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Extraction of bioactive compounds from beach-cast brown algae: a review on accelerated solvent extraction and subcritical water extraction

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Brown algae accumulation on beaches, or beach-cast, can lead to negative environmental impacts. However, beach-cast brown algae harvested from coastlines is a potential resource of bioactive compounds for use in food, biomaterial, cosmetic, and pharmaceutical industries. The extraction and subsequent separation and purification of bioactive compounds using conventional Solid–Liquid Extraction (SLE) requires improvement for sustainability and efficiency. Subcritical water processes are a potential "greener" approach in extraction without a decrease in process performance. This review outlines the bioactive compounds (alginate, fucoidan, laminarin, phenolic compounds, and fucoxanthin) in beach-cast brown algae and summarizes and compares conventional SLE and pressurized water methods: Accelerated Solvent Extraction (ASE) and Subcritical Water Extraction (SCWE). ASE is typically used in characterization/analysis, while SCWE is more appropriate for production. Extraction rate models and challenges related to scale-up in ASE and SCWE are also reviewed. ASE and SCWE can selectively extract bioactive compounds by modifying temperature/pressure and solvent combinations, and minimize extraction time, maximize yields and rates, and reduce chemical/solvent usage compared to SLE. However, kinetic modeling and scaling up of pressurized systems for brown algae valorization is still in its infancy. Future research is required to determine the green solvent combinations, develop batches into continuous processes, balance extraction conditions with product quantity and purity, and scale up for industrial-scale production.

Sustainability spotlight

The accumulation of beach-cast brown algae represents value loss and environmental challenges for ecosystems and communities, such as foul odors, potential harm to local organisms, and greenhouse gas emissions. However, employing green technologies to extract more value (alginate, fucoidan, laminarin, phenolics, and fucoxanthin) from less offers a sustainable solution for valorizing this "waste" biomass. These value-added compounds have various applications in food, biomaterials, cosmetics, and pharmaceuticals. This work reviews recent advancements in pressurized liquid processes, focusing on accelerated solvent extraction and subcritical water extraction for extracting bioactive compounds from small to large-scale applications and integrating them into the biorefinery concept. Aligned with UN SDG 7 for affordable and clean energy, it promotes renewable biomass development for a more sustainable future.

1 Introduction

Marine bioeconomy innovations are underway in Newfoundland and Labrador, Canada, with a focus on sustainably utilizing raw and underused marine biomass resources to create value-added products. This innovative approach aims to advance a circular economy by extracting more from less while minimizing energy consumption and waste generation.[1] One promising avenue is the sustainable utilization of beach-cast algae, typically considered waste but increasingly being recognized as a potential source of bioactive compounds (comparable to aquaculture/wild-harvested algae) such as polysaccharides, phenolic compounds, proteins, lipids, and pigments. These compounds provide health benefits, including antioxidant, anti-inflammatory, antitumor, and antibacterial properties, with applications in animal feed, human food, biomaterials, cosmetics, and pharmaceuticals.[2–4] However, the full potential of beach-cast algae remains untapped, as they are often disposed of in landfills, leading to value loss, environmental concerns, and greenhouse gas emissions.[5]

Global macroalgae production (aquaculture and wild harvesting) reached 38 million tonnes (wet weight) in 2022, marking a 4% increase from 2020 and approximately a 217% increase from 2000 (12 million tonnes). This growth was primarily driven by macroalgae aquaculture growth, particularly

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in Asia. China leads global macroalgae production, accounting for 60%, followed by Indonesia (25%), the Republic of Korea (5%), and the Philippines (4%).[6] Marine macroalgae can be classified into three groups depending on pigmentation and chemical structures: red (Rhodophyta), brown (Ochrophyta), and green (Chlorophyta) algae. Among these, brown algae, with over 1500 known species, are the most consumed globally, representing approximately 66.5% of algae consumption.[7,8] Brown algae are rich sources of bioactive components such as alginate, fucoidan, laminarin, phenolics, and fucoxanthin and contain compounds that act as nutrients, antioxidants, antivirals, and antimicrobials.[9,10] In order to determine the "best" processes and products from beach-cast brown algae, the material must be characterized in terms of bioactive concentration and physicochemical properties.

Extraction is a crucial step for the separation and purification of bioactive compounds for both quantification/characterization and industrial production purposes. Conventional methods for extracting bioactive compounds from algae biomass involve multiple steps influenced by factors such as temperature, extraction time, solvent choice, liquid-to-solid ratio/flow rate, and pre-treatment (drying and grinding).[11] Solid–liquid extraction (SLE) is the most common method, using liquid solvents such as methanol, chloroform, ethanol, acetone, and aqueous solution at ambient/elevated temperatures and atmospheric pressure. However, conventional SLE methods are often time-consuming and have safety/toxicity issues associated with large quantities of organic solvent usage.[12]

More recent developments in pressurized liquid extraction (PLE) aim to increase extraction efficiency, reduce extraction time, and minimize chemical/solvent usage to mitigate the negative impacts of toxic solvents on human health and the environment and potentially improve the overall sustainability of the process.[13] Two promising technologies that employ pressure are accelerated solvent extraction (ASE) and subcritical water extraction (SCWE).[8,14] ASE utilizes liquid solvents under elevated temperatures and very high pressure (40–200 °C and approximately 100 bar), which is particularly effective for lab-scale analysis and quantification. Elevated temperature and pressure enhance mass transfer rates, promote solvent penetration into solids and increase the solubility of target compounds, leading to faster extraction rates.[13,15] SCWE is a specific case of PLE, using subcritical water (SCW) as the solvent, as with ASE. However, the pressure of the system is typically set by the temperature, resulting in SCWE pressures <100 bar at the same temperature as ASE. The lower operating pressure makes SCWE more suitable for industrial-scale recovery *versus* the analytical scale of ASE.[16,17]

Although extensive works have reviewed advanced PLE technologies, including ASE and SCWE of bioactive compounds from marine macroalgae,[8,11,13,18–21] there is little study focused on beach-cast brown algae and ASE and SCWE processes at both small and large scales. Beach-cast algae will be weathered relative to the fresh counterpart, and therefore, process conditions using fresh algae may not be a good match for beach-cast.

In this context, this review will bridge the knowledge gap by highlighting beach-cast brown algae and their bioactive compound extraction using two "green" pressurized technologies (ASE and SCWE), focusing on quantification/characterization and industrial scaling-up. It will first provide an overview of biomass availability and potential bioactive compounds in beach-cast brown algae. This review will then focus on the extraction of these compounds using SLE, ASE, and SCWE. The comparisons of ASE and SCWE and their advantages and disadvantages are discussed. Studies on the economic and environmental sustainability of using these techniques for brown algae valorization will also outlined. Given the growing interest in ASE and SCWE as emerging alternatives to conventional SLE, understanding their extraction kinetics and mechanisms becomes crucial for predicting properties on a large scale. This review will summarize the scale-up and kinetic models of plant-based compound extraction using ASE and SCW to highlight the use of these techniques to obtain active compounds from beach-cast brown algae for a large-scale process.

2 Beach-cast brown algae

The accumulation of beach-cast algae has significantly increased in recent years, potentially due to climate change. The generation rate was estimated as 1 kg per square meter per year on a dry weight (dry wt) basis, with a turnover rate of around 2.6% per day.[22] Therefore, this substantial accumulation of beach-cast algae plays an essential ecological role within marine ecosystems.[1] Harb and Chow[2] comprehensively reviewed beach-cast algae, emphasizing their ecological significance and potential environmental issues, health concerns, and financial losses. For example, extensive algae left on beaches leads to waste accumulation, unpleasant odors, greenhouse gas emissions from decomposition, and adverse effects on the tourism industry in coastal regions worldwide.

Beach-cast brown algae can be harvested as a valuable resource for renewable materials and innovative products. Pardilhó *et al.*[3] explored the feasibility of zero-waste biorefinery approaches on the valorization of algae waste into products, aligning with circular and blue economy principles. Applications of beach-cast brown algae include human food, animal feed, fertilizers, biochemical production, gelling agents, biofuels, and novel biomaterials.[2,23,24] Brown beach-cast *Laminaria hyperborea* is commercially harvested in Scotland to produce soaps and glasses.[25] In Ireland, alginate extracted from beach-cast brown algae *Ascophyllum nodosum* is used in human food, animal feed, and cosmetic industries.[26] Bertagnolli *et al.*[27] harvested beach-cast brown algae *Sargassum filipendula* from Brazilian beaches for alginate extraction. Canada has engaged in the commercial harvesting of brown algae by OrganicOcean, including *Ascophyllum nodosum*, *Saccharina longicruris*, and *Fucus vesiculosus*. Australia also reported commercial beach-cast brown algae harvesting for high-value alginate and low-value products such as fertilizer and animal feed.[28] The global market for algae hydrocolloid alginate was valued at 345 million USD in 2015. Non-hydrocolloid polysaccharides (fucoidan and laminarin) have high market prices at 390 USD per kg and 52 USD per kg, respectively, due to their biological activities.[29,30] The global market size by sales volume for fucoidan and

laminarin is estimated at 17–18 t per year and 25–26 t per year, projected to grow at 3.8% and 8.7% compound annual growth rate, respectively.[31] Thus, the high value and growing markets make brown algae valorization a promising business case.

The suitability of beach-cast brown algae for commercial applications depends on several factors, including biomass quality, species, target compound concentration, resource availability, and local market demands.[3,4] Applications such as bioenergy, biofertilizers, and animal feed often do not require high-quality or homogenous quantities of brown algae. However, higher-value products demand high-quality feedstock. Due to the nutritional profiles and rich content of bioactive compounds in brown algae, the food, cosmetic, and pharmaceutical industries are typically the target market.[3,32] Recent reviews suggest that beach-cast brown algae may have similar potential to fresh brown algae for downstream applications.[2,33] Therefore, beach-cast brown algae could offer economic and ecological advantages, making them a sustainable biomass resource that improves environmental preservation and human health.

3 Potential bioactive compounds in beach-cast brown algae

3.1 Biomass availability and bioactive compounds concentration

Brown algae comprise a diverse group of over 1800 species classified into 20 classes. Among these, species belonging to the genera *Ascophyllum*, *Sargassum*, *Fucus*, *Laminaria/Saccharina*, and *Undaria* stand out for commercial value and bioactive

potential.[34] *Ascophyllum nodosum* is mainly cultivated/harvested from beaches. They are widely distributed on the rocky shores throughout the North Atlantic, including the northeastern coast of North America from New York to Newfoundland.[35] Brown algae genera *Fucus*, *Sargassum*, *Laminaria/Saccharina*, and *Undaria* can be cultivated and wild-harvested.[18] A comprehensive review by Pardilhó *et al.*[3] summarized global beach-cast algae accumulations, detailing species, quantities, and current commercial applications.

Brown algae are a source of nutrients (lipids, carbohydrates, proteins, minerals, and vitamins) and bioactive compounds (polysaccharides, phenolic compounds, and fucoxanthin) with various biological activities (Fig. 1). As shown in Table 1, brown algae genera *Ascophyllum*, *Sargassum*, and *Fucus* are rich in polysaccharides and phenolic compounds, accounting for up to 66–70 dry wt% and 12.7–14.0 dry wt% in gallic acid equivalents (GAE), respectively.[18,34] Fucoxanthin is present in the highest concentrations in the *Fucus* and *Undaria* genera, reaching up to 4.36 and 5.41 mg per g dry wt, respectively.[18] Bioactive compound concentrations vary among brown algae species and are influenced by environmental factors such as harvesting time, geographic habit, water temperature, light intensity, and nutrient levels.[10,27]

3.2 Polysaccharides

Beach-cast brown algae bioactive polysaccharides (alginate, fucoidan, and laminarin) have been extracted by SLE, ASE, and SCWE methods and are potentially used in functional foods, cosmetics, and medical industries.[21,37] The chemical structures of these polysaccharides are depicted in Fig. 2.

Fig. 1 The composition of brown algae with their potential bioactive compounds. Created with https://www.biorender.com/.

