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Authors	Jerome, Rifna E.;Sivapragasam, Nilushni;Gupta, Vijai K.;Tiwari, Brijesh K.;Rajauria, Gaurav
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Role of deep eutectic solvents for the extraction of polysaccharides from seaweed for food applications

Rifna E. Jerome [a,b,c,*], Nilushni Sivapragasam [c], Vijai K. Gupta [d], Brijesh K. Tiwari [e], Gaurav Rajauria [a,b,c]

[a] SUSFERM Centre for Sustainable Fermentation and Bioprocessing Systems for Food and the Bioeconomy, University College Cork, Cork, T12 YN60, Ireland
[b] School of Microbiology, University College Cork, Cork, T12 YN60, Ireland
[c] School of Food and Nutritional Sciences, University College Cork, Cork, T12 YN60, Ireland
[d] School of Biotechnology, Dublin City University, Glasnevin, Dublin, D09 K20V, Ireland
[e] Teagasc Food Research Centre, Department of Food Chemistry and Technology, Ashtown, D15 KN3K, Dublin, Ireland

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ABSTRACT

The accelerating demand for green bioprocessing has positioned seaweed polysaccharides as expensive bio-resources owing to their conformational diversity and varied bioactivities. Their relevance in functional foods and pharmaceuticals further emphasises the need for efficient and sustainable extraction strategies. The majority of existing extraction techniques frequently negotiate polysaccharide integrity, purity, and yield. In response, deep eutectic solvents (DES) have arisen as promising sustainable solvents, advancing tunable physicochemical characteristics and improved selectivity on polysaccharide functional groups. This review methodically assesses recent progress in the extraction of crucial seaweed polysaccharides, comprising alginate, fucoidan, laminarin, and carrageenan, employing DES/DES-assisted advanced technologies. The importance of Kamlet-Taft (KT) parameters is in-depth explored to understand DES-polysaccharide interactions and justify differences in solubilization and recovery proficiencies. Among the reviewed mixtures, choline chloride:glycerol and choline chloride:urea steadily displayed superior performance, with the former accomplishing advanced yields and the latter supporting careful solubilization. The relative insights presented emphasise that extraction results are affected by DES mixtures, seaweed species, and energy-assisted techniques such as microwave- and ultrasound-assisted extraction. Overall, this review highlights the possibility of DES-based green extraction approaches to attain competent and sustainable retrieval of seaweed polysaccharides, along with delivering a mechanistic knowledge for impending solvent design.

1. Introduction

The exploration of diversity in marine ecosystems for commercial uses has placed seaweeds as a critical reserve for the extraction of polysaccharides, as well as other bioactive compounds. Seaweeds are broadly classified into three primary categories: brown, green, and red. They are rich in polysaccharides such as fucoidan, alginate, laminarin, ulvan, carrageenan, agar, and cellulose, which play a vital role in determining the structural and functional properties of seaweeds (Ahmed et al., 2024). These polysaccharides exhibit noteworthy advancements in food, pharmaceuticals, cosmetics, and biotechnology due to their remarkable physicochemical and biological properties (Flores-Contreras et al., 2023). Polysaccharides extracted from seaweeds are peculiarly differentiated through their physical, chemical, and structural characteristics. Alginate, primarily extracted from brown seaweeds, is composed of guluronic and mannuronic acid, showcasing gelling and high viscosity behaviour (Veronica, Heng, & Liew, 2023). Fucoidan, a sulphated polysaccharide found in brown seaweeds, is recognised for its anti-inflammatory and antioxidant potential (Pradhan et al., 2020). Likewise, red seaweeds contain agar and carrageenan, predominantly applied as gelling agents, whereas green seaweeds comprise ulvan, a sulphated polysaccharide known for its antimicrobial and antioxidant

* Corresponding author at: SUSFERM Centre for Sustainable Fermentation and Bioprocessing Systems for Food and the Bioeconomy, University College Cork, Cork, T12 YN60, Ireland.
E-mail addresses: relenjikkaljerome@ucc.ie (R.E. Jerome), NSivapragasam@ucc.ie (N. Sivapragasam), vijaikumar.gupta@dcu.ie (V.K. Gupta), brijesh.tiwari@teagasc.ie (B.K. Tiwari), grajauria@ucc.ie (G. Rajauria).

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activities (Hentati et al., 2020; Premarathna et al., 2024). Additionally, cellulose, an abundant component across various seaweed species, occurs in multiple crystalline configurations (Doh, Lee, & Whiteside, 2020). Considering these wide-ranging bioactive properties and structural attributes, the extraction of polysaccharides from seaweeds is of significant industrial and scientific relevance. However, efficiently isolating targeted polysaccharides is challenging due to the structural complexity of seaweed and the intricate nature of its biochemical components. Hence, polysaccharide extraction methods must aim to preserve delicate biochemical structures while attaining increased yields, a task often hindered by robust cell matrix and compactly bound polysaccharide-protein complexes.

Traditional approaches for extracting seaweed polysaccharides, for example, hot water extraction, acid hydrolysis, and alkali treatment, are frequently constrained by minimal selectivity, high energy utilisation, enhanced processing times, and noxiousness (Quitério, Grosso, Ferraz, Delerue-Matos, & Soares, 2022; Sadeghi et al., 2024). As an alternative, ionic liquids (ILs) - salts in the liquid phase, comprised of large organic cations and distinct anions have been studied for their capability to dissolve dense polysaccharides effectively. ILs exhibit advantages like decreased volatility, combined with great solvation power, supporting the breakdown of dense cell walls (Das, Sequeira, Maity, & Prasad, 2021). For instance, Moradiya, Pereira, & Prasad, 2024reported that aqueous solutions of ILs efficiently extracted alginate from *Sargassum tenerrimum*, yielding up to 54% and isolating polysaccharides with comparable physicochemical properties to those extracted through conventional methods. Correspondingly, (Das et al., 2021) described that bio-ionic liquids enhanced the careful coagulation of k-carrageenan from *Kappaphycus alvarezii*, augmenting extraction efficiency without the requirement for alkaline treatment. Nevertheless, the practical application of ILs is limited by constraints such as elevated synthesis costs, limited recyclability, and probable environmental hazards (Ražić, Gadžurić, & Trtić-Petrović, 2024; Ventura et al., 2017). Moreover, most ILs are not GRAS (Generally Recognised as Safe), and given that the primary applications of seaweed polysaccharides lie in the food and pharmaceutical sectors, their discussion is not pursued further in this review. These limitations highlight the need for more sustainable and biodegradable alternatives, paving the way for deep eutectic solvents (DESs) as promising alternatives.

