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REVIEW

Carbohydrate Biolubricants from Algae and Cyanobacteria

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Abstract

Lubricants are used to prevent friction that causes resistance and heating up in oil drilling; ocular and orthopaedic implant materials; with Metal Working Fluids (MWF) and in general anti-wears. Conventional lubricants are either non-renewable petroleum-based or environmentally unfriendly synthetic materials, while biolubricants are renewable and eco-friendly of 'biological origin'. Biolubricants are derived from either lipids/oils or carbohydrates obtained from living sources like animals (Chitosan, Hyaluronic acid), plants (Gum arabic, Guar gum), algae/cyanobacteria (oil, polysaccharide) and other microorganisms like bacteria (Gellan, Xanthan gum, Dextran, Lichenysin, Surfactin), yeast (single cell oil), filamentous fungi (esters). Lipids/Oils have varied uses in energy (biodiesel), food and other sectors, and are therefore in high demand, while extracellular polysaccharides (EPS) are of limited use at present. Biolubricants from animals have limitations. Similarly, the use of higher plants also has limitations as they require large arable land; only a part of their biomass, not the entire plant useful, and have long-life cycles compared to microorganisms. However, microorganisms like bacteria need specialized equipment and techniques to cultivate, increasing production costs. But, Algae and Cyanobacteria are photoautotrophs with minimal growth requirements and easy to cultivate. The viscous algal/cyanobacterial polysaccharides have remarkable rheological properties useful in reducing friction. Among algae, the seaweed products like agar, carrageenan and alginic acids are shown to provide lubrication, but they are needed more for other uses, and the macroalgae cultivation has its own limitations. Instead, Microalgae and Cyanobacteria pose relatively less problems and produce polysaccharides with remarkable rheological properties and physico-chemical characteristics, fit for lubrication. They can be cultivated round the year, some with seawater or even with wastewater or effluents (resulting also in bioremediation), reducing the cost of biomass production. This review highlights the emerging importance of carbohydrates especially the extracellular polysaccharides (EPS) of Algae and Cyanobacteria with commercial potential as Carbohydrate biolubricants. In addition, algal/cyanobacterial biomass production, together with optimizations required to maximize polysaccharides have been reviewed and the physicochemical properties including molecular weight, crystallinity, thermal characteristic and rheology of polysaccharides useful as biolubricants are discussed.

Keywords Algae · Biolubricant · Cyanobacteria · Polymer · Polysaccharide

Introduction

Lubricant can be a substance that is a solid/liquid/ solid–liquid/ liquid–liquid or gas that can reduce friction amid two surfaces and usually increase smooth functioning; decrease heat; act as a rust protector; resist fire and also temperature extremes [1, 2]. Additives, are mostly polymers, which improve viscosity; reduce temperature dependence; disperse impurities; reduce foam; stabilize emulsion; prevent oxidation, corrosion, rust; inhibit metal catalytic effect and act as biocides to increase durability by preservation of the fluid [3]. These are useful in reducing friction between rough surfaces, machines, synovial joints, blood capillary flow, ocular lubricants and also in oil drilling (Table 1).

Lubricants are of three types, viz. conventional, synthetic and biolubricants. Conventional lubricants are mostly petroleum oils, developed by hydrotreatment, deasphalting along with solvent extraction [4]. Mineral oil

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Table 1 Carbohydrate-biolubricants and their applications

Biolubricant Source	Application	References
Guar gum (guar beans)	Oil drilling, corrosion inhibitors, dispersants	[101]
Chitosan (Shrimp and other crustacean chitin)	Oil drilling, biomedical applications	[102]
Xanthan gum (‘*Xanthomonas campestris’*)	Oil drilling, emulsion, tribology	[103]
Gellan (‘*Sphingomonas paucimobilis’*)	Anti-wear, oil drilling, orthopaedic implant materials, mud thickener in drilling	[104]
Cellulose ‘nanocrystals’ and derivatives	Oil drilling, biodegradable ‘lubricating greases’	[105, 106]
Dextran (‘*Leuconostoc mesenteroides’* and ‘*Streptococcus mutans’*)	Ocular lubricant, artificial tears	[107]
‘Hyaluronic acid’ (HA) (rooster combs, streptococcal fermentation like ‘*Streptococcus zooepidemicus’,* engineered ‘*Synechococcus* sp. PCC 7002′)	Tribology, joint lubrication	[108]
Emulsan (*Acinetobacter calcoaceticus*/ lipopolysaccharides)	Oil emulsion lubrication	[109]
Surfactin (*Bacillus subtilis*)	Oil emulsion lubrication, ‘microbial enhanced oil recovery’ (MEOR)	[51]
Biosurfactant (*Pseudomonas aeruginosa*)	Oil emulsion lubrication, oil recovery	[110]
Polysaccharide from red algae *Porphyridium cruentum/ Rhodella maculata/ Rhodosorus marinus;* Green algae *Schizochlamydella capsulata/ Chlorella stigmatophora*	Drag reduction, tribology / arthritis	[53, 111]
Carrageenan (‘*Gigartina skottsbergi’*)	Tribology, film lubrication	[50, 112]
Alginate	Joint lubrication	[113]
Polysaccharide from Green alga *Ulva* sp.	‘Tissue engineering’ and ‘regenerative medicine’	[114]

lubricants (1.5% of crude), obtained from crude petroleum distillation /refining are composed of complex hydrocarbons with traces of sulphur, nitrogen and oxygen as contaminants. Present day market products (food; cosmetics; pharmaceuticals) widely use white mineral oils [5]. Synthetic lubricants, synthesized chemically, are to provide better lubricity, oxidative stability, low/high temperature fluidity/stability, and are priced higher than petroleum lubricants. Examples are—polyphenyl ethers (heat resistant, applied in high temperature hydraulic fluid); silicate esters (useful in low temperatures); hydrogenated polyalphaolefin (Mobil oil); phosphate esters (fire resistant, air compressor); Polyalkylene glycols (refractory kiln bearings, gear and compression, fibre lubricant) etc. [2, 6].

Environmentally, the conventional and synthetic lubricants are not very friendly. For instance, the acute toxicity of mineral oil, though regarded as low, can at a concentration of ≥ 100 mg/m^3 on a long-term cause microgranulomas in lungs [7]. Petroleum products are used as lubricants typically in machines. The toxic aliphatic/aromatic compounds emanating from technological processing, released to the environment can lead to bioaccumulation and be carcinogenic. Although synthetic lubricants are efficient, they are both expensive and toxic [8]. Consequently, there is need for a low cost; renewable; easily biodegradable; non-toxic lubricant of biological origin (Biolubricants), to replace the petroleum-based and synthetic lubricants.