Table 1 Composition of major bioactive compounds in brown algae genera

	Ascophyllum spp.	*Sargassum* spp.	*Fucus* spp.	*Laminaria* spp./*Saccharina* spp.	*Undaria* spp.	Ref.
Polysaccharides (dry wt%)	42–70	68	62–66	38–61	35–45	34
Fucoidan (dry wt%)	3.9–12	1–4.5	16–20	2–55%	1.5–33%	18
Alginate (dry wt%)	18.3–23.7	0.6–35	25	31.1–40.5	Not applicable	36
Laminarin (dry wt%)	1.2–10	0.3	84% of total sugars	22–34	3	18
Phenolics (dry wt% GAE)	0.5–14	0.063–12.7	0.4–12.2	0.032–5.3	0.08–0.4	18
Fucoxanthin (mg per g dry wt)	0.172–1.78	0.0133–2.023	0.172–4.36	0.22–1.06	2.81–5.41	18

3.2.1 Alginate. Alginate is a natural polysaccharide made of a linear copolymer of α-L-guluronic acid (G) and β-D-mannuronic acid (M) bounded by β-1-4 glycosidic bonds. The molecular weight (MW), monomer frequency (M/G ratio), and the distribution of M and G units in the polymer chain affect the physical properties of alginate, such as viscosity and gel formation.[38] Typically, alginate with a high M/G ratio forms elastic gels, while a low M/G ratio results in brittle gels. Furthermore, G units have a higher affinity for divalent ions than M units due to their binding to G blocks. Gel stiffness increases in the
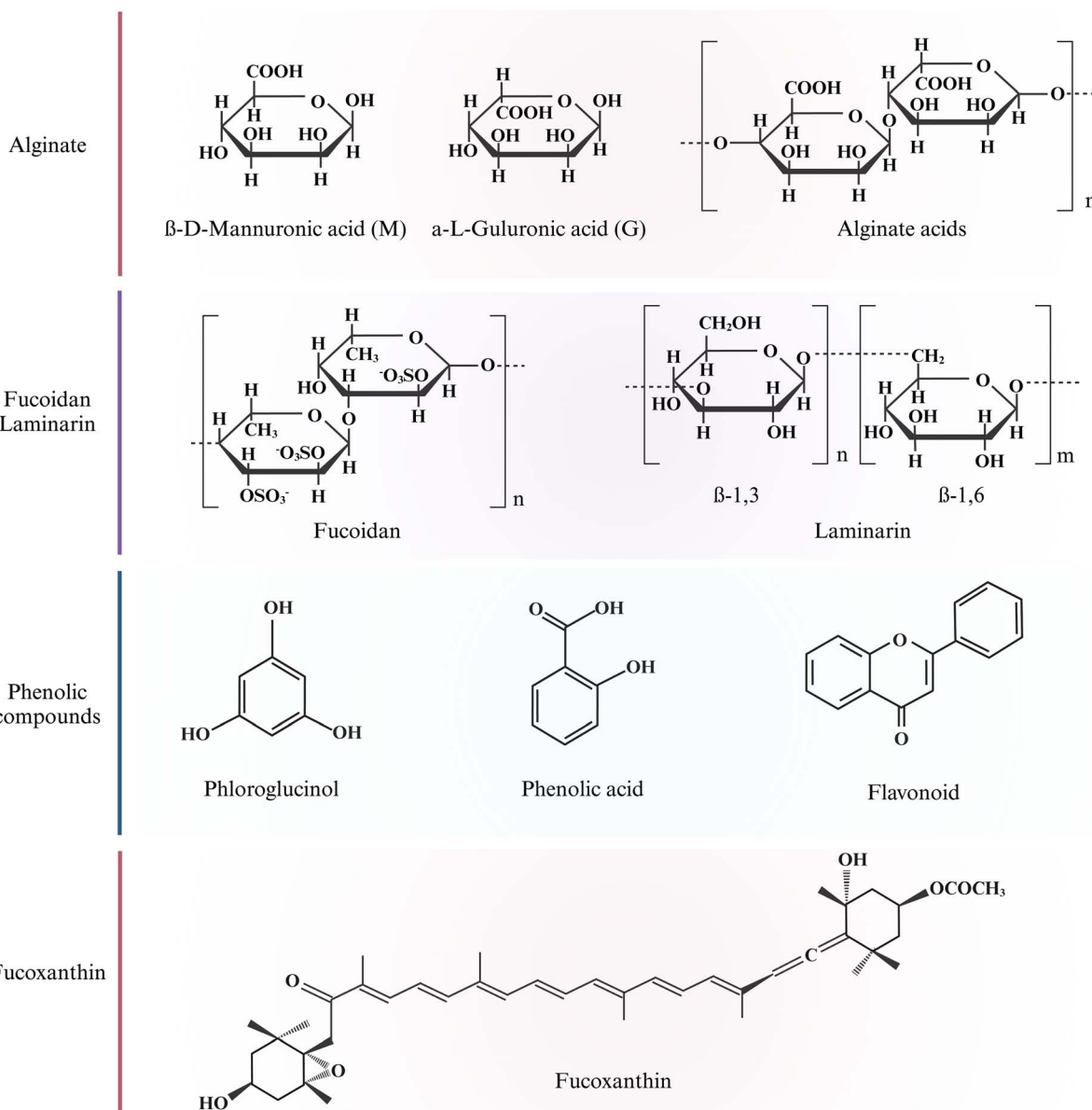
Fig. 2 Chemical structure of bioactive compounds in brown algae. Created with https://www.biorender.com/.

following order: MG blocks < MM blocks < GG blocks, whereas elasticity increases in the order GG blocks < MM blocks < MG blocks.[38,39] Alginates are found primarily in cell walls, up to 40.5 dry wt%, as a mixture of alginate salts (calcium, magnesium, and sodium). Commercial sodium alginate, with a MW of 32–400 kDa, is mainly extracted from brown algae genera *Ascophyllum*, *Laminaria*, and *Macrocystis*. The typical alginate extraction process involves several steps:[36] (i) soaking ground brown algae overnight in 2 wt% formaldehyde solution with a liquid-to-solid ratio ranging from 10 to 20 mL g^{-1}, (ii) pre-treating the collected solid algae with acid at 40–60 °C, with a liquid-to-solid ratio (10–30 mL g^{-1}) for 2–4 hours, (iii) extracting alginate with Na$_2$CO$_3$ (2–4 wt%) at 40–60 °C, with a liquid-to-solid ratio of 10–30 mL g^{-1} for 2–3 h, (iv) precipitating the resulting liquid phase with 95% ethanol at a 1 : 1 volume ratio, and (v) drying the solid sodium alginate in an oven at 50–60 °C.

Alginate offers diverse properties and biological activities, including high viscosity, gelation, biodegradability, biocompatibility, and antibacterial and anticancer abilities. Alginate has applications in thickening/emulsifying agents, wound dressings, and functional food ingredients across industries.[36]

3.2.2 Fucoidan. Fucoidan, a sulfated polysaccharide, consists of an L-fucose backbone with other monomers such as mannose, galactose, glucose, xylose, and uronic acid.[40] Fucoidan is typically located in intercellular spaces and cell walls. The chemical composition of fucoidan varies among species, locations, and extraction methods, affecting their functional properties. They are commonly extracted from beach and coastal brown algae using SLE with hot water or diluted acid/alkaline at 70–100 °C for several hours, with an initial organic solvent soaking step to remove impurities.[41] Brown algae mozuku, kombu, limu moui, bladderwrack, and wakame are some sources of fucoidan. Extraction methods, sulfate content, structures, and MW (ranging from 21–1600 kDa) can affect biological activities and potential applications.[21,42] Reported biological activities include antioxidant, anticancer, anti-inflammatory, and anticoagulant abilities.[39,43,44]

3.2.3 Laminarin. Laminarin, a storage polysaccharide and bioactive compound found in cell vacuoles, is primarily extracted from genera *Laminaria* and *Saccharina*, with lesser extraction from genera *Ascophyllum*, *Fucus*, and *Undaria*. Laminarin is a low MW polysaccharide (approximately 5 kDa) and is composed of β-(1,3)-d-glucan and some β-(1,6)-intrachain links. It has both soluble and insoluble forms depending on the level of branching. Highly branched laminarin dissolves in cold/hot water, while laminarin with a low branching level only dissolves in hot water.[29] Laminarin exhibits various biological activities, including antioxidant, anticoagulant, anti-inflammatory, and anticancer properties, making it a promising source for functional food ingredient exploration.[29,44]

Several studies have attempted to integrate the extraction pathways of fucoidan, alginate, and laminarin, demonstrating the valorization potentials of brown algae species.[45–48] Abraham *et al.*[45] reported a method for co-extracting sodium alginate, fucoidan, and laminarin from beach-cast brown algae *Durvillaea potatorum*, incorporating an acid extraction step followed by an alkaline extraction. Similarly, Kostas *et al.*[46] extracted alginate and fucoidan from *Laminaria digitata*. They also explored the potential of the solid residue as feedstock for bioethanol production and characterized the antioxidant and antimicrobial activities of the waste liquid stream. Yuan and Macquarrie[47] developed a microwave-assisted step-by-step process for producing fucoidan, alginate, sugars, and biochar from *Ascophyllum nodosum*. Lorbeer *et al.*[48] compared the sequential extraction of fucoidans and alginates from different beach-cast brown algae (*Ecklonia radiata*, *Macrocystis pyrifera*, *Durvillaea potatorum*, and *Seirococcus axillaris*), demonstrating process effectiveness when using different feedstocks. These studies are essential for maximizing the value of "waste" brown algae through zero-waste biorefinery approaches.

3.3 Phenolic compounds

Phenolic compounds are a group of secondary metabolites in plants consisting of one or multiple aromatic rings bonded to one or more hydroxyl groups. Brown algae are rich in phenolic compounds such as phlorotannins, phenolic acids, and flavonoids.[49] Phlorotannins are derived from the polymerization of phloroglucinol (1,3,5-trihydroxybenzene) unit. They are highly hydrophilic across a wide range of MW range (126–650 kDa).[50] Phenolic acids are a sub-class of phenolic compounds characterized by one carboxylic acid group.[51] Flavonoids have 15 carbon skeletons and actively defend algae against oxidative damage.[52] Fig. 2 shows phloroglucinol, phenolic acid, and flavonoid chemical structures. Phenolic compounds are widely used ingredients in healthy food due to their strong antioxidant abilities. Antioxidant compounds have a wide range of applications in food, supplements, and medicinal industries. The interaction between brown algae and environments will affect the distribution and concentration of phenolic compounds produced.[8]

3.4 Fucoxanthin

Fucoxanthin is a xanthophyll carotenoid abundant in brown algae and is responsible for its coloration.[53] It has a unique chemical structure that contains nine conjugated double bonds, an allenic bond, epoxy, hydroxyl, carbonyl, and carboxyl groups in the molecule, as shown in Fig. 2. Fucoxanthin is a linear polymer with lower polarity, typically extracted from brown algae genera *Undaria*, *Sargassum*, and *Laminaria* using organic solvents.[54] The concentration of fucoxanthin varies depending on species, geographical location, and harvesting season. For example, higher fucoxanthin levels are observed during winter when sunlight exposure and ocean temperatures are low. Fucoxanthin demonstrates diverse potential health benefits, including antioxidant, anti-inflammatory, anticancer, anti-obesity, and anti-diabetic effects, providing broad applications as a promising bioactive compound.[55]

4 Solid–liquid extraction

4.1 Extraction mechanisms

Conventional SLE, also referred to as leaching, is a widely used method for extracting bioactive compounds for characterization

Table 2 SLE of bioactive compounds from beach-cast brown algae[a]

