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Integration of membrane technology in microalgae biorefineries

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ABSTRACT

The future of microalgae as a sustainable feedstock for biofuel and other products is still uncertain. Although productivity and environmental benefits surpass that of many other types of feedstock, the associated costs with production and downstream processing hinder this type of technology. The microalgae biorefinery approach addresses many of these issues in which upstream and downstream processes are important. Upstream technologies associated to nutrient recovery from waste effluents have been reviewed and discussed. Potentially, waste-derived nutrients will enable the formulation of optimal growth media from wastewater at lower costs. Microalgae dewatering is still seen as a major burden. A thorough review of the associated membrane processes in the literature has highlighted lack of consistency in terms of the influence of pore size and membrane materials. Moreover, only very few pilot-scale cost estimates could be found. The fractionation of microalgae products is perhaps the less developed area in the context of a microalgae biorefinery. Membrane filtration for the recovery of lipids, proteins and carbohydrates from microalgae is still an infant technology and major developments are expected to take place within the next few years. This review highlights the achievements, potential and future challenges of integrating membrane technology into microalgae-based biorefineries.

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1. Introduction

Motivated by market demand for sustainable sources of fuel and energy, biofuels have become a priority for most governmental energy agendas. Nevertheless, in recent times the analysis of the environmental implications in terms of farmland loss and CO_2 emissions has changed our perception of crop-derived biofuels. This has led the EU to reduce the 10% target for renewable energy in the transport sector by 2020, down to 5% [1,2]. Moreover, in order to feed a growing population, farmland is continuously extending into tropical forest areas which threatens biodiversity and the global environment [3,4]. Seemingly, there are divided efforts between growing crops for fuel and energy or for human nutrition.

The need for alternative and sustainable sources of both food and energy has led microalgae to be regarded as a potentially viable feedstock [5–7]. Through a photosynthetic process, microalgae are able to uptake metals and nutrients like carbon (as CO_2), nitrogen (as NH_4^+/NH_3 and NO_3^-/NO_2^-) and phosphorous (as PO_4^{3-}) for their growth and transform these into valuable products such as proteins, carbohydrates, lipids and silica nanomaterials (in the case of diatoms). Whilst algal proteins and poly-unsaturated fatty acids (PUFAs) are driving the use of microalgae as feed and "foodstuff", the biofuel focus is uniquely related to the level of lipids which can be chemically transformed into biodiesel [8–10]. Other forms of fuel such as methane from the anaerobic digestion of algae biomass [11,12] and bioalcohol [13,14] have also been reported in the literature. Apart from fuel commodities, a handful of high-value products have been related to microalgae. These tend to be poly-unsaturated fatty acids (PUFA's) such as eicosapentaenoic acid (EPA) [15,16] and decosahexaenoic acid (DHA) [17], antioxidants such as astaxanthin [18], proteins [19,20], pigments such as chlorophyll and carotenoids [21] and a mixture of polysaccharides [22,23]. EPA and DHA are known to have a variety of health benefits such as hypotriglyceridemic and anti-inflammatory properties [24,25]. Astaxanthin is a potent antioxidant carotenoid also known for anti-inflammatory, antitumor and cardio-protective effects [26,27]. Due to their functionality, emulsifying and enzymatic properties, proteins are very useful in both the food and cosmetic industries [19,20,23]. Certain carotenoids such has beta-carotene, lycopene and astaxanthin are an important dietary source of vitamin A and used to treat certain skin diseases [28]. Chlorophyll is regarded as a colourant and functional ingredient for food processing [29] and also has known antioxidant properties [30,31]. Polysaccharides may represent both an additional ingredient in food processing and a carbohydrate source for bacteria and yeast [14]. The overall composition of algae can be simplistically divided in to three main biochemical groups: proteins, lipids and carbohydrates, although authors also

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include ash and carotenoid content in their work [20,32,33]. Nonetheless, the biochemical composition is highly dependent on numerous environmental and nutritional factors within the growth strategy implemented. These include the composition and supply strategy of the growth media [34–36] and light intensity [37,38]. This variability of the biochemical composition may represent an added challenge for membrane filtration processing but most importantly allows a very flexible product-orientated feedstock.

Due to the photosynthetic ability to take up CO_2, metals and nutrients from waste effluents microalgae are also regarded as a bioremediation tool. On CO_2 sequestration, it has been reported that microalgae could capture 1.8 kg CO_2/kg biomass (absorbed via photosynthesis) [8,39] and have very high capability to remove nitrogen, phosphorous and sulphur compounds from wastewater [40,41]. Furthermore, cultivation technologies of microalgae biomass do not normally compete for arable land which would otherwise undermine the efforts to meet food demand [42,43]. As a result, microalgae appear to be a more socially and environmentally responsible source of biofuel and organic chemicals.