Biolubricants

Biolubricants are preferred because of higher biodegradability, less toxicity and safety in disposal to the environment [9]. Biolubricants can be classified into two main categories viz. oil biolubricants and carbohydrate biolubricants.

Oil Biolubricants

To achieve the environmental standards and non-toxicity, vegetable oils with biodegradability of 70%–100% were introduced as lubricants [8]. These are triacylglycerols and their derivatives like diacylglycerols, monoacylglycerols, free fatty acids, and liquid glycerol. Biolubricant production from oleaginous feed-stocks generally involves transesterification, esterification, epoxidation/ring opening, hydroesterification and catalysis [10, 11]. Homogenous catalysts are low-cost, however difficult to regenerate. Heterogenous biocatalysts like immobilized lipases are advantageous over homogenous/heterogenous chemical catalysts as these are regenerable, continuous, more active, less corrosive and eco-friendly as well [11]. Lubrication characteristics are mostly dependent upon carbon chain length, fatty acids and polarity [10]. Titanium isopropoxide was used as a catalyst to transesterify castor and rapeseed oil to develop biolubricants [12]. The biolubricant property was greatly influenced by the fatty acids viz. oleic acid and ricinoleic acid. Microbial oil from yeasts like *Rhodotorula mucilaginosa, Cryptococcus* *curvatus, Rhodosporidium toruloides, Yarrowia lipolytica* etc. were useful for biolubricant production [13–15]. Triglycerides from *C. curvatus* were initially converted into free fatty acids and finally into polyol esters by a biocatalyst (lipase Lipomod 34MDP) [14]. The viscosity (23.84 mm/s^2) of *C. curvatus* derived biolubricant was comparable to International Standards Organization Viscosity Grade (ISO VG 22) and rich in saturated fatty acids. Ester based biolubricants are also derived from filamentous fungal mat of *Fusarium* and *Rhizopus* sp. with lipid content 39% at least [16]. Oil biolubricants are comparable to ISO VG32 for parameters like Viscosity index (VI), Pour point (PP), Flash point (FP) etc. [ASTM D2422-97(2018)]. Different vegetable oils – Rice bran oil; Coconut oil; Sunflower oil and even oils from algae like *Nannochloropsis* sp., *Chlorella vulgaris* etc. are suitable as biolubricants [17–21]. Oil biolubricants can also be derived from non-edible plants like Jatropha oil (61%–64% fatty acids), Neem oil (oleic acid-43.9%), Karanja oil (oleic acid—30%–40%) [10]. Modified microalgal (*Chlorella* sp.) oil blend (MMO) with poly-alpha-olefin (10%) was found to be an excellent lubricant in reducing friction (10.1%) and heat dissipation in a hydrogen powered engine [22]. Interestingly, all blends fulfilled ISO VG 68 standards except MMO-20. Main components in MMO were Tetrahydrofuran, 2,2-dimethyl-, 4-Butoxy-2-butanone, Hydroperoxide, 1-methylhexyl, Hydroperoxide, 1-ethylbutyl, Hydroperoxide, 1-methylpenthyl, Cyclopentane, 1-acetyl-1,2-epoxy-, Hexadecanoic acid- methyl ester, 9,12-Octadecadienoic acid methyl ester, Heneicosanoic acid, methyl ester etc. Among all these, algal oils can be promoted because they are not so much in demand for food and other applications; their eco-friendliness; lesser toxic emissions and round the year production possibilities. Vegetable oils are added to base oils as additives. Also, additives are required to improve cold flow behaviour and thermo-oxidative stability of bio-oil lubricants. These are anti-oxidants, corrosion inhibitors, detergents and dispersants, extreme pressure viscosity modifiers, nanoparticles, pour point depressants and anti-wear additives [10]. Polysaccharides are also useful as additives to oil lubricants. Schiff base derivative of chitosan (SBC) additive in paraffin oil lubricant was found to reduce friction coefficient significantly [23]. But the major issue in using lipids and oils as biolubricants is their use as raw material for biodiesel production; in cooking food and also in industries producing soaps and other products. Therefore, they are already in short supply to meet these demands. Hence, an alternate source of raw material for biodegradable and eco-friendly biolubricant production is required.

Industrially, carbohydrates are potential sources for biolubricant production. Carbohydrate biolubricants from cluster beans (guar gum), crustaceans (chitosan) and microorganisms like bacteria (*Xanthomonas campestris, Leuconostoc mesenteroides, Streptococcus zooepidemicus, Acinetobacter calcoaceticus* etc.) are with excellent viscous properties for large number of applications (Table 1). However, these have their own limitations in raw material availability and production costs. Chitosan requires crustacean shells and their supply is neither abundant nor continuous. Hyaluronic acid is biologically important as a joint lubricant, produced from animal tissues and microorganisms like *Streptococcus zooepidemicus,* but it is otherwise in high demand pharmaceutically. Plants like cluster beans, useful also as a vegetable limit their production by land availability and seasonality. Microorganisms like bacteria and fungi require expensive, skilled and sophisticated techniques to cultivate, and unsuited to inexpensive open outdoor cultivation. Therefore, an alternative raw material (biomass) that is available round the year with simpler production methods would be ideal. Carbohydrates useful as biolubricants can be extracted from cyanobacteria and diverse groups of algae like Chlorophyceae, Rhodophyceae, Phaeophyceae etc. of marine and freshwater habitats.

Macroalgae (Seaweeds)

Macroalgae grow wild and can also be cultivated in coastal areas. The cultivation and collection of seaweeds provide an alternate livelihood for the poor living in coastal areas. Gulf of Mannar and Palk Bay of South India are commercially important for alginophytes and agarophytes with earnings of about US $1000 per annum per person to the women and teenagers among impoverished rural communities [24]. Algal polysaccharides, in general, are extracted from macroalgae like *Gelidiella acerosa*, *Enteromorpha prolifera*, *Ulva fasciata*, *Gracilaria intermedia* etc. growing in wild or cultivated [25–28]. The phycocolloids agar, carrageenan and alginate from seaweeds are known for their viscosity and lubricating properties (Table 1, 3). However, extended and extensive macroalgal harvest from wild as well as cultivation could cause adverse effects on the marine ecosystem, and pollute the sea [29, 30].