Country, source	Target bioactive compounds and biological activity	Extraction conditions	Brown algae species	Solvents: total extraction yield*; bioactive compound yield**1; bioactive compound content**2	Ref.
Brazil, beach-cast	Phenolics polysaccharides antioxidant	Methanol: RT, 72 h, 30 mL g⁻¹, Water: 80 °C, 9 h, 30 mL g⁻¹	D. jolyana (ES)	Methanol: 4.49 *; 77.30 mg PGE per g **1; Water: 30.04 *; 69.51 mg PGE per g **1	57
			D. jolyana (PB)	Methanol: 2.66 *; 141.55 mg PGE per g **1; Water: 29.67 *; 118.51 mg PGE per g **1	
			D. polypodioides	Methanol: 2.55 *; 58.59 mg PGE per g **1; Water: 9.51 *; 79.82 mg PGE per g **1	
			Z. tournefortii	Methanol: 4.12 *; 89.85 mg PGE per g **1; Water: 12.02 *; 98.42 mg PGE per g **1	
Spain, coast	TPC antioxidant antibacterial	50 °C, 24 h, 20 mL/0.6 g	U. pinnatifida	Ethanol: 38.80 *; 3.68 mg GAE per g **2; Acetone: 3.40 *; 41.50 mg GAE per g **2	58
			H. elongata	Ethanol: 27.00 *; 30.26 mg GAE per g **2; Acetone: 3.60 *; 162.22 mg GAE per g **2	
			B. bifurcata	Ethanol: 24.10 *; 11.39 mg GAE per g **2; Acetone: 10.80 *; 86.08 mg GAE per g **2	
			S. muticum	Ethanol: 17.90 *; 8.31 mg GAE per g **2; Ethyl acetate: 0.30 *; 41.63 mg GAE per g **2	
			L. ochroleuca	Ethanol: 19.20 *; 2.81 mg GAE per g **2; Ethyl acetate: 1.40 *; 32.46 mg GAE per g **2	
			S. latissima	Ethanol: 18.00 *; 2.44 mg GAE per g **2; Acetone: 2.90 *; 16.53 mg GAE per g **2	
			P. canaliculata	Ethanol: 15.60 *; 49.49 mg GAE per g **2; Acetone: 12.20 *; 87.32 mg GAE per g **2	
			F. spiralis	Ethanol: 14.60 *; 95.75 mg GAE per g **2; Acetone: 7.80 *; 184.22 mg GAE per g **2	
			A. nodosum	Ethanol: 18.20 *; 117.2 mg GAE per g **2; Ethyl acetate: 10.30 *; 211.83 mg GAE per g **2	
Ireland, coast	TPC antioxidant	Organic solvent: RT, 24 h, 10 mL g⁻¹, Cold water: RT, 24 h, 20 mL g⁻¹, Hot water: 60 °C, 24 h, 20 mL g⁻¹	L. digitata	Ethanol/water (80:20): 35.20 *; 1.39 µg GAE per mg **2; Methanol/water (70:30): 36.50 *; 2.93 µg GAE per mg **2; Cold water: 39.50 *; 2.24 µg GAE per mg **2; Hot water: 7.90 *; 5.06 µg GAE per mg **2	59
			F. serratus	Ethanol/water (80:20): 24.90 *; 75.96 µg GAE per mg **2; Methanol/water (70:30): 26.30 *; 80.70 µg GAE per mg **2; Cold water: 35.90 *; 81.17 µg GAE per mg **2; Hot water: 6.20 *; 79.49 µg GAE per mg **2	
Korea, coast	Fucoxanthin Fatty acids Antioxidant Antimicrobial Antihypertensive	RT, 20 h, 20 mL g⁻¹	S. horneri	Hexane: 1.42 *; 0.05 mg fucoxanthin per g **2; Ethanol: 1.36 *; 0.08 mg fucoxanthin per g **2; Acetone/methanol (1:1, v/v): 1.29 *; 0.71 mg fucoxanthin per g **2	60
			S. japonica	Hexane: 1.24 *; 0.16 mg fucoxanthin per g **2; Ethanol: 1.22 *; 0.12 mg fucoxanthin per g **2; Acetone/methanol (1:1, v/v): 1.19 *; 0.48 mg fucoxanthin per g **2	
China, coast	Polysaccharides	84 °C, 4.3 h, 27 mL g⁻¹	A. nodosum	Water: 9.15 *	61

Table 2 *(Contd.)*

Country, source	Target bioactive compounds and biological activity	Extraction conditions	Brown algae species	Solvents: total extraction yield*; bioactive compound yield**1; bioactive compound content**2	Ref.
China, coast	Antioxidant Immunostimulatory Polysaccharides Antioxidant	80 °C, 4 h for water/8 h for citric acid/NaOH, 50 mL g^{-1}	*L. japonica*	Water: 10.25 * Citric acid (pH 2): 11.23 * NaOH (pH 10): 44.63 *	62

^{a} * total extraction yield on a dry wt basis (dry wt%); **1 bioactive compound yield in g of dry wt basis of algae; **2 bioactive compound content in g of dry wt basis of algae; **2 bioactive compound content in g of extract; RT = room temperature; TPC = total phenolic compounds; PGE = phloroglucinol equivalents; GAE = gallic acid equivalents.

or production. It involves the transfer of solutes (one or more substitutes) from a solid or semisolid matrix to the liquid phase. The mechanism of SLE is made up of five steps:[56] (i) wetting the sample matrix with liquid solvents; (ii) desorption of compounds from the solid matrix, including the breakdown of chemical bonds between solutes and solids; (iii) dissolution of compounds into the solvent; (iv) diffusion of solutes from the matrix to the external surface of the solids; (v) mass transfer of solutes from the solid surface into bulk solvents.

Typically, the mass transfer of solute through the solid matrix is the rate-limiting step. Internal diffusion can be enhanced by reducing particle size and breaking down cell walls. External mass transfer can be improved by mixing/stirring in batch systems or increasing the flow rate in continuous-flow systems. The efficiency of solvent extraction (rate and yield) is a function of the target compound(s), liquid solvents, extraction time, temperature, liquid-to-solid ratio/flow rate, and particle size of the solid matrix. Among these factors, the liquid solvent is critical as it influences the solubility, selectivity, and sustainability.[56] Organic solvents are commonly used for extracting phenolics, fucoxanthin, and antioxidants due to the medium-to-high polarity of phenolics and the low-to-medium polarity of fucoxanthin. Conversely, due to the water-soluble nature of polysaccharides, acid/alkaline water is a common solvent for recovering fucoidan, alginate, and laminarin from beach-cast brown algae.[21] Table 2 summarizes recent studies on optimizing SLE with organic/aqueous solvents for components extraction from beach-cast brown algae worldwide.

4.2 SLE of bioactive compounds using organic solvents

Organic solvents are extensively used to extract bioactive compounds from brown algae harvested from beaches, coasts, and wild environments (Table 2). Brown algae contain diverse metabolites with varying concentrations and unique biological activities.[10]

As shown in Table 2, extraction yields vary across algae species and solvent systems. Harb *et al.*[57] analyzed the antioxidant activities and chemical composition of four beach-cast brown algae and nine green/red algae from Brazilian beaches. Results showed that extracts from beach-cast brown algae (*Dictyopteris jolyana*, *Dictyopteris polypodioides*, *Zonaria tournefortii*) exhibited the highest antioxidant activities, followed by eight red algae and one green algae. Similarly, Harb *et al.*[63] found that extracts from four tested Brazilian brown algae wastes displayed the highest antioxidant activity, followed by two red and one green algae. Heffernan *et al.*[59] also reported that beach-cast brown algae (*Fucus serratus*) had total phenolic content (TPC) and antioxidant activities thirty times higher than the other beach-cast red algae (*Gracilaria gracilis*) and green algae (*Codium fragile*). The above three studies observed a positive correlation between TPC and antioxidant activity.

Harb *et al.*[57] evaluated four organic solvent systems, and methanol exhibited higher extraction yields compared to hexane, dichloromethane, and ethyl acetate. Methanol extracts were rich in phenolic compounds and sulfated polysaccharides,

showing potential for antioxidant applications. However, this study only analyzed the highest-yield extracts (methanol), and the highest yield does not always translate to the highest quality (extract composition and functionality). Silva et al.[58] compared five organic solvents (ethanol, acetone, ethyl acetate, chloroform, and hexane) for extraction yield, TPC, antioxidant capacity, and antibacterial abilities of nine brown algae. The highest extract yield was achieved when using ethanol as a solvent, while ethyl acetate/acetone extracts exhibited the highest TPC and antioxidant capacity. Heffernan et al.[59] extracted phenolics and antioxidants from Brazilian beach-cast brown algae *Laminaria digitata* and *Fucus serratus* using 80 vol% ethanol and 70 vol% methanol as solvents. Slightly higher extract yields and TPC were observed with 70 vol% methanol, while ferric-reducing antioxidant power (FRAP) was higher in 80 vol% ethanol. Periaswamy Sivagnanam et al.[60] investigated fucoxanthin extraction from Korean brown algae (*Saccharina japonica* and *Sargassum horneri*) collected from the coast. Three solvents (hexane, ethanol, and a 50 : 50 vol% mixture of acetone/methanol) were compared in SLE at room temperature for 20 h. While the acetone/methanol mixture exhibited lower extraction yields compared to hexane and ethanol, it yielded higher fucoxanthin contents for both *Saccharina japonica* and *Saccharina horneri*. Specifically, the fucoxanthin content in the acetone/methanol mixture was three times the value of the hexane extract (0.48 mg g^{-1} *vs.* 0.16 mg g^{-1} of crude extract) and four times the ethanol extract (0.12 mg g^{-1} of crude extract) for *Saccharina japonica*. This difference was more pronounced in *Saccharina horneri*, where hexane and ethanol extracts were 10–12% of the acetone/methanol fucoxanthin. This study also noted crude extracts were rich in phenolics, fatty acids, and fucoxanthin exhibiting antioxidant, antimicrobial, and antihypertension effects.

4.3 SLE of bioactive compounds using aqueous solvents

Water-based solvents are potentially greener options compared to organic solvents. As shown in Table 2, water has been widely used in bioactive extraction from beach-cast brown algae, mainly for polysaccharides. Aqueous extracts from four Brazil beach-cast brown algae showed 3–13 folds higher extraction yields compared to methanolic extracts. These aqueous extracts also exhibited higher ABTS$^+$ scavenging and metal chelating activities for all four studied beach-cast brown algae compared to methanolic extracts.[57] Similarly, another study on beach-cast algae (*Fucus serratus*) demonstrated that SLE using water at room temperature had higher extraction yield (35.90 dry wt%) and TPC (81.17 μg GAE per g extract) compared to organic solvents ethanol (yield of 24.9 dry wt% and 75.96 μg GAE per g extract) and methanol (yield of 26.3 dry wt% and TPC of 80.70 μg GAE per g extract).[59]

Polysaccharides are highly soluble in water but insoluble in organic solvents such as ethanol and acetone. Therefore, the typical process is water extraction followed by ethanol precipitation. Chen et al.[61] optimized water extraction of polysaccharides from *Ascophyllum nodosum* using the Box–Behnken design (BBD). The "best" crude polysaccharide yield of $9.15 \pm$

0.23 dry wt% was obtained at an extraction time of 4.3 h, a temperature of 84 °C, and a water-to-solid ratio of 27 mL g^{-1}. Sun et al.[62] studied the impact of acidic, water, and alkaline effects on polysaccharide yields, structural features, and antioxidant activities from brown algae *Laminaria japonica*. Alkaline extraction (NaOH, pH 10) achieved the highest polysaccharide yield (44.63 dry wt%), surpassing pH 2 citric acid (11.23 dry wt%) and water (10.25 dry wt%) extraction. SLE under acidic and alkaline conditions showed extracts with irregular and rough particles and stronger antioxidant activities, including free radical scavenging, Fe^{2+} chelating capacity, and lipid peroxidation inhibition. Peasura et al.[64] observed similar trends in green algae *Ulva intestinalis*, where alkaline extraction yielded higher sulfated polysaccharide yields (14 dry wt%) compared to distilled water (10 dry wt%) and 0.1 M HCl (12 dry wt%) at the same conditions (80 °C, 6 h, and a liquid-to-solid ratio of 20 mL g^{-1}). However, polysaccharides extracted at acidic conditions exhibited better antioxidant activity than those from water and alkali. These results suggest that adding acid/alkali can help break down chemical bonds between cellulose in brown algae cell walls, facilitating the release of polysaccharides into the solvent. However, caution is needed in conventional acid/base treatments due to the potential risk of breaking covalent bonds in the targeted solute of interest.[52]

5 Accelerated solvent extraction

Bioactive compound extraction using liquid solvents is common in analytical laboratories due to its simple setup. However, the process is often time-consuming (usually 4–72 h) and requires large volumes of organic solvents (approximately 10–50 mL per g biomass). Concerns about organic solvent usage, associated human exposure, and increased purchase and disposal costs have highlighted the need for more efficient extraction methods. In response to these concerns, ASE was introduced. ASE is a higher-pressure variation (40–200 °C, approximately 100 bar) of conventional SLE where the same solvents can be used. However, the increased pressure and temperature produce high-diffusion liquids. The resulting faster extraction rates lead to reduced extraction time, solvent savings, and increased yields. The automatic ASE system does not typically require an extra pre-treatment step (separation or concentration), making it ideal for analytical analysis (quantification/characterization).[13] This section discusses recent developments in ASE for extracting bioactive compounds from beach-cast brown algae.