The importance of algae as a potentially viable feedstock has prompted the development of associated processing technologies which allow maximising product output and reduce costs. Across many industry sectors membrane technology has become a pivotal technology in meeting the demand for a wide range of commodities such as water, food, energy, speciality products and even in wastewater treatment [44–48]. Membrane separation is a process which selectively allows mass transfer of materials from one phase to another, usually driven by pressure, concentration, chemical or electrical potential gradient [49,50]. In simple terms, membranes are classified according to their pore size which range from micron pore size to angstroms, e.g. microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). These can also be distinguished according to the fabrication material (e.g. zeolite, organic and inorganic) and configuration (e.g. spiral-wound, fibres and tubular) [51]. One of the earliest studies of membrane phenomena dates back to the middle of the eighteenth century and referred to the selective passage of water using a pig's bladder [52]. Nevertheless, only in the 1960s, with the development of synthetic membranes by Loeb and Sourirajan [53], membranes were seen as a valuable technology for the process industries. Only 20 years later membranes were effectively being applied at industrial scale. Today, membranes are widely used throughout industry and have become the dominating technology in some cases [50]. Particularly for desalination, technologies such as reverse osmosis have overtaken thermal desalination in terms of metric tons of fresh water produced and account for around 60% of the worldwide production capacity [54,55]. Table 1 summarises some of the documented applications of membrane separation and the specific membrane types used. The rise of membrane technology is a consequence of their own merits over competing technology. Such advantages which account for this success include the ease of scaling up, chemical free separations, low operating and maintenance costs, compact and modular design, automated and continuous operation whilst allowing for highly selective separations [49–51,56,57]. In many cases, dewatering using membranes is preferable to thermal processes due to the reduced minimum work versus energy demand for a phase change.

One of the most recent challenges for membrane filtration is the integration into biorefineries. The biorefinery concept is often described as a facility which converts biomass and biomass wastes into valuable commodities such as fuel, solvents, plastics and added-value chemicals [112–114]. Seemingly, biorefineries represent an opportunity for membrane technology since many of the downstream processes can be realised using available membrane methods. Abels et al. [115] and He et al. [116] have thoroughly reviewed the membrane technologies associated to bioenergy and biorefining. When focused on the utilisation of lignocellulosic materials as a biorenewable feedstock, Abels et al. [115] reported the exploitation of membranes for the production of sugars, lactic acid, proteins, amminoacids, bio-ethanol, biodiesel, lignin and antibodies. In addition, a more extensive review by He et al. [116] also covered the application of membrane technology in biogas and hydrogen production, extraction of bio-oil, purification of biodiesel and bioethanol processing. Many of the opportunities and challenges for integrating membrane technology in biorefineries have been highlighted by these authors, however, the availability of feedstock and the market value of the products generated will drive the decision making process. Setting aside the environmental considerations, microalgae have a very favourable composition with only 4–10% ash matter [32,33] and low lignin present in the cell wall which contains poly-ionic saccharides [117]. Therefore at least 90% of the algae biomass could be processed for marketable products. Table 2 summarises the biochemical composition of different feedstocks used for fuel, energy, feed and food. Although the productivity of microalgae surpasses that of any other feedstock, the reported 100 ton/ha/year of microalgae is yet to be demonstrated at full scale. The world's largest microalgae production plant is 250 ha set up in a series of artificial ponds and is found in Hutt Lagoon, Australia. *Dunaliella saline* is cultivated for the extraction of beta-carotene. A few companies such as Cyanotech corp. (Hawaii, USA) and Nature Beta Technologies (Israel) supply a range of microalgae based products such as skin-scare and food supplements.

Table 1
Examples of the application of each type of membrane filtration in specific industry areas. MF – microfiltration, UF – ultrafiltration, NF – nanofiltration, RO – reverse osmosis, FO – forward osmosis, PV – pervaporation, ED – electrodialysis, and GS – gas-solid.

Applications	Membrane type	Reference
Food and biotechnology		
Cell harvesting, e.g. algae, bacteria and yeast	MF/UF	[58–61]
Juice, wine and beer clarification	MF/UF	[62–65]
Milk processing and fractionation	MF/UF	[66,67]
Recovery and fractionation of protein and peptides	MF/UF/ED	[68–73]
Sugar refining and clarification	MF/UF/NF/RO	[74–78]
Concentration of foodstuff and pharmaceuticals	NF/RO/FO	[79–84]
Energy, fuels and solvents		
Extraction and purification of bio-oils and biodiesel	MF/UF/NF	[85–89]
Recycling and purification of organic solvents	NF	[90–93]
Extraction and purification of alcohols	PV	[94,95]
Biogas processing and upgrading	GS	[96,97]
Environment and water treatment		
Wastewater remediation	UF/NF	[98–100]
Heavy metal removal/recovery	NF/ED	[101–103]
Desalination for fresh water supply	NF/RO/FO	[104–107]
Recovery of resources from wastewater	MF/UF/NF/RO	[108–111]

1.1. Key challenges for microalgae processing

As the research community attempts to unlock the potential of microalgae, many technical and non-technical challenges hinder the feasibility of this novel *green technology*. Commercially, microalgae struggle to become viable since microalgal economics are fundamentally based on the extraction of algal-oil [5,9]. Thus far, only a handful of technologies have been reported for the extraction of microalgae products. Moreover, these uniquely target on one product (typically lipids) and thus do not account for the viability and value of the remaining products in the biomass [16,138]. The prospects in marketing microalgae-based products seem to rely on the cost reduction of the inputs such as energy, water and nutrients but also in maximising the range of products. Only an integration of upstream and downstream processes will

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