Agar, a sulphated phycocolloid, extracted from members of Rhodophyceae is an efficient lubricating agent, predominantly composed of the monosaccharide galactose. As a lubricant, coating of agar (1 mm) in a rectangular pipe reduced 40% drag with Reynolds number 2,600 [31]. Similarly, the red seaweeds of the families Gigartinaceae, Hypneaceae, and Solieriaceae are harvested for the sulphated polysaccharide carrageenan. The known carrageenophytes are *Chondrus, Gigartina, Eticheuma, Kappaphycus, Hypnea, Laurencia, Solieria, Agardhiella, Sarconema* etc. Commercially, carrageenan are of three different types based on gelation properties viz. 'iota', 'kappa' and 'lambda'. Of these, kappa (25–30% ester sulfate) forms strong gel with potassium salt, and usually extracted from '*Kappaphycus alvarezii'*, useful as oil drilling lubricants [32].

Alginate/algin is produced from the macroalgae belonging to the class Phaeophyceae, such as *Macrocystis pyrifera, Sargassum vulgare, Laminaria hyperborea, L. japonica, Ascophyllum nodosum.* Alginates even from bacteria like *Azotobacter* sp. and *Pseudomonas* sp. are reported [33]. Alginates are linear anionic polysaccharides. Apart from oil drilling, alginates are also marketed as cleaner lubricant spray. A composite of Sodium alginate and N-Succinyl chitosan was proved to be an excellent aerogel in separation of oil–water (99%) due to super oleophobicity and more porosity [34].

Starch composed of glucose is of two types, viz. amyloses (linear) and amylopectins (branched) depending on the arrangement of glucose units. Starch associated dispersant lubricating muds with a pour point of 20 °C to − 25 °C are generally prepared with polyalkenes and water by a steam jet cooker. However, it needs additional exploration for commercial biolubricant applications [35]. Starch is a major constituent in plastids of *Chlorophyceae* (green algae), often comprising 10%–60% of total carbohydrates [36, 37]. Cell wall of *Ulva* is composed of 8%–29% dry weight of polysaccharides [38]. *Ascophyllum nodosum,* a brown alga has 9.15% polysaccharides by dry weight [39]. Floridean starch from Rhodophyceae, known as semi-amylopectin, is reported to contain amylopectin, and occasionally amylose, e.g. *Glaucosphaera vacuolata* [40, 41].

All these polysaccharides have potential for development as biolubricants. However, the seaweed products like agar, alginates and carrageenans are already in short supply for different industrial and laboratory applications and hence may not be available in sufficient volumes for lubricant production. Further, the macroalgal biomass production is restricted by seasonal growth and cannot be continued year-round. In addition, production could also be affected by overharvesting and diseases like "ice-ice".

Microalgae and Cyanobacteria

Microalgae and Cyanobacteria are thalloid photosynthetic, oxygenic microorganisms. Among them, the cyanobacteria are prokaryotic and colonize extreme habitats like saltpans due to their physiological adaptability. Often, they form blooms in freshwater as well as oceans spreading to several miles [42–44]. Microalgae and cyanobacteria are biotechnologically important in food; feed; phycoremediation; pharmaceuticals; biofertilizer and biofuel production [45, 46]. The extracellular polysaccharides (EPS) are possible to get as a byproduct in industries employing microalgae and cyanobacteria for biodiesel manufacturing and other products. EPS with bioactivity due to sulfate group, can be extracted, and applied as biolubricant, for drag reduction by turbulence damping during movement of the fluid [31, 47, 48]. The multi-functional capabilities of the polysaccharides from microalgae and cyanobacteria could replace synthetic lubricants [49]. Aqueous polysaccharide lubrication is studied, combining their adsorption, tribology and rheological behaviour [50]. Microbial enhanced oil recovery (MEOR), mostly from bacteria like *Bacillus subtilis* is in use in oil industries [51]. Biolubricants can be applied as drag reducers in both closed and open pipe systems [31]. According to European Union standards (EN 16807), biolubricants for EU Ecolabel require 25% carbon in the formulation.

Microalgae

Microalgal starch is a byproduct in bio-oil refineries, and could be utilized in biolubricant production. A minimum of 44.8 g polysaccharides per kg dw can be extracted from *Chlorella pyrenoidosa* [52]. The polysaccharides from the microalga *Schizochlamydella capsulata* were found to be an efficient drag reducer (type-B) with a slight variation in Reynolds number 9,000–10,000 [53]. The glucose polymers like polyglucans (α/β) are distributed differently among algae of different taxonomic positions. Paramylon bodies observed in many heterokontophyta and *Euglena* sp. are storehouses of β-1, 3 glucan, an efficient ocular lubricant. Cellulose glucan, useful for biolubricant production, is present (β-1, 4-linked; β-1, 3-/ β-1, 4-linked) in cell walls of algae [54]. Extracellular polysaccharide (EPS) production is common in algae and cyanobacteria. An acidic, sulphated heteropolysaccharide as EPS was obtained from the unicellular fast-growing alga *Porphyridium* sp. of Rhodophyceae [55]. The EPS (0.5–2% w/w) was found useful as a viscosupplementation lubricant to reduce friction and pain when injected into human joints like the knee, which otherwise often require total knee replacement which is expensive and durable for 10–15 years only [56]. The sulphated polysaccharides have been found to be a lubricant for arthritis, and an alternate for hyaluronic acid [48, 56]. The adhesive polysaccharide hydrogels with low friction coefficient are useful as drug delivery biolubricants, biocompatible, and useful in tissue engineering [57]. This biolubricant is comparable to lubricin and useful in reducing the allergic effect of hyaluronic acid.