DES belong to a category of “designer solvents” due to their tunability to tailor the extraction process. They are synthesised through mixing a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) at a particular molar ratio, to suppress the melting point, compared to the individual constituents (Gan & Baroutian, 2022; Sharma et al., 2024). In addition, DES are less volatile and GRAS because of their biodegradability and non-toxicity; therefore, often labelled as a “green designer solvent”. The efficiency of DES to extract seaweed polysaccharides depends on its robustness and the ability to disintegrate seaweed cell walls to facilitate the extraction of polysaccharides (Dai, Van Spronsen, Witkamp, Verpoorte, & Choi, 2013a; Florindo, McIntosh, Welton, Branco, & Marrucho, 2018). DES forms intermolecular interactions with the seaweed matrix through van der Waals forces, hydrogen bonding, and dipolar exchanges, which enhance the selectivity of DES for polysaccharide extraction. Thus, recently, a significant amount of research has been focused on using DES for seaweed polysaccharide extraction. Further, the rise of DES is part of a pronounced trend towards sustainable extraction advances, where solvents and processing technologies are designed to minimise environmental impact while maximising efficiency. In line with this, researchers have explored innovative green extraction techniques, such as microwave-assisted, ultrasound-assisted (UAE), supercritical fluid, and high-pressure homogenization, that complement or enhance DES-based extraction methods. Coupling DES with these green technologies has shown remarkable promise for extracting a wide range of bioactive compounds, including polyphenols, carotenoids, polysaccharides, and other phytochemicals from diverse agricultural and food matrices.

Recently, DES-assisted extraction of bioactive compounds from other biomass, namely plant and food-derived sources, illustrated their extraction versatility and effectiveness, providing a foundation for their subsequent application in seaweed polysaccharide extraction. For instance, the extraction of bioactive compounds from apple pomace using NADES and UAE, emphasising total flavonoid content, total phenolic content, lipid peroxidation inhibition, and antioxidant potential (Airouyuwa, Mostafa, Riaz, & Maqsood, 2022); Hashemi, Rahimi, and Arjmand (2023); (Rashid, Wani, Manzoor, Masoodi, & Dar, 2023). Whereas supercritical fluid extraction with DES under mild conditions retains the functional characteristics of heat-labile biomolecules present in the *Lentinus edodes* (Zhang et al., 2022). Likewise, microwave-assisted deep eutectic solvents were used to extract polysaccharides from leaves of *Lithocarpus litseifolius* (Wu et al., 2022). The mechanism comprised the interactive influence of microwaves and DES that aided in the rupture of the cell wall, facilitating enhanced extraction efficiency. Furthermore, most recently, high-pressure-assisted deep eutectic solvents were employed to extract pectic polysaccharides from Tartary buckwheat sprouts (Wang et al., 2024). This approach successfully interrupted cell walls, increasing the extraction of rhamnogalacturonan-I (RG-I)-augmented pectic polysaccharides. The obtained extract possessed enhanced antioxidant activities and anti-glycosylation properties attributed to elevated bound flavonoid content.

Building on the confirmed strengths of pairing DES with novel extraction techniques for distinct bioactive compounds, mounting attention is now being directed towards the seaweed polysaccharides extraction under related principles. DES interactions with each discussed polysaccharide from seaweed in this review are explained using Kamlet-Taft (KT) parameters. Seaweed polysaccharides exhibit distinctive structural density owing to their sulfation models, branching, and firm cell wall organisation, which make their selective and efficient extraction challenging. Despite the growing application of DES and DES-assisted green technologies in other biomass systems, comprehensive reviews dedicated to seaweed polysaccharide extraction remain scarce. Addressing this gap, the present review critically examines recent advances in green extraction strategies for seaweed polysaccharides, with particular emphasis on the structure-reactivity relationships and selective extraction behaviour of DES as interpreted.

2. Understanding the structural diversity of seaweed polysaccharides for efficient extraction

Polysaccharides extracted from seaweeds are bioactive macromolecules with enormous industrial and scientific potential owing to their structural diversity and adaptable functionality. Previous studies have reported that seaweed polysaccharides display exclusive biological and physicochemical characteristics driven by their glycosidic associations, degree of branching, monosaccharide composition, and functional substitutions, such as acetylation or sulfation (Akter et al., 2024; Cosenza, Navarro, Ponce, & Stortz, 2017). The main polysaccharide components of brown seaweed are fucoidan, alginate, and laminarin. Fucoidan, dense, sulphated complex polysaccharides, exhibit potential bioactivities, mainly antiviral and anticoagulant properties, emphasising their significance in therapeutic applications. On the other hand, alginates holding mannuronic (M) and guluronic (G) acid form gel linkages with divalent cations, making them essential in biomedical and food applications (Song et al., 2024; Zhou et al., 2024). In addition, polysaccharides isolated from green seaweed, such as ulvan, demonstrate unique bioactivities on account of their rhamnose-rich sulphated organisations, supporting potential in nutraceutical applications. Similarly, red seaweeds, abundant in agar and carrageenan, are principally utilised as stabilising and gelling agents in food and pharmaceuticals. The gelling properties of these polysaccharides are dictated by the sulphate content (Cosenza et al., 2017; Lee, Xie, Ng, & Suleria, 2025; Zhang, Ye, et al., 2022). The essential polysaccharides and the fundamental molecules present in brown, green and red seaweed, alongside their

medicinal properties, are outlined in Table 1.