5.1 Principles and mechanisms

The ASE technique was first introduced in 1996 by Richter et al.[65] The Dionex Corporation (Thermo Fisher Scientific, USA) subsequently commercialized extraction units, including ASE 150, 200, and 350 systems, which have been widely used by many laboratories worldwide. As noted above, ASE operates at 40–200 °C and approximately 100 bar. The extraction is modeled as a four-stage process:[14] (i) solvent penetration into solids, (ii) solute(s) desorption/dissolution, (iii) internal

Fig. 3 (A) Mechanism of ASE technique. (B) Schematic of the ASE Process. (C) Commercial automated accelerated solvent extractor. Created with https://www.biorender.com/.

diffusion of solute(s), and (iv) external mass transfer of solute(s) into the bulk flowing fluid (Fig. 3). Elevated temperature increases solvent diffusivity by reducing solvent viscosity and surface tension, accelerating the extraction rates. Pressure maintains the solvent in a liquid state at temperatures above its boiling point, facilitates a more rapid extraction cell filling, and more effective solvent penetration. Furthermore, the pressurized solvent enhances the solubility of targets, resulting in increased extraction rates and yields. The degree of enhancement is a function of not only pressure and temperature but also the solvent(s) of choice. For instance, when the solvent is water in ASE conditions, water is subcritical, and the process is low-polarity water extraction. However, high temperatures can degrade thermolabile compounds such as pigments and alginate.[66] Therefore, optimization of extraction conditions, especially temperature, is vital to maximize the quality and quantity of yield(s).

ASE has three operation modes: static, dynamic, and semidynamic.[14] Most ASE studies involving bioactive compounds from brown algae focus on static mode (Table 3). In this mode, pressurized solvent reacts with the solid matrices for a fixed time at constant pressure and temperature before collection. Although the static mode uses less solvent than other modes, the extraction efficiency is limited once equilibrium concentration in the solute is achieved. Thermal degradation and undesirable chemical reactions can occur after equilibrium. Dynamic ASE employs a continuous supply of fresh pressurized liquid, avoiding equilibrium but potentially requiring more solvent and reducing contact time for desorption and diffusion. Semi-dynamic extraction, also known as the multiple rinse cycle mode, combines static and dynamic features. It begins with a static period ensuring desorption/internal diffusion, followed

by dynamic flow by introducing fresh solvent to shift equilibrium.

5.2 ASE of bioactive compounds from beach-cast brown algae

The studies outlined below include bioactive compound extraction from dried and ground brown algae powder and ASE combined with separation (e.g., precipitation and purification) to extract phenolics and polysaccharides. Antioxidant activity is one of the most extensively studied biological properties. As shown in Table 3, overall crude extract yields vary with species and extraction parameters. The effects of solvents and temperatures are the most extensively studied. Getachew et al.[67] investigated ASE using water for bioactive compound extraction from beach-cast brown algae *Fucus vesiculosus*. They found the highest yield (25.99 dry wt%), TPC (51.04 mg GAE/g extract), and antioxidant activities were achieved between 190-200 °C. However, the highest alginate yield (2.08 dry wt%) and fucoidan yield (12.52 dry wt%) were observed at 140 °C and 160 °C, respectively. The decrease in polysaccharide yield at higher temperatures may be due to thermal degradation or Maillard reactions, leading to polysaccharide breakdown into small organic acids. Dobrinčić et al.[68] reported a comparable temperature range for sulfated polysaccharide extraction from brown algae *Fucus virsoides* harvested from the southwest coast of the Novigrad Sea, Croatia. The highest polysaccharide yield (24.22 dry wt%) was achieved at 140 °C, with a liquid-to-solid ratio of 22 mL g^{-1}, 103 bar pressure, over 37 min, using 0.1 M H$_2$SO$_4$ as a solvent.

Plaza et al.[69] studied ASE as an analytical method to characterize bioactive compounds for antioxidant and antimicrobial

Table 3 ASE extraction of bioactive compounds from beach-cast brown algae[a]

Country, source, species	Extractor	Extraction parameters					Bioactive compounds	Yields	Ref.
		Solvents (v/v)	T (°C)	P (bar)	t (min)	L/S (mL g^{-1})			
Denmark, beach, F. vesiculosus	ASE 350	Water	190	103	14	10	Crude extract	25.99 dry wt%	67
			140	103	12	10	Alginate	2.08 dry wt%	
			160	103	13	10	Fucoidan	12.52 dry wt%	
			200	103	14	10	Phenolics	51.04 mg GAE per g extract	
			150	103	12	10	Phlorotannin	2.24 mg per g extract	
Croatia, coast, F. virsoides	ASE 350	0.1M H_2SO_4	140	103	37	22	Polysaccharides	24.22 dry wt%	68
Spain, H. elongata	ASE 200	Hexane	50	103	25	11	Crude extract	3.41 dry wt%	69
			100	103	25	11	Crude extract	3.50 dry wt%	
			150	103	27	11	Crude extract	4.72 dry wt%	
			200	103	29	11	Crude extract	7.59 dry wt%	
		Ethanol	50	103	25	11	Crude extract	8.29 dry wt%	
			100	103	25	11	Crude extract	10.56 dry wt%	
			150	103	27	11	Crude extract	19.23 dry wt%	
			200	103	29	11	Crude extract	36.91 dry wt%	
		Water	50	103	25	11	Crude extract	9.51 dry wt%	
			100	103	25	11	Crude extract	15.08 dry wt%	
			150	103	27	11	Crude extract	46.43 dry wt%	
			200	103	29	11	Crude extract	51.56 dry wt%	
Spain, H. elongata	ASE 200	Hexane	100	103	25	13.8	Crude extract	—	70
		Ethanol	100	103	25	7.3	Crude extract	—	
		Water	100	103	25	11	Crude extract	—	
Denmark, beach, F. vesiculosus	ASE 350	Ethanol/water (58.65 : 41.35)	137.18	103	10	10	Crude extract	31.16 dry wt%	71
			137.18	103	10	10	Phenolics	3.69% GAE	
Ireland, coast, F. serratus	ASE 200	Water	120	103	25	8.8	Crude extract	33.40 dry wt%	59
		Water	120	103	25	8.8	Phenolics	21.32 µg GAE per g extract	
		Ethanol/water (80 : 20)	100	69	25	8.8	Crude extract	31.70 dry wt%	
		Ethanol/water (80 : 20)	100	69	25	8.8	Phenolics	56.68 µg GAE per g extract	
		Methanol/water (70 : 30)	90	69	25	8.8	Crude extract	29.20 dry wt%	
		Methanol/water (70 : 30)	90	69	25	8.8	Phenolics	61.11 µg GAE per g extract	
Ireland, coast, L. digitata		Water	120	103	25	8.8	Crude extract	29.80 dry wt%	
		Water	120	103	25	8.8	Phenolics	1.37 µg GAE per g extract	
		Ethanol/water (80 : 20)	100	69	25	8.8	Crude extract	24.80 dry wt%	
		Ethanol/water (80 : 20)	100	69	25	8.8	Phenolics	2.20 µg GAE per g extract	
		Methanol/water (70 : 30)	90	69	25	8.8	Crude extract	28.20 dry wt%	
		Methanol/water (70 : 30)	90	69	25	8.8	Phenolics	2.18 µg GAE per g extract	
France, wild, S. muticum	ASE 200	Ethanol/water (95 : 5)	160	103	26	5.5	Crude extract	21.90 dry wt%	72
			160	103	26	5.5	Phenolics	94 mg GAE per g extract	
			160	103	26	5.5	Phlorotannins	5.02 mg PGE per g extract	
Korea, coast, E. bicyclis	ASE	Ethanol/water (90 : 10)	110	103	11	5.5	Fucoxanthin	0.42 mg g^{-1}	73

Table 3 (*Contd.*)

| Country, source, species | Extractor | Extraction parameters | | | | | Bioactive compounds | Yields | Ref. |
		Solvents (v/v)	T (°C)	P (bar)	t (min)	L/S (mL g⁻¹)			
Spain, coast, *L. ochroleuca*	ASE 350	Hexane	120	103	15	10	Crude extract	9.02 dry wt%	74
			160	103	18	10	Crude extract	7.43 dry wt%	
		Ethyl acetate	120	103	15	10	Crude extract	7.42 dry wt%	
			160	103	18	10	Crude extract	5.29 dry wt%	
		Ethanol	120	103	15	10	Crude extract	15.54 dry wt%	
			160	103	18	10	Crude extract	11.55 dry wt%	
		Ethanol/water (1:1)	120	103	15	10	Crude extract	47.16 dry wt%	
			160	103	18	10	Crude extract	51.91 dry wt%	

^{a} T = temperature (°C), P = pressure (bar), t = total extraction time (min), including ramp-up time and static time, L/S = liquid-to-solid ratio (mL g⁻¹), GAE = gallic acid equivalents, PGE = phloroglucinol equivalents.

activities from brown algae *Himanthalia elongata*. Different solvents (hexane, ethanol, and water) and temperatures (50, 100, 150, and 200 °C) were evaluated for impact on crude extract yield, chemical composition, and biological activities. As with previous work, higher temperatures resulted in increased extract yield. Solvents with higher polarity led to greater extraction yield, indicating major compounds in *Himanthalia elongata* tend to be medium to highly polar. In another antiviral study, Santoyo *et al.*[70] focused on *Himanthalia elongata* and found that ethanol extracts were able to better inhibit virus infection, approximately 90% at a concentration of 75 μg mL⁻¹, compared to water and hexane extracts, which reduced virus infectivity to 78% and 70%, respectively. Subsequent characterization of extracts revealed that the antiviral activity of water extracts correlated with polysaccharides, while ethanol and hexane extracts were associated with fucosterol.

Several studies have explored solvent mixtures to balance yield and quality/biological activity. Studies of ethanol/water mixtures dominate, as ethanol is generally recognized as safe (GRAS) and suitable for use in the food industry. Heffernan *et al.*[59] compared the impact of water, 80 vol% ethanol, and 70 vol% methanol on the extraction yield, TPC, and antioxidant activity from brown algae *Fucus serratus* and *Laminaria digitata* harvested from coastal areas. The highest yield (33.40 dry wt%) was achieved for *Fucus serratus* using water as a solvent, surpassing aqueous ethanol (31.70 dry wt%) and aqueous methanol (29.20 dry wt%). However, ethanol/water and methanol/water extracts showed higher TPC and antioxidant activities compared to water extracts, demonstrating the role operating conditions play in quantity and quality. Sumampouw *et al.*[71] optimized ASE conditions to achieve high extract yield, TPC, and strong antioxidant properties from beach-cast brown algae *Fucus vesiculosu*. Optimal conditions (137.18 °C, 58.65 vol% ethanol in water for 4.68 min) produced a yield of 31.16 dry wt%, phenolic yield of 3.69 g GAE/100 g dry wt, and effective concentrations for 50% inhibition (EC_{50}) of DPPH radical (92.60 μg mL⁻¹), ABTS radical (2.35 mg mL⁻¹), and metal chelating (1.10 mg mL⁻¹). In another study, Sánchez-Camargo *et al.*[72] compared ASE with enzyme-assisted extraction and alkaline hydrolysis, with results showing that ASE alone produced the highest yields and antioxidant activity. The maximum yield (21.90 dry wt%), TPC (94.00 mg GAE/g extract), phlorotannins content (5.02 mg per g extract), and antioxidant activity (1.28 mmol Trolox equivalents per g extract) were obtained at 160 °C and 95 vol% ethanol conditions.