Cyanobacteria

Cyanobacteria produce slime, as they are often covered with sheaths and capsules (Fig. 1). EPS released by cyanobacteria are useful in soft tribology/ microbial enhanced oil recovery (MEOR), and a possible alternative for synthetic surfactants [58]. Optimization of growth medium and physical parameters like light (duration and

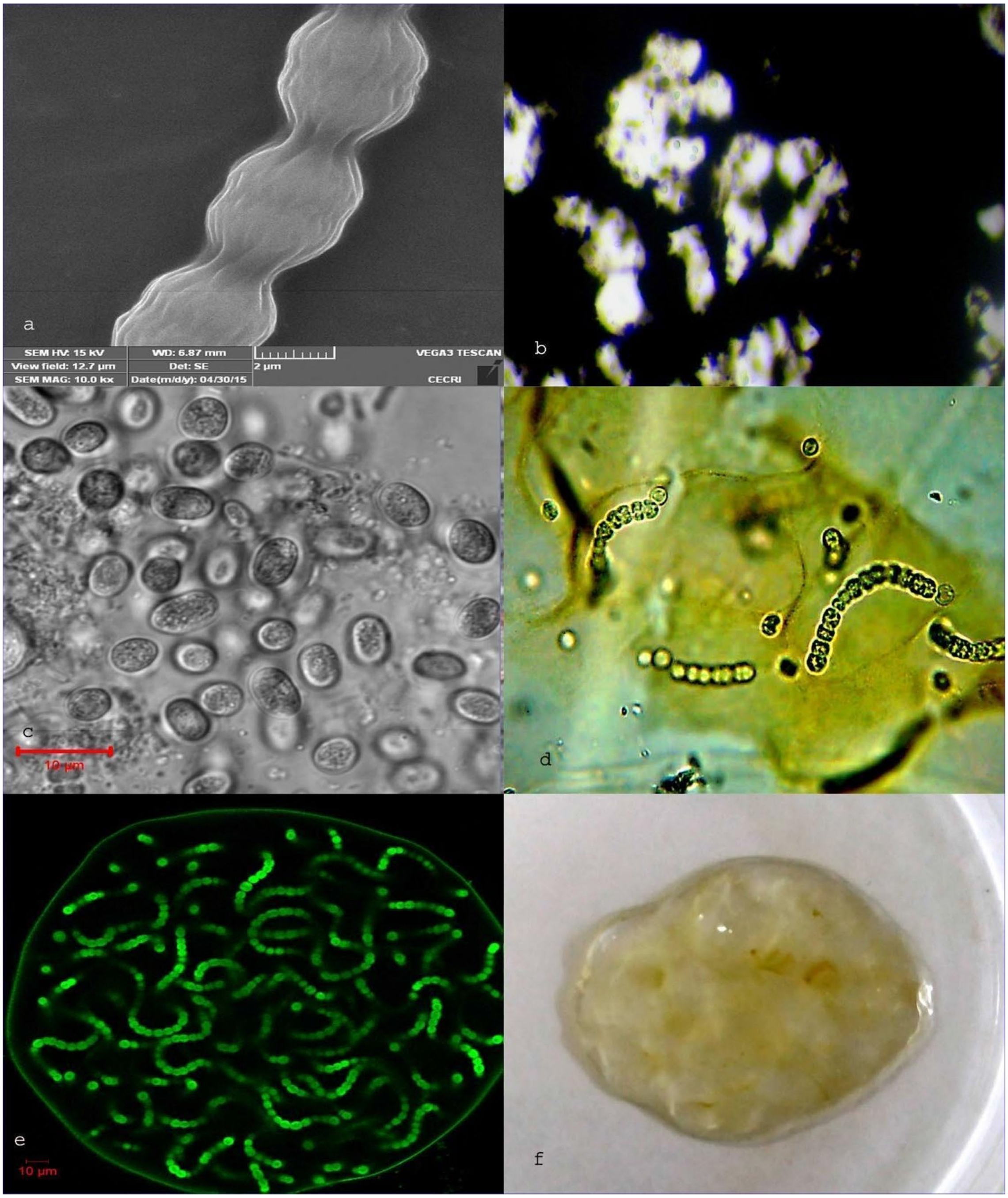

Fig. 1 EPS from cyanobacteria. SEM image of *N. muscorum* with EPS (**a**); India ink staining of EPS of *C. epiphytica* (**b**); differential interference contrast microscopic view of EPS from *C. epiphytica* (**c**); Cells of *Nostoc* sp. with EPS (**d**); Confocal Laser Scanning Microscopy (CLSM) image of Mucilaginous (EPS) ball of *N.commune* (**e**); Extracted EPS (**f**)

intensities) and temperature, maximise EPS production (Table 2). Closed photobioreactors are useful to maintain quality during large scale production of EPS [59, 60]. But carbohydrate biolubricant production for oil drilling can be made inexpensive with biomass from open outdoor ponds. The raceway ponds are economical and upscalable to any level of industrial production [61]. The EPS composition from these organisms, and therefore their applications could be varied. Unlike bacteria, cyanobacterial anionic, highly hydrophobic EPS are heteropolymers extending to 10–12 monomers. The novel polysaccharides nostoflan, cyanoflan and sacran were isolated from *Nostoc flagelliforme*, *Cyanothece* sp. and *Aphanothece sacrum* respectively [62–64]. Nearly 75% of total carbohydrates

Table 2 Polysaccharide production from algae/cyanobacteria

Organism	Condition	PSs yield	Time (d)	References
Anabaena sp. BTA990	N (–)	1.30 mg/mL	26–30	[109]
Arthrospira platensis	LI 180 µmol/m^2 /s; temperature: 33 °C	290 ± 5 mg/ L	21	[115]
Cyanobacterium aponinum	500 µmol photons/ m^2 /s	~20 mg/ L/d	14	[116]
Cyanothece epiphytica	Nutrient starvation; ozonisation	6.33–9.66 µg/mL/day	9	[47]
Limnothrix redekei PUPCCC 116	Radiant flux of 9.8 W/m^2, continuous light	614 µg /mL	21	[67]
Lyngbya stagnina	Salt (NaCl)	88 µg/mL	6	[98]
Microcoleus vaginatus	Light intensity at 80 µE/ m^2 /s	302.41 mg/ g DW	20	[117]
N. flagelliforme TCCC11757	N (–)	37.95 mg/L	16	[100]
N. microscopicum	BG11	0.90 g/L	44	[118]
N. muscorum	Ozonisation	126.73 µg/mL	12	[70]
Phormidium 94a	Continuous illumination by fluorescent lamps~5,000 lx	929.88 mg/g dw	15	[119]
Scytonema tolypothrichoides VB61278	Temperature 28 to 34 °C; Irradiance: 8 to 13 W/ m^2	~500 µg/mL	25	[120]
Synechocystis sp. BASO444	Salt (NaCl)	500 mg/L EPS	15	[121]
Tolypothrix bouteillei VB61268	Temperature: 27–34 °C; Irradiance: 7 to 17 W /m^2	~250 µg/mL	25	[120]
Ulva rigida	Collected alga	20% of DW	–	[122]
Enteromorpha compressa	Collected alga	23% of DW	–	[123]
Sargassum tenerrimum	Collected alga	61% of DW	–	[124]
Gelidiella acerosa	Collected alga	89.5% of DW	–	[125]
Gracilaria caudata	Collected alga	32.8% of DW	–	[126]
Turbinaria conoides	Collected alga	35% of DW	–	[127]
Ascophyllum nodosum	Collected alga	42.31% of DW	–	[39]
Laminaria japonica	Collected alga	7.56%-18.6% of DW	–	[128, 129]
Porphyridium sp.	Continuous illumination (15µE/ m ^{2} /s); 3% CO$_2$; artificial sea water	36% of DW	15	[55]
Chlorella vulgaris	Continuous illumination (3600 lx)	495.44 mg/g	16	[130]
Spirulina platensis	Algal powder	71.65% of DW	–	[131]
Chlorella pyrenoidosa	Algal powder	44.8 g/ kg	–	[52]
Scenedesmus sp.	Constant illumination: 1500 lx	48 mg/L	14	[83]
Scenedesmus obliquus	Varying light intensities (10–60 µmol /m^2/s)	0.14–0.20 pg/cell	9	[132]
Botryococcus braunii	'Laboratory' simulated 'Mediterranean climate' conditions	0.29 g/L/day		[133]