2.1. Conventional extraction methods

Conventional solvent-based extraction approaches, including Soxhlet extraction and heat-coupled solvent extraction, are widely used methods in both laboratory settings and industrial applications for recovering polysaccharides from seaweed. During the Soxhlet extraction procedure, the biomass is subjected to a continuous solvent flow that improves the extraction yield associated with heat-coupled solvent extraction. Interestingly, the solvent used in both of the above methods is hot water, normally varying between 60 °C and 100 °C, with the inclusion of calcium chloride, promoting the precipitation of the extracted polysaccharide (Quitério et al., 2022). Attributing to the continuous flow process, the extraction time is remarkably lowered in Soxhlet extraction, whereas heat-coupled solvent extraction depends on the speed of mixing and temperature to enhance the solubility of the targeted polysaccharide compounds, permitting them to ooze more competently in the selected solvent (Quitério et al., 2022).

Earlier, several solvent mixtures have also been explored for the extraction of seaweed polysaccharides. (Hsiao et al., 2022) extracted fucoidan from *Sargassum crispifolium* by pre-treating biomass with 95% ethanol (feed to solvent ratio, 1:10) to remove lipids and pigments, followed by sequential filtration, and extraction in a water bath at 85 °C to obtain the targeted polysaccharide. (Huang, Wu, Yang, Kuan, & Chen, 2016) extracted polysaccharides by applying a combination of dichloromethane and methanol in a 1:1 ratio, along with hydrochloric acid solutions. The extraction was prolonged for 48 h, at temperatures reaching 100 °C or higher. Further methods consist of acid-and alkali-coupled extractions, principally involving HCl and NaOH, which break the hydrogen bonds within the polysaccharides and promote their solubilization into the solvent. (Chi et al., 2018) used 0.5 M NaOH solution at 60 °C for 3 h to extract polysaccharides from a seaweed species, accomplishing a yield of 24.7%. Likewise, they carried out extraction on *Ulva clathrata*, achieving the maximum polysaccharide yield of 18.3% under optimised extraction parameters of 0.1 M NaOH at 90 °C for 2 h. Similarly, through another study, acid extraction was extensively studied by (Liu, Wu, Jin, & Guo, 2020), where the effect of 0.1 N HCl at 25 °C over 4 h with a feed to solvent ratio of 1:30 was performed. They recognised 0.1 M HCl at 80 °C for 60 min as the optimal extraction condition for extracting polysaccharides from *Enteromorpha prolifera*, ensuing in a yield of 3.62%. Interestingly, after all acid extractions, the polysaccharides were neutralised using NaOH. However, regardless of their extensive use, conventional extraction processes, such as heat-coupled solvent extraction, Soxhlet extraction, and acid-alkali extraction, face numerous challenges. These comprise prolonged extraction times, excessive consumption of solvents, and most importantly, the prospective deprivation of the extracted compounds owing to elevated temperatures throughout the extraction process.

2.2. Paradigm shift to novel green extraction method

The development of novel extraction techniques for seaweed polysaccharides has been driven by the limitations associated with conventional methods, particularly in terms of high energy consumption, prolonged extraction time, and degradation of bioactive compounds. In this context, green extraction technologies have emerged as alternative approaches aimed at improving extraction efficiency while minimising environmental impact and preserving the structural integrity of polysaccharides (Lomartire & Gonçalves, 2022). This section highlights the evolution of these techniques with emphasis on their operational principles, practical applicability, and inherent limitations, thereby providing a foundation for the subsequent discussion on DES.

Green extraction methods, including microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), supercritical fluid extraction (SFE), and high-pressure processing (HPP), have been identified as sustainable techniques (García-Vaquero, Rajauria, O'Doherty, & Sweeney, 2017; Otero et al., 2023). Vázquez-Rodríguez, Gutiérrez-Uribe, Antunes-Ricardo, Santos-Zea, and Cruz-Suárez (2020) explained that the UAE relies on acoustic cavitation to rupture seaweed cell matrix; however, the high viscosity and structural complexity of seaweed polysaccharide matrices can limit mass transfer, thereby reducing extraction efficiency. On the other hand, the MAE of seaweed polysaccharides was found to accelerate the extraction process with the help of localised heating; nevertheless, non-uniform temperature distribution may lead to partial thermal degradation of sensitive compounds (Das et al., 2021; Rodriguez-Jasso, Mussatto, Pastrana, Aguilar, & Teixeira, 2011). Further SFE, which uses supercritical CO_2 and is highly selective, is generally unsuitable for hydrophilic polysaccharides due to their low solubility in non-polar supercritical fluids and requires high capital investment, limiting its practical applicability (Saravana, Cho, Woo, & Chun, 2018). Similarly, HPP, which uses an elevated level of hydrostatic pressure to enhance extraction without triggering heat-induced degradation, was reported to be challenging for substantially cross-

Table 1
Structural composition and therapeutic potential of polysaccharides from brown, green, and red seaweeds.

