.

CRediT authorship contribution statement

MT performed the literature search, MT and NA drafted the manuscript, and GPP and JNK contributed to the narrative and edited the manuscript. All authors approved the final manuscript.

Declaration of competing interest

The authors and funding agencies have no conflicts of interest to declare. No conflicts, informed consent, and human or animal rights are applicable to this paper.

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