synthesized could be released as polysaccharides into the medium. EPS production can be maximized by altering simple factors (Table 2). Emulcyan, an emulsifier EPS of the cyanobacterium *Phormidium* J-1 were maximal in stationary phase [65]. Cyanoflan the polymer from *Cyanothece* sp. form droplets (≤ 200 µm), similar to xanthan gum with an Emulsification Index (EI) of ≥ 50% and stability of more than a month [64]. Also, emulsifier, a biosurfactant from *Nostoc* sp. had an EI of 21.4 to 37.5% with different hydrocarbons and oils [66]. EPS extracted from cyanobacteria *Cyanothece* sp. CCY 0110, *Limnothrix redekei*, *N. flagelliforme* etc. are highly viscous, and comparable to commercial xanthan gum [64, 67–69]. The lubricity provided by EPS (0.1; 5.0% w/w) is similar to grease with remarkable emulsifying activity as shown by *Cyanothece epiphytica* [47]. Also, the EPS from *N. muscorum* with ample uronic acid could be useful in oil drilling operations and paint emulsions [70]. EI for sulphated EPS from *C. epiphytica* at its lowest (0.2%) was 58.24–72.37% [47]. EPS from *N. flagelliforme* (0.45%) showed better EI (27.3–73.8) than xanthan gum in hydrocarbon and oil [69]. Emulsion from EPS of *N. muscorum* was stable for 3 months (EI > 75%), while E24 was > 80% [70]. Emulsifying properties are useful in oil drilling.

Physical and Chemical Properties

Analysis of the physical and chemical properties of the polysaccharides would reveal their utility as biolubricants and will enthuse entrepreneurs to view algal industries as profitable ventures to make multiple products. Some important properties to be considered are:

Molecular Weight

The molecular weight (MW) of a substance can determine the viscosity, and consequently the lubricity. Algal/cyanobacterial polysaccharides are high MW polymers (Table 3). A high MW polysaccharide (> 10,000 kDa) Fucoidan from *Turbinaria turbinata* can be extracted with mild enzymes [71] and the Cell bound polysaccharide (CPS) is of high MW. It can be extracted as efficiently as Released polysaccharide (RPS) [47, 70, 72]. The Natural Algae Based Synthetic Lubricant (NASL) with MW > 300,000 is the slime extracted from a kelp *Macrosystis pyrifera*. Its MW is higher than a typical lubricant and is a superior drag reducer [73]. Due to its high MW, bio-emulsion in low concentration (1:50–1: 1000) produces a stable emulsion [74]. Biomedically, ultra-high molecular weight polyethylene is used for hip and knee replacement which can cause inflammation and this can be reduced by the algal biolubricant.

Sugar Composition

Carbohydrate biolubricants can be both hydrophilic and hydrophobic in nature, depending on the monomeric composition. In general, algal/cyanobacterial polysaccharides are composed of several monomeric units (Table 3). The commercial xanthan gum is composed of mannose, glucose and glucuronic acid. The potential EPS biolubricants of the cyanobacterium *C. epiphytica* is composed of six monosaccharides with sulfate groups [47]. Sulfated polysaccharides are useful as biolubricants for biomedical applications. Based on partition coefficient (K_{av}) (based on sugar partition between aqueous solvents and polystyrene gel) the hydrophobicity of sugars is as D-ribose > D-arabinose > D-xylose > D-mannose > D-glucose > D-galactose [75]. In the formulation of oral tablets/capsules hydrophobicity is not advantageous, but in coating oil drilling pipes hydrophobic lubricants are useful. Hydrophilic tablets were manufactured by co-processing starch/microcrystalline cellulose (MCC) /Chitin polymer and an additive magnesium silicate [76]. Hydrophilic hydroxypropyl methylcellulose is a derivative obtained from cellulose used in tolcapone tablet formulation due to its high viscosity, gelling and swelling ability, inertness, non-ionic property, odourless fillers, and significant impact on release kinetics into the system [77]. Superhydrophobic coatings on oil/ gas pipelines are mostly developed by nanomaterials that protect against corrosion, fouling agents and aggressors [78]. A green superhydrophobic film was developed with cerium chloride (0.038 M) and myristic acid (0.1 M) to coat onto the carbon steel surface [79]. However, hydrophobic lubricants from carbohydrates are less recognized. Peptide moieties and ester linked acetyl groups together with deoxyhexoses (rhamnose/fucose) provide hydrophobicity for cyanobacterial EPS [80].

Thermal Stability

For a lubricant, to work properly, thermal stability is a basic requirement (Table 3). Algal/cyanobacterial polysaccharides are quite stable in a high temperature range due to complexity of their polymeric structures. Released polysaccharides (RPS) from *Cyanothece* sp. CCY 0110 showed 65% loss at 248–300 °C [68]. At 237 to 378 °C, only 39% loss was observed in RPS from *N. carneum*. As revealed by differential scanning thermogram (DSC), the crystallization temperature was 107.4 °C with a latent energy of crystallization of 108.67 mJ [81]. EPS from *C. epiphytica* degraded 50% at 288 °C [47] and that of *Arthrospira maxima* had a weight loss of 66.6% at > 500 °C, while a mass residue of 34% still remained at 700 °C [82]. 80% mass loss of EPS from *Scenedesmus* sp. SB1 took place at 167 °C [83].