Seaweed type	Polysaccharide	Major molecules	Therapeutic effects	Reference
Brown seaweed	Alginate	Mannuronic acid, α-(4)-l-guluronic acid	Immunomodulatory, wound healing, anticancer, antidiabetic	(Alrata et al., 2024)
	Laminarin	Mannitol, (1, 3)-β-D-Glucose (1, 6)-β-D-glucose	Anti-inflammatory, antioxidant, antidiabetic	(Jayapala, Toragall, Kumar, Chaudhari, & Baskaran, 2022)
	Fucoidan	(1, 4)-d-Galactose, β-(1, 4)-d-Mannuronic acid, (1, 2)-α-l-Fucose-l-sulphate	Anticancer, anticoagulant, antiviral, anti-inflammatory	(Senthilkumar, Manivasagan, Venkatesan, & Kim, 2013)
	Xylan	β (1, 4)-d-Xylose	Antioxidant, anticancer, anti-inflammatory	(Konishi, Nakata, Miyagi, & Tako, 2012)
Green seaweed	Ulvan	β-d-Glucuronosyl-(1, 4)-α-l-rhamnose 3-sulphate	Antiviral, antimicrobial, antioxidant, anti-inflammatory	(Kraithong et al., 2024)
	Mannan	Mannose	Antidiabetic, antioxidant, immunomodulatory, anti-inflammatory	(Saraswathy, 2024)
Red seaweed	Carrageenan	Galactose acid and β-(1, 4, 3, 6)-anhydro-d-galactose	Anticancer, immunomodulatory, anti-inflammatory, antiviral	(Das & Bal, 2024)
	Agar	(3, 6)-anhydro-l-galactose	Wound healing, anticancer, anti-inflammatory, antiviral	(Chumsook, Praiboon, & Fu, 2023)
	Mannan	Mannose	Antidiabetic, anti-inflammatory, antioxidant, immunomodulatory,	(Ghosh, Pujol, Damonte, Sinha, & Ray, 2009)
	Starch	Amylopectin, glucose	Antidiabetic, energy source	(Tagliapietra, Borges, Ferreira, & Clerici, 2023)
	Xylan	β (1, 4)-d-Xylose	Antidiabetic, anticancer, anti-inflammatory	(Mune Mune, Hatanaka, Kishimura, & Kumagai, 2024)

linked seaweed polysaccharides (Khan, Aslam, & Makroo, 2019). Collectively, these observations indicate that, although green extraction technologies offer improvements over conventional methods, they still face important operational and scalability challenges. These restrictions have initiated a demand for novel extraction methods allied with doctrines of green chemistry, driving the broader application of DES, prepared through mixing HBDs and HBAs to create a eutectic complex possessing augmented polarity and tunable characteristics.

2.2.1. Critical comparison and evolution of extraction strategies

The progression from conventional to green extraction techniques reflects a shift from yield-driven approaches to sustainability and functionality-oriented processing (Otero et al., 2023; Rifna, Misra, & Dwivedi, 2023; Yara-Varón et al., 2017). Rather than differing only in methodology, these approaches fundamentally vary in their impact on process efficiency, structural integrity of polysaccharides, and industrial feasibility. Conventional extraction methods, although robust and scalable, are often energy-intensive and can compromise polysaccharide structure due to prolonged thermal or chemical exposure (Kadam, Álvarez, Tiwari, & O'Donnell, 2015; Wijesinghe & Jeon, 2012). In contrast, green extraction techniques improve process efficiency and reduce environmental burden, yet introduce new challenges related to operational complexity and scale-up.

A key distinction lies in the balance between extraction efficiency and structural preservation. Techniques such as UAE and MAE enhance mass transfer and reduce processing time, but may induce localised degradation under uncontrolled conditions (Rodriguez-Jasso et al., 2011). Enzyme-assisted extraction offers higher specificity but is constrained by cost and sensitivity (Kadam, Álvarez, et al., 2015). Within this context, deep eutectic solvents (DES) have gained increasing attention as next-generation green solvents due to their tunable physicochemical properties, low volatility, and ability to selectively solubilise complex polysaccharides. Compared to other green technologies, DES offer unique advantages, particularly in terms of solvent design flexibility and compatibility with bioactive compounds (Dai et al., 2013a; Florindo et al., 2018). Nevertheless, DES-based extraction is not without challenges, including high viscosity, difficulties in downstream recovery, and limited industrial scalability, as discussed in later sections. From a practical and industrial standpoint, the selection of an appropriate extraction method must extend beyond extraction yield and efficiency, incorporating considerations such as process scalability, economic feasibility, environmental impact, and preservation of polysaccharide structure and bioactivity. This highlights the need for integrated and hybrid extraction strategies that combine the advantages of different approaches while minimising their individual limitations. Therefore, while green extraction technologies represent a significant advancement over conventional methods, their successful industrial translation requires integrated optimisation of process parameters and comprehensive techno-economic evaluation.

2.2.2. Structure-function relationship of DES for the extraction of seaweed polysaccharides using the Kamlet-Taft parameter

To efficiently utilise DES to facilitate the extraction of polysaccharides in seaweed requires a good understanding in terms of molecular interactions (Krishnan et al. (2024); (Murphy et al., 2023). The Kamlet-Taft (KT) model supplies a strong background for knowing the structural performance connection of DESs, which is regulated through three main factors: α (HBD acidity), β (HBA basicity), and π* (polarizability). However, its application in polysaccharide extraction remains largely interpretative rather than predictive, as KT parameters are often correlated with extraction yield without direct validation of molecular-level interactions. This creates a disconnect between theoretical solvent descriptors and actual extraction performance in complex seaweed matrices (Al-Akayleh, Ali Agha, Olaimat, & Qinna, 2025; Dai, Witkamp, Verpoorte, & Choi, 2015). The α factor denotes the hydrogen bond donor acidity, which plays an important part in rupturing the hydrogen bonds present in polysaccharides (Kalhor & Ghandi, 2019; Orellana, 2020; Subedi, 2021). Mechanistically, higher α values enhance the disruption of intra- and intermolecular hydrogen bonding networks within the seaweed matrix, facilitating the release of bound polysaccharides. However, exceptionally high α values, specifically in acidic DES, may promote hydrolytic cleavage of glycosidic bonds, ensuing in decreased molecular weight and subsequent loss of bioactivity. Notably, most studies infer the role of α based mainly on extraction yield rather than direct structural characterisation (e.g., molecular weight or sulphation degree), restricting the competence to conclusively establish regulated hydrogen-bond disruption versus undesired depolymerisation, thus demonstrating a trade-off between extraction efficiency and structural preservation (Teles et al., 2017; Vilková, Płotka-Wasylka, & Andruch, 2020). Alginates consist of carboxyl and hydroxyl groups, and these functional groups can form strong intermolecular interactions with DES, especially at elevated α values, to efficiently extract polysaccharides (Asghari et al., 2023; Shete, 2024). Correspondingly, the β factor exhibits the HBA basicity in DES that facilitates associations among the acidic networks on polysaccharides, namely carboxyl and sulphate groups occurring in fucoidans and carrageenans (Guidi, 2019; Kundu, Rao, & Banerjee, 2020). DES systems with higher β values demonstrate enhanced affinity towards sulphated polysaccharides due to stronger hydrogen bonding and electrostatic interactions, thereby improving selectivity. DESs with high β values, such as choline chloride, are effective for obtaining the sulphated polysaccharides through hydrogen bonds between HBA-HBD and the polysaccharide (Er & Orakdogen, 2024). However, overly strong DES-polysaccharide interactions may hinder downstream recovery, as strong binding can reduce precipitation efficiency during anti-solvent addition, highlighting an important process limitation (Teles et al., 2017). From a process engineering viewpoint, this characterises a critical trade-off, as greater selectivity during extraction may inversely impact recovery efficiency, demanding higher anti-solvent input and increasing process cost and environmental burden (Hessel et al., 2022; Jessop, 2011). In addition, the DES's polarizability (π* factor) also affects the extraction by augmenting the solvent potential to diffuse through extremely cross-connected as well as intricate polysaccharide structures (Kundu et al., 2020). Few polysaccharides, for example, ulvans and fucoidans, which display a branching and sulphur-containing framework, are remarkably approachable to DESs with great polarizability (Hardiningtyas et al., 2024; Otero et al., 2023). However, the individual influence of π* stays less distinctly defined, as its effects are often linked with viscosity and solvent structuring. Therefore, its predictive utility in DES design for polysaccharide extraction is still regulated and demands additional validation via mutual experimental and computational studies (Bhar, Errehymy, & Ray, 2023). Furthermore, DESs formulated with hydrogen bond donors such as ethylene glycol or urea exhibit strong intermolecular interactions with polysaccharides. When coupled with enabling techniques such as MAE or UAE, which disrupt the seaweed cell wall, these DESs can penetrate the biomass more effectively, bind to polysaccharides, and thereby facilitate efficient extraction. The combined influence among π*, β, and α factors permits DESs to aim polysaccharide configurations and rupture them selectively, steering to polysaccharides extraction with marginal degradation along with the greatest functional safeguarding (Er & Orakdogen, 2024).