ASE has been studied to extract fucoxanthin and fatty acids. Shang *et al.*[73] optimized the extraction conditions for fucoxanthin from brown algae using a design of experiment approach. Solvent and temperature were the most significant factors, achieving a maximum fucoxanthin yield of 0.42 mg g⁻¹ at 110 °C with 90 vol% ethanol. Otero *et al.*[74] assessed fatty acids and TPC extracted from brown algae *Laminaria ochroleuca* using ASE. Four solvent systems (hexane, ethyl acetate, ethanol, and ethanol/water 1 : 1, v/v) were compared, with the ethanol/water mixture giving the highest yield (51.91 dry wt%), TPC (173.65 mg GAE per g extract), and antioxidant activity at 160 °C and 18 min extraction time. While ASE has shown excellent

utility in characterizing and high yields of bioactive compounds in algae, running a system at over 100 bar can be challenging as one scales up. As such, SCWE, which runs at lower pressures, maybe a better option for production.

6 Subcritical water extraction

Subcritical water (SCW) is defined as water at pressures and temperatures to maintain the water in the liquid phase even though above the normal boiling point of water. This translates to pressures between 10-221 bar and temperatures between 100–374 °C.[75] Subcritical water extraction (SCWE) utilizes SCW as a green solvent, also known as pressurized hot water extraction (PHWE) or superheated water extraction. When water is used as the sole solvent in an ASE system under operational conditions of 100–200 °C and approximately 100 bar, ASE can also be considered SCWE in this specific context. Both ASE and SCWE offer faster extraction rates, reduced solvent usage, and higher yields compared to conventional SLE methods.[13] However, unlike ASE, SCWE is more readily scalable for industrial use due to its ability to operate at lower pressures (water vapor pressure).[52]

6.1 Principles and mechanisms

The SCWE of bioactive compounds from solid/semisolid samples can generally be described as the same five stages as SLE,[56] as outlined in Section 4.1. Operation parameters such as temperature, pressure, extraction time/flow rate, and particle size influence the five extraction stages. Fig. 4 shows the P–T diagram for water and the subcritical region and depicts a typical lab-scale pressurized reactor.

6.1.1 Temperature. Temperature optimization is crucial in SCWE as it determines the physicochemical properties of water and impacts all five extraction steps.[56] Heating water weakens hydrogen bonds, leading to the dissociation of water into H_3O^+ and OH^-, increasing the ionic product (K_w). As temperature increases from room temperature to 300 °C, at a constant pressure of 250 bar, the ionic product increases from 10^{-14} to 10^{-11} (mol L^{-1}).[2] The high ionic product water translates to the water acting as an acid/base catalyst, favoring ionic reactions. The dielectric constant (ε) decreases with temperature increase and shifts water from a polar to a semi-polar/nonpolar solvent and impacts the solvation power.[76] For instance, as temperature increases from 25 to 200 °C, the dielectric constant decreases from 78 to 35 at a constant pressure of 15 bar, which makes it comparable to methanol ($\varepsilon = 33$) and ethanol ($\varepsilon = 24$) at ambient conditions.[52]

As noted in ASE, the elevated temperature reduces water viscosity and surface tension while enhancing diffusivity, allowing deep solvent penetration into the solid matrix and improving mass transfer. The temperature increase also reduced intermolecular forces between solutes and solids, resulting in faster desorption of solutes from the matrix.[17] However, the solubility effect can impact both target and nontarget compounds, resulting in a less selective process. In addition, other chemical reactions and thermal degradation may occur under high temperature and pressure conditions.[52]

6.1.2 Pressure. The pressure has limited effects on liquid water properties and extraction efficiency in SCWE.[17] However, high pressure may help wet the solid sample and break the cell wall structures, increasing extraction rates and yields. Elevated pressure also results in high costs and difficulty scaling.
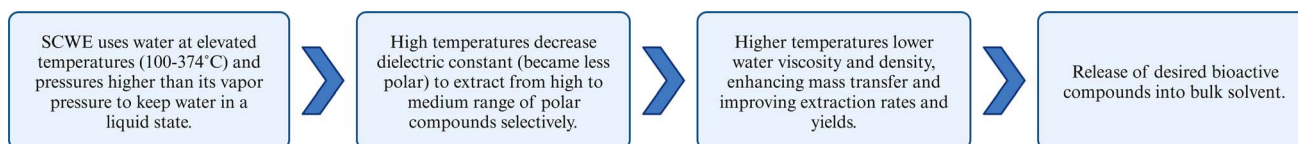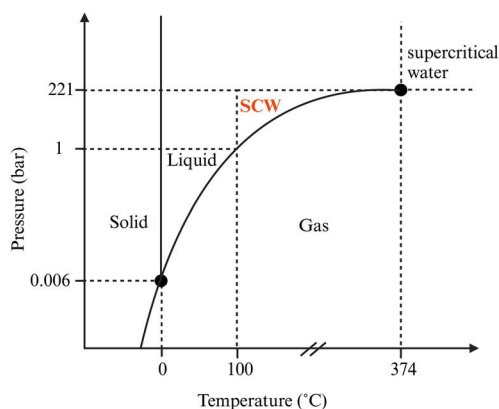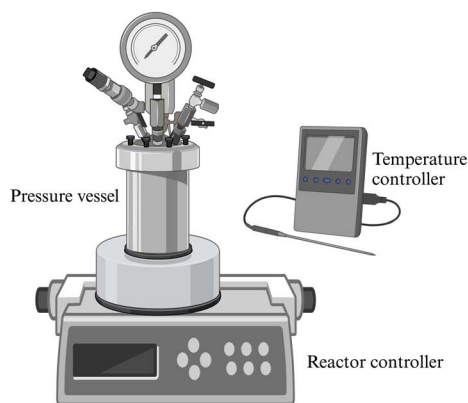
Fig. 4 (A) Mechanism of SCWE technique. (B) Water phase diagram. (C) Lab-scale SCW Batch reactor. Created with https://www.biorender.com/.

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6.1.3 Extraction time and flow rate. Similar to the ASE, SCWE can operate in static or dynamic mode. In static mode, extraction time must be optimized to reach equilibrium. The extraction efficiency will not increase after the equilibrium point, while thermal degradation and undesirable chemical reactions can occur due to the reactivity of SCW. Some studies use non-isothermal processing, where the extraction time is the ramp-up time required to reach an extraction temperature without allowing for an isothermal static time.[39,77,78] Many studies also conducted isothermal processing to extract alginate, fucoidan, phenolics, and phlorotannin, with isothermal static times ranging from 5 to 30 min, as summarized in Table 4. While isothermal conditions are achieved during the reaction stage of hydrothermal processing, the heating and cooling rates are typically slow in most lab-scale reactors. Generally, the ramp-up time required to reach the desired temperature in the subcritical range is 15 to 80 min, with heating rates varying from 2 to 7.1 °C min^{-1}.[85]

As with ASE, operating in dynamic mode can increase extraction yield, staying below equilibrium concentrations and minimizing the risk of degradation or chemical reactions.[52] The flow rate optimization is a function of a number of factors, including whether the extraction rate is external mass transfer controlled or internal mass transfer controlled.[86] If external mass transfer dominates, then higher flow rates induce more turbulence and better mass transfer. However, this may result in diluted extracts (due to contact time). Internal mass transfer control is a function of diffusion rate, which is less sensitive to flow. It should be noted internal mass transfer resistances can be minimized by optimizing particle size.

6.1.4 Particle size. Particle size is crucial in extraction efficiency because it influences mass transfer rates. Smaller particles offer a larger surface area per unit mass, facilitating better water accessibility to solids. Mechanical particle size reduction can enhance desorption and diffusion by potentially breaking cell walls and structures. Additionally, smaller particle size shortens the internal diffusion path, leading to faster diffusion rates.[16] However, optimal particle size is essential to maximize surface area while avoiding channeling effects. Further, very small particles that are densely packed in a column can impact pressure (through pressure drop) as one scales up.

6.2 SCWE of bioactive compounds from beach-cast brown algae

The bulk of SCWE work has focused on the recovery or production (*versus* characterization as in ASE) of bioactive compounds from brown algae, using a laboratory batch scale reactor from 200 mL to 3.7 L (Table 4). Crude extract yield varies considerably depending on the species and SCW conditions. Korean coastal-harvested brown algae *Undaria pinnatifida* showed a higher extract yield (62.37 dry wt%) compared to *Laminaria japonica* (35.53 dry wt%) or *Hizikia fusiforme* (18.55 dry wt%) under the same SCW conditions (210 °C, 30 bar, water-to-solid ratio of 20 mL g^{-1}, and non-isothermal processing).[87] Higher extract yields were reported from brown algae *Himanthalia elongata* (70.70 dry wt%)[77] at 180 °C and *Laminaria*

ochroleuca (80.0 dry wt%)[78] at 220 °C using non-isothermal processing. A similar high yield (76.02 dry wt%) was produced in the South African brown algae *Ecklonia maxima* at 180 °C, 40 bar, water-to-solid ratio of 30 mL g^{-1} for 23.75 min isothermal static time.[82] These crude extracts typically contain different compounds with medium to high polarity, such as antioxidants, phenolics, phlorotannin, fucoidan, and alginate. More selective extraction requires more precision in operating conditions and solvents.

Gan and Baroutian[79] reported the highest yields of phenolics (29.90 mg GAE per g dry wt) and phlorotannin (0.99 mg phloroglucinol equivalents (PGE) per g dry wt) at 210 °C and 15 or 20 min static time. These results were higher than conventional hot water extraction, where the phenolic yield was 1.27 mg GAE per g dry wt and the phlorotannin yield was 0.69 mg PGE per g dry wt. In a study of brown algae *Laminaria ochroleuca*, the highest phlorotannin content (3.20 g/100 g extract) in the extract was reported at 220 °C.[78] Na *et al.*[87] obtained the highest phenolic yields for *Undaria pinnatifida* (14.30 mg per g dry wt), *Laminaria japonica* (10.90 mg per g dry wt), and *Hizikia fusiforme* (18.10 mg per g dry wt) at 210 °C. Bordoloi and Goosen[82] found the highest TPC (41.20 mg GAE per g extract) at 180 °C and 23.75 min static time. Cernadas *et al.*[77] observed an increase in the TPC from 4.10 mg GAE per g extract at 120 °C to a maximum of 45.50 mg GAE per g extract at 220 °C. The above five studies have noted that the optimal temperature range for antioxidant activities aligns with the optimal TPC and phlorotannin content. Jacobsen *et al.*[18] also reviewed a positive correlation between phenolics/phlorotannins and their antioxidant potential.