Crystallinity

Carbohydrate biolubricants are mostly amorphous in nature. However, sodium alginate is crystalline with its peak 2 θ of 13.5 and 21.9°, while calcium alginates show different semi crystalline peaks [84]. Polysaccharides from cyanobacteria like *Cyanothece* sp. CCY 0110, *C. epiphytica*, *N. flagelliforme*, *N. muscorum* are reported to be amorphous [47, 68, 70, 85]. But X-Ray diffraction' analysis of EPS from the microalga *Scenedesmus* sp. SB1 found them both amorphous (84.8%) and crystalline (15.2%) as presented (Fig. 2) [83]. Amorphous materials have generally been used for lubrication in a large number of applications including tablet formulations and earthquake lubrication [86, 87].

Rheological Property

In tribology, under hydrodynamic, boundary and mixed regime, aqueous polysaccharide lubrication is important, and dependent on viscosity, adsorption and both [50]. In drilling muds, often, water alone is used as a lubricant, but the efficacy could be enhanced with carbohydrate biolubricants. These are mostly thixotropic, pseudoplastic and non-Newtonian. The carbohydrate biolubricants from microalgae and cyanobacteria are comparable to seaweeds and commercial polysaccharides like Xanthan gum of bacterial origin (Table 3). The Newtonian lubricants are useful in hydrodynamic, elastohydrodynamic and also in mixed regimes. Rheological properties are affected by temperature, pH, MW, chemical structure, concentration, and extraction processes which are evaluated prior to different applications for its conformity. The flow index of Cell bound polysaccharides (CPS) and RPS from *Anabaena* sp. CCC 745 were < 1, indicating pseudoplastic and non-Newtonian characteristics [72]. Consistency index was high for RPS (90.92 PaS), compared to CPS (67.35 PaS). The polysaccharide

Table 3 Physico-chemical properties of extracellular polysaccharide from algae/cyanobacteria

Organism	MW (KDa)	Sugar composition	Thermal stability	Rheology	References
Ulva fasciata	–	Rh; Xy; Gl; Ma; U acid; sulfated	–	Viscosity: 1.27 to 10.37 mPa s; increased from 0.1to 1.0% (w/v); shear-thickening with temperature, pH, concentration, and salinity	[26]
Enteromorpha prolifera	55–511	Rh; Xy; Ma; Ga; Gl; U acid; Sulfated		Pseudoplastic; thixotropic; intrinsic viscosity (0.37 mL/mg) less effected by pH, temperature, ionic strength	[27]
Laminaria digitata (Sodium alginate)	114	Linear binary copolymers of (1–4)-linked ‘β-d-mannuronic acid’ (M) and ‘monomeric α-l-guluronic acid’ (G)	–	Intrinsic viscosity: 2.542 dL/g; ‘soft’ and ‘elastic’ gels	[134]
Macrocystis pyrifera (Alginate)	56–396	–	–	Newtonian; low shear rate; loss modulus ($G^{//}$) > > storage modulus ($G^{/}$); dependent on molecular weight; Intrinsic viscosity (η) ranged from 150 to 1185 mL/g	[135]
Turbinaria turbinata	224–326	Rh, Fu, Ar, Xy, Ma, Ga, Gl; sulfated	Degradation stages were 25–200, 200–500, and 500–800 °C for all fractions	Viscosity (2.0%) Newtonian; weak pseudoplastic; increase in concentration from 0.25–1.00% increased consistency index; Intrinsic viscosity: 0.0016–0.0086 Pas	[71]
Cladosiphon okamuranus (Fucoidan)	–	–	–	Shear-thinning (< 1.5%) at 25 °C; plastic at 2.0%; increased with concentration > 1%; decreased with temperature; increased with NaCl and $CaCl_2$; stable over pH5.8 to 9.5 (0 °C and 25 °C)	[136]
Gelidiella acerosa (Agar)	179–289	–	Gelling (T_{gel}) and Melting temperature (T_m): 36–42 °C and 82–88 °C	Viscosity for agar (1.5%): 42cp-45cp in at 80 °C; predominantly elastic gel; $G^{/} > G^{//}$ (1%) agar; Newtonian at steady shear flow (1%) at low shear rate limiting region	[25]
Gelidium sp. (Agar)		Ga; sulfated	–	Strong gel formation with 0.1 M KCl; $G^{/} > > G^{//}$ at 10 g/L and low temperature; decrease over 50 °C; crossed over at 83 °C	[137]
Gracilaria intermedia		Ga; sulfated	–	$G^{//} > G^{/}$ at concentrations 0.75–1.5%; pseudoplastic; viscosity decreased with increase in shear rate	[28]
Anabaena sp. CCC 745	30.29 (CPS) 19.57 (RPS)	Gl; Xy; Rh; Glu U acid	–	Viscosity decreased with shear rate; low detraction of viscosity for CPS; pseudoplastic; non-Newtonian; fluid nature; consistency index: 67.35 and 90.92 PaS	[72]

Table 3 (continued)