The DES-extracted polysaccharides are further stabilised by the DES (Nie, Chen, & Lu, 2020; Saravana, Cho, et al., 2018). This stabilisation is critical to retain the bioactivity of the extracted polysaccharides (Dheyab et al. (2021); (Ferreira & Sarraguça, 2024; Kim, Kim, & Yoon, 2024). However, such stabilisation is highly dependent on the balance of KT parameters, as inappropriate solvent design may lead to structural modification rather than preservation. A recent work carried out by Guerrero-Higareda and Carrillo-Nieves (2025) showed that functional attributes and molecular weight polysaccharides extracted using DES were preserved. Few studies have identified that through regulating the viscosity of DES, it is likely to enhance the properties of extracted

polysaccharides with improved purity, efficiency and yield (Ling & Hadinoto, 2022; Meng et al., 2023; Yahaya et al., 2024; Zhang et al., 2021). Recent studies have demonstrated that hydrated DES systems can significantly reduce viscosity and improve mass transfer; however, excessive hydration may compromise solvent structure and reduce extraction selectivity (Dai et al., 2015; González-Laredo et al., 2023; Şahin et al., 2026; Vilková et al., 2020). For instance, hydroxyl-rich polysaccharides, namely alginates, could be efficiently extracted with DES mixtures with high α values, whereas those possessing elevated β values are beneficially appropriate for fucoidan or any sulphated seaweed polysaccharides (Ling & Hadinoto, 2022). This demonstrates that KT parameters can act as practical design tools for tailoring DES composition towards specific polysaccharide targets; however, their implementation requires balancing extraction efficiency with downstream processing feasibility and structural preservation.

Curiously, this versatility in solvent design permits the desired polysaccharide extraction of seaweed. In addition, current research on experimental and computational works has enriched the insights into the structure-function correlation of DES mixtures for polysaccharide extraction (Dwamena & Raynie, 2020; Teles et al., 2017). Molecular dynamics simulations have shown energy distribution of hydrogen bonding and the associations among DESs and polysaccharides, to map the extraction process. Nevertheless, KT parameters alone may not fully capture the complexity of DES systems, particularly in hydrated or multi-component environments, and therefore should be complemented with computational and spectroscopic analyses for more accurate prediction. Overall, Kamlet-Taft parameters provide a valuable framework for understanding and predicting DES-polysaccharide interactions; however, their true significance lies in enabling rational solvent design. The interplay between α, β, and π* governs not only solubilization efficiency but also selectivity, structural preservation, and recovery behaviour. From a practical perspective, these parameters can guide the development of task-specific DES systems tailored to target specific polysaccharides while minimising degradation and co-extraction.