Whereas overall yields, TPC, phlorotannin, and antioxidant activity were favored at elevated SCW temperatures (>180 °C), polysaccharide yields were highest at lower temperature ranges (<160 °C). Optimal fucoidan yield (4.60 dry wt%) was obtained at lower temperatures and shorter isothermal static times (120 °C and 5 min) compared to TPC (210 °C and 15 min).[79] Bordoloi and Goosen[82] obtained the maximum alginate yield of 15.65 dry wt% at 120 °C with a 5 min static time. Slightly higher temperatures were also reported for the recovery of fucoidan (13.15 dry wt%)[81] at 150 °C and alginate (14.94 dry wt%)[78] at 160 °C. The highest fucoidan yield (25.98 dry wt%) from beach-harvested brown algae *Nizamuddinia zanardinii* was obtained at 150 °C, with a water-to-solid ratio of 21 mL g^{-1} and 29 min static time. This value was much higher at a much shorter residence time than the yield *via* conventional SLE (5.20 dry wt%) at 65 °C, with a water-to-solid ratio of 20 mL g^{-1} over 6 h.[80] In another study, Alboofetileh *et al.*[81] compared SCWE with other extraction methods. Results showed SCWE had the highest fucoidan yield (13.15 dry wt%) compared to enzyme-assisted extraction (4.28–5.58 dry wt%), ultrasound-assisted extraction (3.60 dry wt%), microwave-assisted extraction (6.17 dry wt%), enzyme-ultrasound-assisted extraction (7.87 dry wt%), and microwave-ultrasound-assisted extraction (5.53 dry wt%).

Adding organic and inorganic solvents may enhance the solubility of target compounds in SCW and affect the sample matrix structure.[52] Saravana *et al.*[40] investigated the effect of various solvents (water, 0.1% NaOH, 0.1% formic acid, 25–75%

Table 4 SCWE of bioactive compounds from beach-cast brown algae[a]

Country, source, species	Batch reactor	Target compounds	Solvents	P (bar)	T (°C)	Ramp-up time (min)	Static time (min)	L/S (mL g⁻¹)	Yields	Ref.
New Zealand, wild, U. pinnatifida	1 L	Phenolics	Water	30	210	15–20	15–20	100	29.90 mg GAE per g	79
		Phlorotannin	Water	30	210	15–20	20	100	0.99 mg PGE per g	
Iran, beach, N. zanardinii	500 mL	Fucoidan	Water	30	120	15–20	5	50	4.60 dry wt%	80
		Fucoidan	Water	7.5	150	5	29	21	25.98 dry wt%	
Iran, coast, N. zanardinii	500 mL	Fucoidan	Water	7.5	150	5	20	30	13.15 dry wt%	81
South Africa, coast, E. maxima	1 L	Crude extract	Water	40	180	NG	23.75	30	76.02 dry wt%	82
		Phenolics	Water	40	180	NG	23.75	30	41.20 mg GAE per g extract	
Spain, algamar, H. elongata	3.7 L	Alginate	Water	40	120	NG	5	30	15.65 dry wt%	77
		Crude extract	Water	10.03	180	NG	0	30	70.70 dry wt%	
		Phenolics	Water	23.18	220	NG	0	30	45.50 mg GAE per g extract	
		Fucoidan	Water	6.2	160	NG	0	30	9.05 dry wt%	
		Carbohydrate	Water	6.2	160	NG	0	30	38.88 dry wt%	
Spain, algamar, L. ochroleuca	3.7 L	Crude extract	Water	7.5	220	NG	0	30	80.00 dry wt%	78
		Phlorotannin	Water	7.5	220	NG	0	30	3.20 g/100 g extract	
		Proteins	Water	7.5	220	NG	0	30	18.00 g/100 g extract	
		Fucoidan	Water	7.5	160	NG	0	30	41.38 g/100 g extract	
		Alginate	Water	7.5	160	NG	0	30	14.94 g/100 g extract	
Korea, S. japonica	200 mL	Alginate	Water	5	80	10	5	16.58	8.21 dry wt%	40
		Alginate	0.1% NaOH	5	80	10	5	16.58	10.31 dry wt%	
		Alginate	0.1% formic acid	5	80	10	5	16.58	8.22 dry wt%	
		Alginate	70% ethanol	5	80	10	5	16.58	4.10 dry wt%	
		Alginate	50% ethanol	5	80	10	5	16.58	1.75 dry wt%	
		Alginate	25% ethanol	5	80	10	5	16.58	6.00 dry wt%	
		Fucoidan	Water	50	140	15	5	16.58	6.52 dry wt%	
		Fucoidan	0.1% NaOH	50	140	15	5	16.58	8.23 dry wt%	
		Fucoidan	0.1% formic acid	50	140	15	5	16.58	7.00 dry wt%	
		Fucoidan	70% ethanol	50	140	15	5	16.58	0.50 dry wt%	
		Fucoidan	50% ethanol	25	110	10	5	16.58	1.95 dry wt%	
		Fucoidan	25% ethanol	25	110	10	5	16.58	2.90 dry wt%	
Korea, S. japonica	200 mL	Fucoidan	0.1% NaOH	80	127.01	12	11.98	25	13.56 dry wt%	83
Korea, S. japonica	200 mL	Phenolics	Ionic liquids (0.25 M)	50	175	25	5	32	58.91 mg PGE per g	84
		Phenolics	Water	50	175	25	5	32	39.27 mg PGE per g	
Korea, S. japonica	200 mL	Fucoidan	30% DESs	19.85	150	25	0	36.81	14.93 dry wt%	39
		Alginate	30% DESs	19.85	150	25	0	36.81	28.12 dry wt%	
Spain, beach-cast, D. dichotoma	15 L	Glucose	Water	5.12	150	NG	30	8	2.29 g L⁻¹	5
		Xylose	Water	5.12	150	NG	30	8	3.11 g L⁻¹	
		Arabinose	Water	5.12	150	NG	30	8	1.27 g L⁻¹	

[a] T = temperature (°C), P = pressure (bar), Ramp-up time is the extraction time needed to reach the specified extraction temperature; Static time represents the isothermal extraction time after reaching the specified extraction temperature; Cooling time was not given by most studies; NG = not given; L/S ratio = liquid-to-solid ratio; GAE = gallic acid equivalents, PGE = phloroglucinol equivalents.

aqueous ethanol) on SCWE of fucoidan from *Saccharina japonica*. The best combination of crude fucoidan (8.23 dry wt%) and alginate (10.31 dry wt%) yields were obtained at 140 °C and 50 bar when using 0.1% NaOH, compared to pure water, 0.1% formic acid, and 25–75% aqueous ethanol. Alkaline water (0.1% NaOH) might induce cellulose swelling, which disrupts the hydrogen bonds within hemicellulose and cellulose in the cell wall structure, facilitating the release of polysaccharides. In subsequent work, Saravana et al.[83] optimized fucoidan SCWE with 0.1% NaOH. The studied parameters included temperature (100–180 °C), pressure (20–80 bar), solvent/solid ratio (11–25 mL g^{-1}), agitation speed (100–300 rpm), and static time (5–15 min). The optimal fucoidan yield (13.56 dry wt%) was at 127 °C, 80 bar, 25 mL g^{-1}, 300 rpm, and 11.98 min.

Dinh et al.[84] studied the combination of SCW with ionic liquids (ILs) in the extraction of phenolics from brown algae *Saccharina japonica*. SCW was compared to SCW+1-butyl-3-methylimidazolium tetrafluoroborate; concentrations of IL at 0.25 M led to an increased phenolic yield (58.91 mg PGE per g dry wt) compared to SCW without the addition of IL (39.27 mg PGE per g dry wt) at 175 °C. However, IL concentrations >0.25 M reduced yields due to a significant increase in solvent viscosity. Saravana et al.[39] studied the addition of seven deep eutectic solvents (DESs) in SCW; component one of the DES was choline chloride, and component two was varied (1,2-propanediol, glycerol, ethylene glycol, 1,3-butanediol, 1,4-butanediol, urea, and propanedioic acid) at a 1 : 2 ratio of component one to two. Choline chloride:glycerol showed the highest overall yield of alginate and fucoidan and was therefore used in subsequent optimization studies (temperature, pressure, solvent-to-solid ratio, and water content in DES). The optimized alginate (28.12 dry wt%) and fucoidan (14.93 dry wt%) yields were obtained at 150 °C, 19.85 bar, 70% water content in choline chloride: glycerol, and a solvent/solid ratio of 36.81 mL g^{-1}. These results were higher than SCWE without DES, where yields were 70% lower for alginate (8.21 wt% dry basis) and 56% lower for fucoidan (6.52 wt% dry basis).

7 Comparison of ASE and SCWE techniques

7.1 Similarities, differences, advantages, and disadvantages of ASE and SCWE

ASE and SCWE are two advanced pressurized techniques that can both use water at subcritical conditions; however, in ASE,

the pressure is typically set at approximately 100 bar (system design), while in SCWE, the pressure is set by the system temperature (vapor pressure of water). In this context, ASE can be considered a form of SCWE, particularly when water is the sole solvent and conditions align with those of SCWE. Both ASE and SCWE are designed to enhance extraction efficiency, resulting in faster extraction rates, reduced solvent usage, and higher yields compared to conventional SLE methods. These two techniques aim to minimize harmful organic solvents, adhering to green chemistry principles. Although ASE and SCWE share some similarities, they are distinct methods with unique operational parameters and applications. Table 5 outlines the typical operating conditions of ASE compared to SCWE in terms of solvent usage, temperature and pressure conditions, average extraction time, and application scales.

Despite their advantages, as outlined in Table 6, ASE and SCWE have some limitations. The analytical-scale ASE system has a high instrument cost and operates under very high-pressure conditions (approximately 100 bar), making it challenging to scale up.[88] In contrast, SCW equipment operates at lower pressures (typically 5–80 bar) and is much simpler than ASE systems or supercritical fluids. Therefore, it is less expensive and more readily scalable for industrial applications.[17,89] However, the main challenge of ASE and SCWE is the need for high temperatures, which can lead to the thermal degradation of heat-sensitive compounds. Additionally, SCW is more reactive and corrosive, potentially complicating processing control due to accelerated hydrolysis and oxidation of some compounds. Static SCW processes may increase the residence time of compounds compared to dynamic modes, making thermally labile compounds more susceptible to degradation.[52] Moisture in the extraction solution is not always easily removed in SCWE, requiring additional processing such as separation, dehydration, and precipitation steps. Zhang et al.[17] also noted that SCW equipment is not easy to clean, possibly due to potential char buildup.

7.2 Economic and environmental sustainability perspective of ASE and SCWE

Pressurized liquid extraction using ASE and SCW extraction technologies offers several advantages over conventional solvent-based methods, particularly reducing the use of harmful organic solvents and producing less waste. Economic and environmental sustainability analysis of ASE and SCWE can give insights into beach-cast brown algae valorization design economically and environmentally friendly.

Table 5 Typical operating conditions of ASE compared to SCWE. Data was obtained from Zhang *et al.*[17] and Giergielewicz-Możajska *et al.*[88] with a summary of the typical SCWE operating pressure from this review work

	ASE	SCWE
Solvent	Solvents and/or water	Water, water and co-solvents
Temperature	40–200 °C	100–220 °C
Pressure	Approximately 100 bar	5–80 bar
Average extraction time	12–18 min	10–60 min
Application scale	Lab extraction/characterization or small scale	From lab to industrial scale

Table 6 Advantages and disadvantages of ASE and SCWE

	ASE	SCWE
Advantages	- Fully automatic extraction and cleaning cycles	- Water as green, cheap, and readily available solvent
	- Low solvent consumption (about 10–25 mL g^{-1}) and extraction time (usually 12–18 min)	- Can use wet biomass, reducing drying costs and energy consumption
	- Suitable for a wide range of solvents	- Can extract polar, moderately polar, low-polar, and non-polar compounds separately
	- Possibility of extraction of 24 samples in one batch cycle	- Less expensive equipment than ASE systems
		- Higher efficiency than SLE
		- Continuous operation possible
Disadvantages	- High equipment costs	- Moisture removal from extracts may require additional steps (e.g., separation, dehydration, precipitation)
	- High-pressure settings make scaling up difficult	- Thermal degradation can occur at higher temperatures
	- Potential thermal degradation of heat-sensitive compounds	- Static SCWE may increase the residence time of compounds compared to dynamic modes, making thermally labile compounds more susceptible to degradation
		- Equipment is not easy to clean

ASE and SCWE can potentially lower operational costs by increasing extraction efficiency, reducing organic solvent consumption, management, disposal, and shortening extraction times. However, the initial investment in pressurized equipment can be significant. As developed by Dionex Corporation, ASE systems are designed for laboratory-scale extraction and offer automated extraction and cleaning cycles, saving on labor and time but high instrument costs.[88] The high-pressure settings (approximately 100 bar) of the ASE system also make scale-up difficult and costly. In contrast, SCWE uses pressurized reactors and water as a solvent, which is cheaper and readily available. Vendors such as Parr Instrument Company, Amar Equipment, and Milestone Company provide pressurized vessels. SCWE can also process high-moisture or wet biomass without requiring energy-intensive drying operations, thereby reducing pre-treatment costs associated with drying.[90] Furthermore, SCWE operates at water vapor pressure, is more readily scalable for industrial applications, and potentially offers long-term cost benefits than ASE systems.