Organism	MW (KDa)	Sugar composition	Thermal stability	Rheology	References
Arthrospira maxima	81–98	Gl; Ga; Rh; Xy; Ma; Ar; U acids	34% residue remained (< 700 °C)	Pseudoplastic, gel-like; shear-thinning; resist thermal cycle	[82, 138]
Cyanothece epiphytica	–	Ar, Xy, Gl, Ga, Ma, Fu	50% weight loss at 288 °C	G' and G'' traversed at 58℃; thereafter $G' > G''$; viscoelastic; non-Newtonian and thixotropic	[47]
Cyanothece sp. CCY 0110	> 1000	Cyanoflan—carbohydrate content: 71%; neutral sugars and U acids: 56.8; 13.7%; sulfate: 11%	A weight loss of 12% (20 ◦C to 110 ◦C); constant weight till 248 ◦C, decomposed at 300 ◦C	Cyanoflan viscosity was shear thinning started with values of '66.6′ (0.1%), '922.1′ (0.5%) and '1594.0′ (1%) mPa.s at 'shear rate' of 10 s^{-1}, reached '13.0′, '102.7′ and '229.5′ mPa.s respectively,	[64, 68]
Limnothrix redekei PUPCCC 116		Gl/Ma; Ri; Rh; U acid	–	Non-Newtonian shear thinning (0.2% w/v; 0.4% w/v); high effect till shear rate 350/s; increased with concentration; comparable to xanthan; pseudoplastic	[67]
N. carneum		Xy; Ma	22.8% weight loss at 340 –530 °C	Intrinsic viscosity (η): 6.9	[139]
N. calcicola	–	D-Ri; D-Ar; L-Rh; L-Fu; D-Xy; D-Ma; D-Gl; D-Ga; and 3-methyl-D-Arabinose	–	A low viscosity (55-65cps) polymer (0.4% w/w) pseudoplastic; non-Newtonian	[140]
N. carneum	–	Gl; Xy; U acids; sulfated	237 °C	Pseudoplastic non-Newtonian fluid; shear rate to maxima of 24.2, 70.1 and 140 cP	[81]
N. commune	–	Ar; Rh; Fu; Xy; Ma; Ga; Gl; Glu U acid	–	Kinematic viscosity (0.1%): 3.4101 mm^2/s	[141]
N. flagelliforme	~279	Gl; Ga; Ma; Ri; Xy; Ar; Rh; Fu; Glu U acid	–	Pseudoplastic (1%); stable emulsions more than xanthan gum; shear-thinning	[69]
N. muscorum	–	Gl, Ga, Ma, Ar, Xy, Fu, Rh Gal U acid, sulfate (trace)	Mass loss 94% at 240℃	G' and G'' increased with oscillation; cross over > 50 Hz; pseudoplastic, thixotropic; Non-Newtonian weak gel	[70]
Lyngbya stagnina	–	Ma/Gl; Xy; Rh; Ga; Gal U acid	–	Non-Newtonian (0.2% w/v), pseudoplastic; viscosity maximum at pH 10; lowest at pH 6	[98]
Phormidium 94a	2,000	Ga; Ma; Ar; Ri; Gal U acid	–	'Newtonian' behaviour (0.1%) similar to Arabic gum; concentrations > 0.1% was 'non- Newtonian', shear thinning, pseudoplastic	[119]

Ga Galactose, *Ma* Mannose, *Ar* Arabinose, *Ri* Ribose, *Gl* Glucose, *Xy* Xylose, *Fu* Fucose, *Rh* Rhamnose, *Glu U* Glucuronic acid, *Gal U* Galacturonic acid

Cyanoflan (MW > 1 MDa) from *Cyanothece* sp. CCY 0110 exhibited better rheological property than Xanthan gum [64]. For instance, 1% solution of Cyanoflan has a viscosity of 1594.0 mPa.s while Xanthan gum (1%) has a viscosity of only 1113.0 mPa.s. Xanthan gum was more plastic than viscous compared to Cyanoflan. EPS from *Limnothrix redekei* PUPCCC 116 (0.2%) and Xanthan gum presented comparable shear thinning characteristics [67]. Interestingly, viscosity of Xanthan gum decreased with rise in temperature (15–55 °C) but no change in the EPS.

Advantages of Microalgae/Cyanobacteria

Generally algal Carbohydrate biolubricants are formulated from seaweed products like agar, alginic acid, and carrageenans (Table 1). However, the critical factor in using macroalgae is their cultivation, and related environmental issues. Apart from seasonal dependence on light and temperature in 'spring' and 'autumn', overharvesting from the wild reduces the genetic pool of Macroalgae. They are cultivated on surface sea water, and shadowing affects the productivity of other marine resources like phytoplanktons and microalgae of benthic regions [29]. In sea, primary productivity is dependent upon phytoplanktons in a major way [43]. Tropical seawater is limited by NO_3-N. Cultivation of seaweeds in natural seawater may further decrease the nutrient status, and affect the marine biota. As nitrogen source is essential for algal growth, urea is often applied in offshore cultivation of algae [30]. The microalgal/cyanobacterial biomass production can be coupled to bioremediation of industrial effluents (Fig. 3). Microalga *Chlorella vulgaris* and *C. protothecoides* presented short lag phase in biomass production and complete NH_4^+ (40 mg/L) removal in 10 days from 'anaerobic digestion effluent' [88]. *C. minutissima* was cultivated in 'saline aquaculture wastewater', and fivefold increase in cell density was achieved [89]. Both total N and P were decreased up to 88% and > 99% respectively. NO_3-N, NO_2-N, dissolved orthophosphates were reduced by 88.6, 74.3, 99% respectively. 'Dairy wastewater' was useful in increasing biomass productivities of *C. pyrenoidosa*, *Anabaena ambigua* and *Scenedesmus abundans* while effectively reducing biological oxygen demand-BOD (56%), chemical oxygen demand-COD (77%), NO_3-N (88%), phosphate (85%) in 25 days [90]. *Chlorococcum* sp. SL7B, *Chlorella* sp. SL7A and *Neochloris* sp. SK57 were cultivated in 'pharmaceutical effluent' contaminated river water. *Neochloris* sp. SK57 reduced COD in 10 days with efficiency 90% [91]. Also, *Chlorococcum humicola* cultivated in undiluted 'textile mill effluent' reduced NO_3-N and NO_2-N below detectable limit in 3 days [92]. Maximum biomass was produced in TE (90%) + $NaNO_3$ (0.15%) with growth rate 0.37/d. Microalgae and cyanobacteria used for bioremediation, also called phycoremediation, can result in biomass with EPS [92–94]. Remarkably, microalgae and cyanobacteria can grow in both low nutrient waters as well as nutrient loaded industrial effluents, reducing nutrients and water requirement as well. Cultivation in wastewater is the most economical way of biomass production [92]. The cyanobacterium *Oscillatoria boryana* BDU 92181 was reported to break down 'melanoidin', a recalcitrant pigment from distillery effluent and utilized it as carbon and nitrogen source [95]. Conversion of nutrients into biomass is contributed by light and inorganic carbon [96]. Flue gases from industry can also be utilized by microalgae and cyanobacteria, and about 513 tons of CO_2 can be converted to 100 tons of dry algal biomass [97]. Algal/ cyanobacterial biomass production excludes arable land requirement, and are capable of growing in wastewater and the biomass would be available irrespective of seasons in a much shorter time period compared to higher plants. Hence, for any biotech industry including biolubricant production, microalgae/cyanobacteria cultivation is desirable for continuous supply of raw materials. Marine microalgae/cyanobacteria can be cultivated in seawater, which minimizes freshwater requirement. *Porphyridium* sp. was cultivated on supplementation of CO_2 (3%), and a continuous illumination of 15μE/m^2/s in artificial seawater medium (ASW). Production of biomass can be enhanced by photobioreactors, and an economical photobioreactor is a raceway pond for mass production of biomass. Even harmful algal/cyanobacterial blooms can be harvested and the different components of the biomass can be used for different purposes [44]. Growth rate is high for microalgae and cyanobacteria compared to seaweeds. Physico-chemical properties of the carbohydrates are also comparable to seaweeds (Table 3). Chosen marine microalgal strains can be cultivated in seawater both indoors and