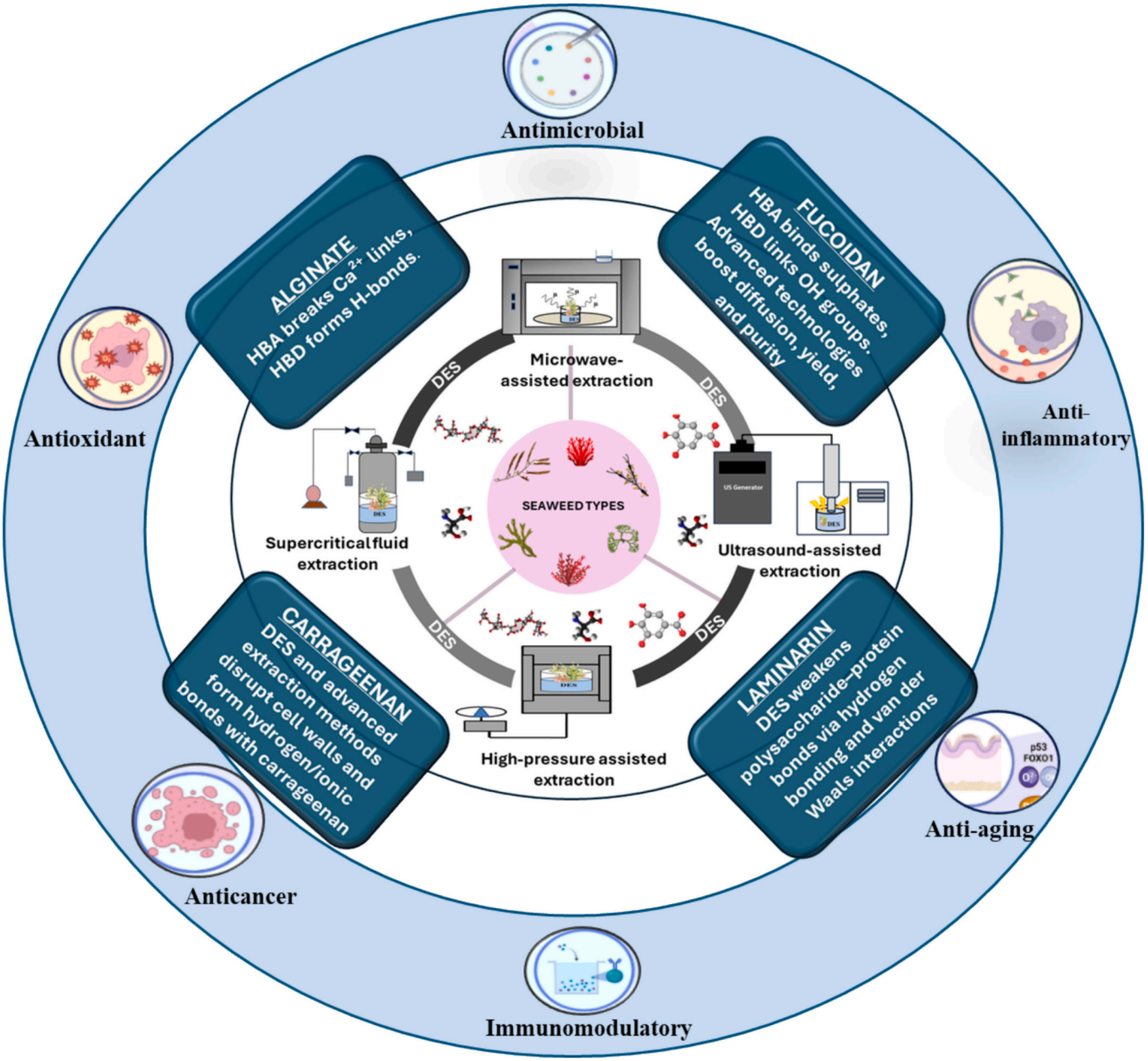


Fig. 1. Targeted seaweed polysaccharides, their mode of action with DES, and the therapeutic properties displayed by DES-extracted polysaccharides.

Nevertheless, their standalone application remains limited, and integration with experimental validation and molecular modelling is essential for advancing scalable and efficient DES-based extraction processes.

The subsequent sections will continue with elucidating the extraction of specific polysaccharides present in seaweeds with the application of DESs, containing alginate, fucoidan, laminarin, carrageenan, ulvan, agar, and cellulose. Further, the sections also delve into characteristics of targeted polysaccharides, their biological significance, and the most effective formulation of DESs for their effective extraction from seaweed matrix. Fig. 1 illustrates the seaweed polysaccharides of interest, their interaction mechanisms with DES, and the therapeutic properties exhibited by DES-extracted polysaccharides.

3. Extraction of seaweed polysaccharides using DES and their integration with advanced techniques

3.1. Alginate

Alginate is an important polysaccharide found in considerable amounts in the cell walls of brown seaweeds, where it functions as both a mechanical stabiliser and a natural resistance to environmental challenges. Structurally, alginate is a straight-chain, linear copolymer formed of β-D mannuronic acid (M) and α-L-guluronic acid (G) units connected by (1,4) glycosidic bonds. These monomers are arranged into three structural sequences: homopolymeric G-blocks, homopolymeric M-blocks, and heteropolymeric MG-blocks (Teng, An, Chen, Zhang, & Zhao, 2021). The relative proportion and configuration of these blocks, which vary among seaweed species and environmental surroundings, significantly affect the polymer's physicochemical properties, principally its ability to form gels through divalent cation binding (Kumar, Hart, & Thakur, 2024). Also, alginate contains (-OH) and ($-COO^-$), which are essentially accountable for its viscosity, solubility, gelation and play a substantial role throughout the extraction and purification process. Also, these functional groups uphold the polymer's structural stability and applicability in food, pharmaceutical, packaging, and biomedical industries (Saji, Hebden, Goswami, & Du, 2022). Building on this importance, numerous studies have explored seaweed alginate extraction using DES and DES-coupled technologies, emphasising their potential as an efficient and sustainable extraction method.

3.1.1. Mode of action of DES for alginate extraction

Alginate extraction using DES starts as the solvent diffuses into the structural matrix of seaweed. The increased polarity and adjustable viscosity of DES enable it to form intermolecular linkages with the alginate functional groups. The HBA, usually choline chloride, networks with the negatively charged ($-COO^-$) groups of alginate via its quaternary ammonium cation, thus weakening ionic bonds with cations such as Ca^{2+}, Mg^{2+}, Na^+, or K^+, in alginate (Bojorges, López-Rubio, Martínez-Abad, & Fabra, 2023; Saji et al., 2022); Alginate from seaweed can contain cations that are naturally found in marine. Concurrently, the HBD forms robust hydrogen bonds with the ($-COO^-$) and (-OH) present in the backbone of alginate. When combined with advanced extraction technologies such as MAE or UAE, the competence of alginate recovery is further enhanced. These methods promote molecular diffusion by disrupting the cell wall, while also reducing DES viscosity, which facilitates intermolecular interactions and improves overall extraction yield (Reynaga-Navarro, Wijffels, Eppink, & Kazbar, 2024).