Todd and Baroutian[91] conducted a techno-economic comparison of SCW (125 °C and 100 bar), supercritical CO$_2$ (40 °C and 150 bar), and conventional organic solvent extraction (50 °C) for phenolic compounds from grape marc. The techno-economic analysis showed that the cost of manufacture by SCWE (NZ$89.60/kg product) is comparable to the current solvent extraction techniques (NZ$87.00/kg product) but significantly lower than supercritical CO$_2$ extraction (NZ$123.40/kg product). While the study assumes equal phenolic extraction capacity (25 mg GAE per mg dry wt feedstock) across all methods for simplicity, it acknowledges that actual yields may vary in practice. Thakhiew et al.[92] also performed a techno-economic analysis comparing SCW hydrolysis and lipase-catalyzed hydrolysis for continuous fatty acid production, using palm oil splitting as a model. Their results indicated that SCW hydrolysis (350 °C and 200 bar) requires higher capital investment and energy consumption than lipase-catalyzed hydrolysis, while the annual operating costs for both methods are comparable.

Another techno-economic feasibility study[93] on microalgal biofuel production suggested that incorporating biorefinery approaches, which valorize by-products and co-products, can improve overall economics. This contrasts with producing biofuel as a sole product, which is not economically viable. However, there is limited information on the economic assessment of SCWE application in brown algae valorization.[94] Future case studies and experimental data at both lab and large scale are needed to establish the economic feasibility of beach-cast brown algae valorization using the SCW technique.

To evaluate and improve the environmental sustainability of ASE and SCWE techniques for beach-cast brown algae valorization, Life Cycle Analysis (LCA) provides valuable insights into the environmental impacts of different extraction methods, materials, and energy sources.[95] Todd and Baroutian[91] conducted a "gate-to-gate" analysis to quantify the potential environmental impact (PEI) of SCWE, supercritical CO$_2$ extraction, and conventional organic solvent extraction methods using energy and material balances. They compared eight PEI categories: human toxicity by ingestion (HTPI), human toxicity by inhalation/dermal exposure (HTPE), terrestrial toxicity potential (TTP), aquatic toxicity potential (ATP), global warming potential (GWP), ozone depletion potential (ODP), photochemical oxidation potential (PCOP), and acidification potential (AP). The results indicated that supercritical CO$_2$ had the highest PEIs (209 PEI per tonne product) and greenhouse gas emissions (11.8 kg CO$_2$-equivalent per kg product), followed by SCWE with 178 PEI per tonne product and 10.0 kg CO$_2$-equivalent per kg product and conventional solvent extraction with 175 PEI per tonne product and 9.8 kg CO$_2$-equivalent per kg product. In

another study,[31] a comprehensive ex-ante "harbor-to-gate" LCA was conducted to evaluate the environmental sustainability of two biorefinery systems using the South African brown algae *Ecklonia maxima*. Two biorefinery systems co-produce alginate, laminarin, and fucoidan through SCWE (100 °C and 40 bar) and hot water extraction (HWE, 60 °C for 6 h) and were compared to an industrial-scale alginate production system (referred to as "REF"). Four impact categories were selected: climate change, mineral resource scarcity, marine eutrophication, and water consumption. The results showed that the brown algae biorefinery system using SCWE had a higher carbon footprint (25 665 kg CO_2-equivalent per t dry matter feedstock) compared to HWE (13 530 kg CO_2-equivalent per t dry matter feedstock) and the REF system (5188 kg CO_2-equivalent per t dry matter feedstock). The main contributors were the electric energy consumption of the extraction process and spray drying in SCWE and HWE. The total electric energy consumption was 20 MW h per t dry matter feedstock for SCWE and 9.7 MW h per t for HWE. In SCWE and HWE, oven drying of alginate and spray drying of fucoidan and laminarin accounted for 61% and 77% of the total electric energy consumption, while the extraction process contributed 35% and 18%, respectively.

These findings demonstrated that SCWE was not the most holistically eco-friendly method due to its large energy consumption. Four scenarios were further analyzed to explore process optimization opportunities and improve environmental performance: side-stream valorization, optimized product drying process, adoption of a greener electricity mix, and use of more resilient stainless steel.[31] Among these scenarios, the side-stream valorization applied zero waste and closed-loop resource management principles by integrating solid and liquid-side stream valorization, showing overall improvements. The solid-side stream was used for feed supplement production, and the liquid-side stream was passed through a reverse osmosis (PO) membrane to produce liquid fertilizer and recover water. Additionally, using electricity from more renewable sources rather than coal can further enhance the sustainability of the SCWE system.

8 Extraction kinetics and modeling of bioactive compounds using ASE and SCWE from beach-cast brown algae

ASE and SCWE methods offer an alternative to conventional SLE, making the study of extraction mechanisms and modeling essential for scale-up. This section provides insights into the current status of extraction rate/kinetic models and scale-up for extracting bioactive compounds from beach-cast brown algae using ASE and SCWE.

8.1 Design and scale-up status of ASE and SCWE

As noted, ASE operates at fixed high pressures (around 100 bar) to facilitate automatic solvent filling and purging, allowing the solvent (organic or aqueous) to penetrate solid matrices and operate in a fixed bed design. In contrast, SCWE maintains pressure at/slightly above water's vapor pressure, ensuring water remains liquid within designated temperature ranges. The subcritical region for water is characterized by temperatures of 100–374 °C and pressures of 1–221 bar,[17,96] as depicted in Fig. 4. Most SCWE studies on brown algae use batch reactors focusing on lower temperatures and pressures, between 100–220 °C and 5–80 bar, for bioactive compound extraction (Table 4). The pressurized extraction system comprises key components:[52,97] solvent supply, solvent transport pump, heater, pressure vessel, condenser, and collection vessel. Depending on the cost and specific applications, detailed design may have additional features such as autosamplers, gas purge systems, pressure regulators, safety features, and integration with downstream separation systems.

Although SCWE is more readily to scale up compared to the ASE system, most research on SCWE for bioactive compound extraction remains at the laboratory scale, with few pilot-scale studies reported.[16] Kwon and Chung[98] studied the scale-up of a lab-scale 22 mL ASE system (packed bed, 23 mm i.d. × 50 mm long, 1 g sample size with particle size < 10 mm) to a larger 8 L SCW system (stirring pressurized reactor, 143 mm i.d. × 520 mm long, 250 g sample size). They studied turmeric as the solid feedstock to extract curcuminoids. Results showed comparable yields between lab-scale (15.80 dry wt%) and 8 L (13.58 dry wt%) under optimized conditions (135 °C, 5 min isothermal extraction time, and 50% ethanol in water). Varying pressure using nitrogen (from 5 to 100 bar) in the 8 L system did not significantly affect curcuminoid yield (13.50–13.58 dry wt%). This is likely due to minimal changes in water's dielectric constant and density within the pressure range at studied temperatures. In another study, Ko et al.[99] assessed the scaling up of ASE with water as a solvent for flavonoid extraction from agricultural by-product satsuma mandarin peel using the same size, 22 mL lab-scale packed-type ASE and 8 L stirring-type system. The yields of flavonoids obtained at the lab scale (117.80 mg per g dry wt) and 8 L system (113.40 mg per g dry wt) were similar under optimized conditions (130 °C, 15 min isothermal extraction time, and water-to-solid ratio of 34 mL g^{-1}). The above two studies indicate that rate-limiting phenomena common in scale-up (such as poor contact due to fluid dynamics, external mass transfer, etc.) were not encountered; however, the scale of the larger system in 8 L is still relatively small.

To assess the scale-up of batch SCW systems from laboratory (500 mL) to 25 L scale, Trigueros et al.[96] studied the valorization of red algae residue post-agar extraction. SCW treatment was conducted at 175 °C, 20 bar, and 5% (w/v) biomass loading in both lab and 25 L scale systems. The larger system yields were consistently lower for monomer, oligomer, and free amino acids but approximately the same for protein under the same conditions. At lab scale, oligomer yield was 78.6%, monomer at 4.6%, and protein of 37.5% with 17.8 mg free amino acids/g protein compared to 25 L scale with oligomer at 71.4%, monomer at 3.0%, and protein at 37.4% with 14.2 mg free amino acids per g protein. The phenolic yield was 45% higher on the lab scale (17.9 g GAE per kg dry wt) compared to 25 L (10.0 g GAE per kg dry wt) at 175 °C. In another study, Alonso-Riaño et al.[85] compared the valorization of brewer's spent grain

at the same sizes, 500 mL and 25 L system. As in the previous study, maximum yields were similar in both systems. At the 25 L scale (170 °C and 22 min isothermal time), total carbohydrates were 56%, total pentose was 78%, and protein was 64% with 21 mg free amino acids/g protein. The 500 mL lab-scale system yielded a maximum phenolic content of 34 mg GAE/g dry wt, 38% higher than the pilot system. However, the lab-scale operating conditions were not truly comparable to the 25 L system. The lab system was at 174 °C, 15.7 min ramp-up time with slow heating rate from 3–14.4 °C min^{-1}, 45 min isothermal time, 60 min cooling time, and 50 bar, while the pilot conditions were the similar temperature but faster heating rate (13.4–83.4 °C min^{-1}) with 4.5 min ramp-up time to reach desired temperature of 170 °C, half of the isothermal time (22 min), and lower pressure (20 bar).

Moral et al.[5] explored the valorization potential of tidal waste biomass from the Andalusian Mediterranean coastline using a 15 L-scale SCW batch reactor. The waste feedstock comprised beach-cast brown algae (Dyctiota dichotoma) and seagrass (Posidonia oceanica and Zostera noltii). An optimal mixture yield of glucose (2.29 g L^{-1}), xylose (3.11 g L^{-1}), and arabinose (1.27 g L^{-1}) were obtained at a temperature of 150 °C, 30 min isothermal reaction time (without consideration of ramp-up time), and a liquid-to-solid ratio of 8 mL g^{-1}.

8.2 Challenges for large-scale application

Although the above studies demonstrate the potential of SCWE for larger-scale applications, there are limited reports on scaling up bioactive compound extraction from beach-cast brown algae using SCWE. Developing SCW equipment for large-scale use is still in its early stages and presents significant challenges. Key issues include ensuring safety, managing energy consumption, and maintaining the yield and bioactivity of the extracts. Legal regulations are also necessary to establish production standards and standardized usage rules for SCW equipment. Addressing these issues is crucial to overcoming the safety and energy consumption challenges associated with large-scale SCW equipment.[100]

In order to maintain the yield and quality of extract, one of the main limitations in scaling up is achieving uniform mass and heat transfer. In laboratory settings, small-scale reactors using small sample sizes allow for better control of heat (ramp-up) and mass (mixing) transfer resistances, mitigating issues related to ramp-up time and ensuring consistent reaction conditions. However, as the process scales up, maintaining uniform heat and reactant/product distribution becomes challenging. Ensuring rapid ramp-up rates so that the bulk material reaches the desired temperature quickly is difficult, as larger volumes introduce heat transfer resistances. This discrepancy can lead to variations in the reaction time, where some compounds may initiate reactions at lower temperatures, leading to potential decomposition or hydrolysis before reaching the target conditions.