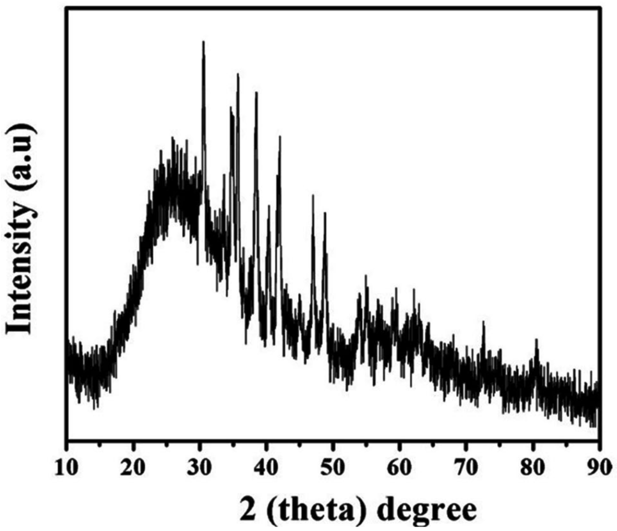

Fig. 2 XRD spectrum of EPS from *Scenedesmus* sp. SB1 [83]

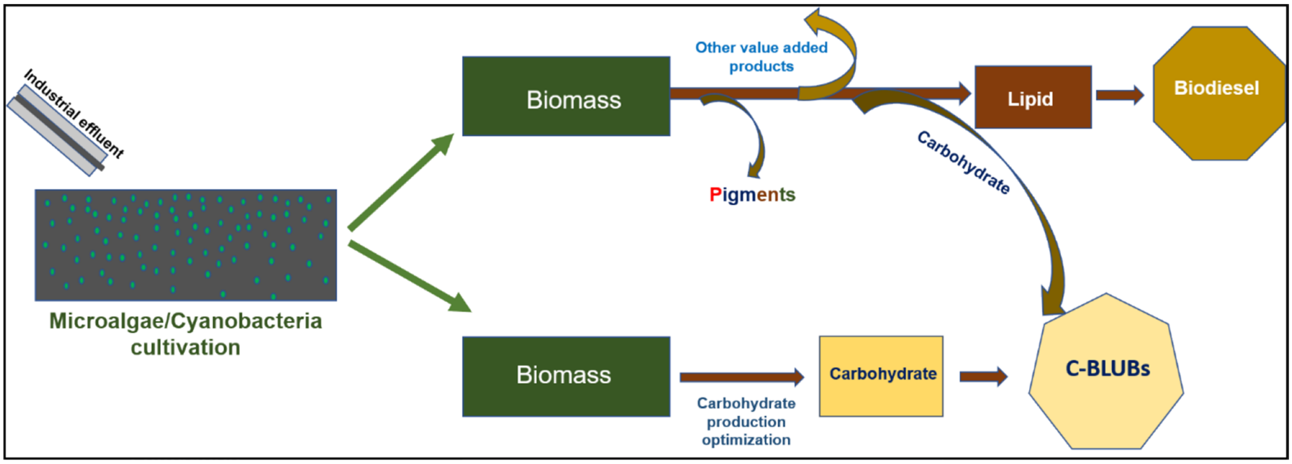

Fig. 3 Carbohydrate biolubricants production routes by cultivation of algae/cyanobacteria in industrial effluent

outdoors depending on the products to be made. Unlike bacteria and fungi, the algae and cyanobacteria can be cultivated outdoors under daylight as they are photosynthetic. In algal biorefineries for energy production, pigments and carbohydrates could become value-added products. Carbohydrate components can be separated and used for biolubricant production which would reduce production costs of both primary and byproducts (Fig. 3). For maximal production of polysaccharides by microalgae and cyanobacteria, mild stress which is often starvation of macronutrients like N/P or increase in salinity or mild ozonation would help [70, 98–100]. Such manipulations are not possible with macroalgae as they are cultivated in the natural sea surface water. Unlike seaweeds, microalgae and cyanobacteria are not so much disease prone. Algal/cyanobacterial strains in open ponds or raceways can compete with bacteria by releasing metabolites with allelopathic effect [92].

Conclusion

Carbohydrate biolubricant production is yet to achieve commercial dimensions and a sustainable market growth. Just as vegetable oil, microbial oil and animal fat are used as a base for biolubricant production, carbohydrates from algae and cyanobacteria are also suitable and have potential in diverse applications. The commercial leads to use eco-friendly microalgae and cyanobacteria for carbohydrate biolubricant production are yet to be used to establish industries comparable to those for mineral oils and synthetics as well as those of seaweeds. Industrially, at present, macroalgae are more in use, although their cultivation is at present only in sea and regarded as a threat to marine biota raising environmental concerns. Marine microalgae cultivation on the other hand, is possible in saline water, artificial sea water, inorganic/organic growth media, and industrial effluents as well. Algal biomass production coupled with bioremediation can substantially reduce nutrients and water requirements. In addition to continuous supply of raw material, it can reduce cost of production. Accumulation of carbohydrates in cells has been shown to be improved by simple stresses like nutrient starvation and ozonisation for short durations. Further, the physico-chemical properties of carbohydrates from algae and cyanobacteria comply with the required properties for a biolubricant. The successful lab level studies reported thus far, are to be scaled up and commercialized, using a multi-disciplinary approach. Uninterrupted supply of the raw materials is assured as mass cultivation technology is available for algal/cyanobacterial biomass. Carbohydrate biolubricant formulations are biodegradable and eco-friendly and therefore to be preferred over mineral oils and synthetic lubricants.

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Declarations

Conflict of interest The authors declare no conflicts of interest.

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