3.1.2. Recent advances in alginate extraction from seaweed using DES/DES-combined with advanced technologies

Hiemstra, Meinema, Eppink, Wijffels, and Kazbar (2024) explored choline chloride-based DES for the extraction of alginate from *Ascophyllum nodosum*. The authors reported that out of the eight DES mixtures, ChCl:Urea (1:2) demonstrated the highest efficiency, yielding 74% intact alginate, whereas conventional alkaline extraction produced only 10–24.5%. The enhanced performance can be rationalised using Kamlet-Taft (KT) parameters; the high hydrogen-bond basicity (β) of urea facilitates strong interactions with the electronegative carboxylate ($-COO^-$) and hydroxyl (-OH) groups of alginates, while the choline chloride cation provides electrostatic stabilisation of ($-COO^-$) moieties. In contrast, other DES with lower α or β values would form weaker interactions, resulting in reduced solubilization and slower alginate release. However, this interpretation is primarily based on extraction yield, and limited information is available on whether the recovered alginate retains its native molecular weight distribution or functional properties, which are critical for industrial applications. Further, (Reynaga-Navarro et al., 2024) reported that alginate recovery from brown seaweed using choline chloride-based DES strongly depends on the hydrogen bond donor used and the precipitation strategy. Interestingly, in their study, ChCl:Urea and ChCl:Ethylene glycol yielded the lowest alginate recovery under acid condition (9.6 ± 1.3% and 21.8 ± 0.6%, respectively), whereas ChCl:Glycerol, ChCl:Sorbitol, ChCl:Xylitol, and ChCl:Glucose produced moderate yields of ~25–29%. This contrast underscores that extraction efficiency is determined not only by DES composition but also by seaweed species, process conditions and precipitation strategy. More importantly, it highlights a key limitation in DES-based systems, where high solubilization does not necessarily translate to high recovery, indicating a disconnect between extraction and downstream processing efficiency. Ethanolic and $CaCl_2$ precipitation steadily enhanced yield, with the highest recovery attained for ChCl:Glycerol (51.2 ± 1.3% with ethanol and 45.7 ± 1.2% with $CaCl_2$), displaying the key part of precipitation in extracting alginate from DES matrices. This also suggests that precipitation strategy must be co-optimised with DES selection, rather than treated as a secondary step, which is often overlooked in current studies. Rationalising these results through KT parameters, ChCl:Urea DES displays elevated β from urea's $-NH_2$ and carbonyl groups and moderate α, which assists powerful linkages with alginate's electronegative ($-COO^-$) and (-OH) groups. While these associations improve alginate dissolution, they can also over stabilise the polymer chains, restricting solubilization and release during precipitation, thus ensuing in depleted recovery (Shete, 2024). Whereas ChCl:Glycerol associations have a comparatively high α and β with reduced viscosity and manifold (-OH) groups, allowing efficient hydrogen bonding with the ($-COO^-$) and (-OH) groups of alginates, though preserving satisfactory molecular mobility. This permits the alginates to be more effectively precipitated, generating greater recovery (Shete, 2024). Likewise, DESs with HBDs for instance, sorbitol, xylitol, and glucose, show moderate α and β values, delivering medium recovery yields. Ethylene glycol, regardless of its ability for hydrogen bonding, offers limited binding sites compared to glycerol, leading to lower solubilization and reduced alginate yield under acid precipitation. Moreover, authors also reported that DES-isolated alginate exhibited a reduced ManA/GulA ratio compared to ethanolic extracts. This decrease may be attributed to the preferential disruption of calcium-guluronate linkages by choline chloride and the strong hydrogen bonding of urea with carboxyl and hydroxyl groups in the alginate backbone, which can selectively destabilise guluronate-rich sequences or promote partial depolymerisation of mannuronic residues (Prates et al., 2025). Such compositional changes may significantly influence rheological behaviour and gel-forming ability, yet these functional implications are rarely assessed in DES-based extraction studies. Future studies may warrant optimising DES composition using HBDs with milder hydrogen-bonding capacity or gentler conditions, coupling advanced extraction technologies to preserve the native ManA/GulA ratio while maintaining efficient alginate solubilization. (Nie et al., 2020) explored the effect of UAE of alginate from *Sargassum horneri* with ChCl:1, 2-propanediol (1:2) at optimised conditions with 30% water, 1:30 solid-liquid ratio, at 70 °C. The researchers stated alginate yield of 11.31% (*w*/w), compared to 8.74% (w/w) obtained with conventional hot-water extraction. They further reported that DES-extracted alginate exhibited greater purity, as evidenced by lower mineral and protein content relative to the hot-

water extract. This variance in purity might be accredited to the specific solvation power of DES, which favourably relates to alginate functional groups while lessening *co*-extraction of non-polysaccharide elements. The diminished mineral and protein matter in the alginate extract features the potential of DES to specifically extract alginate while reducing the co-extraction of untargeted compounds. (Saravana, Cho, et al., 2018) studied the recovery of alginate from *Laminaria japonica* with the aid of DES in subcritical water hydrolysis. It was observed that ChCl: Glycerol showed increased extraction competence evaluated to 1, 2-propanediol. This could be attributed to the healthy α and β values of glycerol-based DES, which add to interactions with the (-COO^-) and (-OH) groups of alginates. Further, the quaternary ammonium cation of ChCl can electrostatically stabilise the negatively charged (-COO^-) groups however, glycerol results in numerous hydrogen bonds with both (-OH) and (-COO^-) groups, improving solubilization and molecular movement of alginate chains. The increased polarity (π*) and decreased viscosity of ChCl: Glycerol further boost dissolution into the algal matrix, aiding to efficient extraction. Likewise, (James, Ramirez, Barner, & Moghaddam, 2024) investigated the extraction of sodium alginate and fucoidan from *A. nodosum* using glycerol and ChCl based DESs coupled with MAE. The ChCl:Glycerol combination achieved an alginate recovery of 46.2% and purity of 33.43%, along with enhanced bioactive potential.