Laboratory work with small-scale reactors is essential for identifying the key parameters needed for scaling up processes, often involving the development of kinetic models.[101] However,

scaling up introduces complexities in maintaining these parameters, especially in terms of heat and mass transfer. Therefore, further research and development are needed to optimize reactor designs and process controls for large-scale applications.

8.3 Mathematical modeling

In modeling the extraction rate of bioactive compounds in ASE/SCWE, the mechanism is collapsed from the five stages outlined above to two stages:[52] (i) a washing stage and (ii) a diffusion stage. The assumption is that the system used to study kinetics is using a small enough sample size that external mass transfer resistances can be ignored or collapsed into the diffusion stage. The washing stage is described as solvent penetration into the porous solids, exposing the solid surface to the solvent, resulting in the rapid dissolution of compounds. In the diffusion stage, compounds diffuse from the interior of the solids to the external surface, followed by the mass transfer of solutes from the solid surface into the bulk solvent.

From an engineering perspective, rate models are crucial tools for process optimization, system control, and scaling up.[101] Although numerous kinetic models are widely used to extract compounds from plant biomass, studies on marine algae biomass remain relatively limited. Commonly used models for investigating the extraction kinetics of bioactive compounds in ASE/SCWE include Fick's law and empirical models such as first-order kinetic, second-order kinetic, two-site kinetic, and Peleg's models (Table 7).

8.3.1 Fick's law model. Fick's second law is used to describe the diffusion process in the non-steady state. Assuming negligible external mass transfer resistance and constant effective diffusion coefficient across solute concentrations. A general solution for Fick's second law was given by Crank[111] for homogenous and porous solid particles with a uniform distribution of bioactive compounds in an isobaric and isothermal system for the sphere in eqn (1).

$$\frac{C - C_0}{C_i - C_0} = 1 + \frac{2R}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{R} \exp\left(-\frac{D_e n^2 \pi^2 t}{R^2}\right) \quad (1)$$

where C_0 is the initial concentration of solute in the sample particle, C_i is the concentration of solute at the surface of the sample particle. R is the average particle radius. D_e represents the effective diffusion coefficient. The mass of solute transferred from the porous solid sample into liquid solvent can be given by eqn (2).[111]

$$\frac{M}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_e t}{R^2}\right) \quad (2)$$

where M is the mass of solute transferred at time t, M_∞ is the total mass of solute transferred after infinite time. For sufficiently long times, only the first term of the series is significant, and eqn (2) can be simplified to eqn (3) and then can be converted into the form of eqn (4).[112]

$$\frac{M}{M_\infty} = 1 - \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D_e t}{R^2}\right) \quad (3)$$

Table 7 Kinetic models applied in ASE and SCWE of bioactive compounds from plant biomass

Raw material	Bioactive compounds	Extraction technique	Type of model	Equation	Ref.
Spent coffee grounds	Oil	ASE	Two-site kinetic	Eqn (10)	102
			Fick's law	Eqn (4)	
			Arrhenius equation	Eqn (6)	
Cocoa bean shell	Fat	ASE	Fick's law	Eqn (4)	103
			Arrhenius equation	Eqn (6)	
Watermelon seed	Oil	ASE	Second-order kinetic	Eqn (9)	104
			Peleg's	Eqn (12)	
			Fick's law	Eqn (4)	
Cocoa bean shell	Flavanols	ASE	Peleg's	Eqn (12)	105
Pomelo peels	Pectin	SCWE	First-order kinetic	Eqn (8)	106
Noni fruits	Scopoletin, alizarin, rutin	SCWE	Two-site kinetic	Eqn (10)	107
Grape skins and defatted grape seeds	Polyphenols	SCWE	Two-site kinetic	Eqn (10)	108
Loquat leaves	Lipids	SCWE	Second-order kinetic	Eqn (9)	109
Grape canes	*Trans*-resveratrol	SCWE	Fick's law	Eqn (3)	110
			Arrhenius equation	Eqn (6)	

$$\frac{M}{M_\infty} = 1 - A e^{-Bt} \tag{4}$$

where A is the model constant, and B is the diffusion constant and can be used to estimate D_e by eqn (5).

$$B = \frac{\pi^2 D_e}{R^2} \tag{5}$$

Fick's law-based solutions are commonly used to estimate D_e of solutes in porous solid samples. These models have found application in various extraction processes, including ASE of oil from spent coffee grounds,[102] fat extraction from cocoa bean shells in the ASE process,[103] and SCWE of *trans*-resveratrol from grape canes.[110] As discussed in previous sections, temperature is the most important parameter in ASE/SCWE. To investigate temperature impact on the extraction process, the Arrhenius equation eqn (6) has been used to describe the D_e as a function of temperature.[112]

$$D_e = D_0 e^{-\frac{E_a}{RT}} \tag{6}$$

where D_0 is a pre-exponential factor. E_a represents the activation energy, R is the gas constant (8.314 J mol^{-1} K), and T is the absolute temperature. However, the Stokes–Einstein eqn (7) explains that D_e is influenced not only by temperature but also by the viscosity of the solution. D_e increases with the temperature but decreases with increasing viscosity.[113] The viscosity of the solution can be affected by the liquid-to-solid ratio. The optimal liquid-to-solid ratio can enhance the mass transfer rate during the external diffusion, increasing equilibrium extraction yields. Beyond the optimal value, higher liquid-to-solid ratios do not significantly impact yields, leading to solvent wastage and dilute extracts.

$$D_e = \frac{K_B T}{6\pi \, \eta r_H} \tag{7}$$

where K_B represents the Boltzmann constant (1.38 × 10^{-23} J K^{-1}), η is the viscosity of the solvent, r_H is the hydrodynamic radius of the matrix, and T is the absolute temperature.

8.3.2 Empirical models. In ASE and SCWE, different empirical models have been employed (Table 7). Although they lack the theoretical rigor of fundamental models, they provide a model that can be used for the design/scaling.[114]

8.3.2.1 First-order kinetic model. The first-order kinetic model, eqn (8), has been applied to describe bioactive compound extraction with assumptions of uniform solute distribution. The model provides the fraction of bioactive compound extracted (C_t/C_∞) at time t. However, the first-order kinetic model fails to account for equilibrium and is valid only when solute concentrations are below the saturation.[106]

$$\frac{C_t}{C_\infty} = 1 - e^{-K_1 t} \tag{8}$$

where C_t and C_∞ are the concentrations of solute extracted in the solvent at time t and at infinite time, respectively. K_1 is the first-order rate constant.

8.3.2.2 Second-order kinetic model. The second-order kinetic model eqn (9) assumes the solute concentration will reach equilibrium in the solvent phase for a given set of conditions.

$$C_t = \frac{C_\infty{}^2 K_2 t}{1 + C_\infty K_2 t} \tag{9}$$

where C_t and C_∞ represent the concentrations of solute extracted from the solid into the solvent at time t and at equilibrium, respectively. K_2 is the second-order rate constant.

8.3.2.3 Two-site kinetic model. The two-site kinetic model developed by So and MacDonald[115] assumes two distinct phases involved in the extraction process where the fast washing step and a slow diffusion step occur simultaneously. The combination of two steps is expressed by the two-site first-order equation, eqn (10).

$$C_t = C_w[1 - \exp(-K_w t)] + C_d[1 - \exp(-K_d t)] \tag{10}$$

where C_w and C_d are the concentrations of solute extracted in the solvent during the washing stage and the diffusion stage, respectively. When the time approaches ∞, $C_\infty = C_w + C_d$. K_w

and K_d represent the rate constants/mass transfer coefficients for the washing and diffusion phases, respectively.

8.3.2.4   Peleg's model. Peleg's model is a well-known kinetic model based on the second-order kinetic model, as shown in eqn (11).[116]

$$C_t = C_0 + \frac{t}{K_1 + K_2 t} \tag{11}$$

where C_0 and C_t are the concentrations of solute extracted in the solvent at the initial time and at any time. K_1 is the model rate constant, and K_2 is the model capacity constant. The term C_0 can be omitted from Peleg's model as the initial concentration of solute in the solvent is zero when fresh solvent is used. Therefore, Peleg's model eqn (11) can be written as eqn (12).[114]

$$C_t = \frac{t}{K_1 + K_2 t} \tag{12}$$

The two-site kinetic model has been successfully applied in ASE and SCWE of bioactive compounds from various biomass sources, including spent coffee grounds,[102] noni fruits,[107] and grape skins/defatted grapes.[108] Toda *et al.*[102] observed that the washing rate (K_w) was 27 times higher than the diffusion rate (K_d) in ASE with absolute ethanol solvent in batch mode at an extraction temperature of 150 °C. In another dynamic SCWE study on the recovery of low methoxyl pectin from pomelo peels,[106] the first-order kinetic model exhibited better agreement with experimental data ($R^2 > 0.94$) than the two-site kinetic model, which failed to fit the data and reverted to the first-order kinetic model. This suggests that the distinction between "fast" and "slow" kinetics is not significant in the pectin SCW extraction process in dynamic mode, and the first-order kinetic model is more appropriate in this case. The second-order kinetic model was effectively used to describe watermelon seed oil extraction in ASE, demonstrating a better fitting ($R^2 > 0.99$) compared to Peleg's model ($R^2 > 0.98$) and Fick's model ($R^2 > 0.85$) at temperatures of 60–80 °C.[104] The second-order kinetic model was also used to model lipids extraction from loquat leaves in dynamic SCWE, showing good agreement between the estimated data and the experimental data ($R^2 > 0.98$).[109] Peleg's model found application in representing the ASE batch mode for extracting oil from watermelon seeds[104] and flavanols from cocoa bean shells,[105] providing a satisfactory fit for the experimental data. Both the second-order kinetic model in eqn (9) and Peleg's model in eqn (12) are hyperbolic equations suitable for estimating the initial extraction rate and maximum extraction yield.

9   Conclusion and future trends

This work provides a comprehensive review of pressurized liquid processes (ASE and SCWE) as a "green" alternative to conventional SLE for extracting bioactive compounds (alginate, fucoidan, laminarin, phenolics, and fucoxanthin) from beach-cast brown algae. These bioactive compounds have broad applications in the food, cosmetic, and pharmaceutical industries. ASE and SCWE are potentially more sustainable extraction

processes compared to conventional SLE in the elimination of harmful organic solvent use, ease in reusing and/or treating the remaining solids, and ease of reuse of produced water. This review compares and outlines the advantages and disadvantages of these two advanced pressurized techniques. ASE is more suited for lab-scale characterization and analysis, while SCWE has better potential for scale-up to production applications. In general, these pressurized techniques can extract key valuable products more efficiently and selectively by modifying process conditions (mainly solvent combinations and temperatures) while minimizing extraction time and chemical usage compared to conventional SLE. However, the higher temperature required in SCWE means costs (environmental and financial) in energy consumption must be balanced against the costs associated with SLE (*e.g.*, waste generation, handling, and consumption of toxic solvents) in larger-scale applications. Work in process optimization, side-stream valorization, and adopting a greener electricity mix would improve the balance in favor of SCWE.

SCWE is more readily scalable than ASE (which is mainly for analytical analysis). However, the bulk of the SCWE work is at the lab scale, with limited scale-up work. While lab scale work is critical for establishing extraction rates, it does not effectively capture the impact transport phenomena (heat and mass transfer effects) will have on overall reaction time (*i.e.*, time material spends at reaction temperature or temperature variability within reactor) and subsequent reactor size and operating conditions. Future research studies should focus on the feasibility of large-scale operation and industrial equipment design, optimizing parameters such as solvent combinations, temperature, and total extraction time (considering ramp-up, isothermal, and cooling time) to balance quantity and quality. This includes establishing kinetic models and incorporating mass and heat transfer models. Such research initiatives are hoped to significantly contribute to the understanding, advancement, and future applications of high-value products obtained from beach-cast brown algae using ASE and SCWE, supporting circular economic developments.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Author contributions

Yu Zhang: conceptualization, visualization, writing – original draft & review & editing. Kelly Hawboldt: supervision, funding acquisition, project administration, conceptualization, writing – review & editing. Stephanie MacQuarrie: writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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