Furthermore, (Wu et al., 2021) used a DES-MAE to recover alginate from the seaweed species *Fucus vesiculosus*. The DES mixture of ChCl:1, 4-butanediol was used in a ratio of 1:5 and optimised for 168 °C, at 32% water content, for 35 min. The work accomplished a significant alginate yield of 116.33 mg/g. In this DES, the (-OH) groups of 1, 4-butanediol form hydrogen bonds with the (-COO^-) and (-OH) groups of alginates, disturbing the intermolecular crosslinks and improving the polymer solubilization. Meanwhile, the choline cation stabilises the negatively charged (-COO^-) groups electrostatically, further promoting chain separation. Microwave pretreatment lowers the solvent viscosity, increases molecular mobility, and ruptures cell walls, facilitating efficient penetration of the DES and improving extraction yield. These interactions reflect the KT parameters; β of 1, 4-butanediol and moderate polarity (π*) enhance alginate solubilization and diffusion, demonstrating how DES composition and functional group chemistry govern extraction efficiency. Nevertheless, recognising that reusability of DES is a major area of interest, (Cai et al., 2020) formulated a temperature-dependent DES design of o-cresol and ethanolamine to extract polysaccharides, mainly alginate, from the seaweed *Ganoderma lucidum,* and the researchers reported that the system continued greater polysaccharide efficiency crosswise multiple sequences, with insignificant deprivation in extract yield afterwards five uses. This work emphasised the reusability along with the green chemistry perspective of DES, which might be later investigated for the extraction of alginate from other seaweed species.

Overall, the discussed studies indicate that DES-assisted extraction of alginate is strongly influenced by the choice of solvent system, precipitation strategy, operating conditions, and seaweed species. ChCl:Glycerol has shown consistent performance across various seaweed species such as *A. nodosum* and *L. japonica*, where its balanced α and β capacities, multiple hydroxyl groups, moderate viscosity, and high polarity facilitated strong interactions with alginate's -COO^- and -OH groups, thereby enhancing solubilization and precipitation efficiency. By contrast, DESs with stronger hydrogen-bond donor properties, such as ChCl: Urea, markedly improved solubilization and over-stabilised alginate chains, leading to variable yields depending on precipitation methods and process parameters (Shete, 2024). Complementary approaches, including microwave- or ultrasound-assisted DES extraction, further improve recovery by reducing viscosity, disrupting cell walls, and increasing molecular mobility. Future research should focus on tailoring DES combinations, HBD/HBA ratios, and extraction conditions to maximise yield and preserve alginate's functional qualities, while also addressing scale-up feasibility and solvent recyclability for sustainable industrial application.

3.2. Fucoidan

Fucoidan is a sulphated complex polysaccharide primarily positioned in the interstitial matrix as well as the fibrous components of brown seaweeds, where it enables cell wall flexibility and controls osmotic equilibrium. Structurally, fucoidan exhibits significant structural diversity, containing primarily α-L-fucopyranose units linked through α(1–3) or alternating α(1–3)/ α(1–4)-glycosidic bonds (Cunha & Grenha, 2016). These fucose units are selectively substituted with sulphated ester groups, principally at the C-2 and C-4 positions, which confer a pronounced anionic charge to the molecule. In parallel, trace monosaccharides like mannose, galactose, uronic acids, and xylose are covalently linked into the main chain or occur as side-chain residues, producing an intricate and highly branched polymer network (James et al., 2024). The structure may be additionally modified by acetyl and occasionally methyl groups, which affect viscosity, solubility, and hydrogen bonding between molecules. Sulphate groups may also occur on side chains as well as the main chain, and the degree of sulfation directly impacts the polymer's bioactive potential (Li, Lu, Wei, & Zhao, 2008). The chemical intricacy of fucoidan is principally determined by aspects for instance, such as the type of seaweed species, seasonal growth environment, ecological origin, and extraction or refining approaches used. This chemical complexity, although vital to fucoidan's biological characteristics, presents notable challenges for extraction, as various solvents used recurrently induce depolymerisation, desulphation, and conformational disruption (Li et al., 2008). In this scenario, the use of DES displays a promising substitute, as their changeable hydrogen-bonding properties and mild environments enable selective solubilization while conserving sulphate ester groups as well as native molecular configuration. Subsequently, DES-based extraction not only boosts recovery efficiency but also preserves the molecular configuration, biological, and physicochemical activity of fucoidan, establishing a green and sustainable approach for the recovery of this multifunctional seaweed polysaccharide.

3.2.1. Mode of action of DES in fucoidan extraction

The mechanism of DES in the extraction of fucoidan is determined through its potential to disrupt the hydrogen-bonded complex and electrostatic bond that stabilise the fucoidan within the seaweed cellular matrix. DES, prepared by combining HBD and HBA, allows the selective solubilization of fucoidan while decreasing the structural degradation (Ale, Mikkelsen, & Meyer, 2011; Chadwick, Carvalho, Vanegas, & Dimartino, 2025). The HBA, typically choline chloride, engages in electrostatic (ionic) interactions with the negatively charged sulphate (-OSO_3^-) groups along the fucoidan backbone. Concurrently, the HBD, such as ethylene glycol or glycerol, forms extensive hydrogen-bonding interactions with hydroxyl (-OH) groups and engages in hydrogen-bonding and ion-dipole interactions with (-OSO_3^-) groups. These combined interactions facilitate solubilization and extraction of fucoidan from the seaweed biomass. Fig. 2 illustrates the mechanisms of DES interaction with sulphated algal polysaccharides using fucoidan as an example. The fucoidan structure from *Ascophyllum nodosum,* illustrated in Fig. 2, was redrawn based on the structure reported by (Ale & Meyer, 2013). The fucoidan structure in the figure shows fucose backbone linked predominantly through α-(1–4) and with a lower proportion of α-(1–3) linkages, while sulphate substitution occurs mainly at the O-2 position. The figure illustrates the potential interactions between DES components and the sulphate functionalities present on the fucoidan backbone.

The extremely branched structure and broad molecular weight distribution of fucoidan (varying between a few kDa to >1000 kDa) generate steric interference and wide hydrogen-bonding links, which DES can penetrate owing to its tunable viscosity and polarity, permitting competent extraction at mild temperatures and conserving native

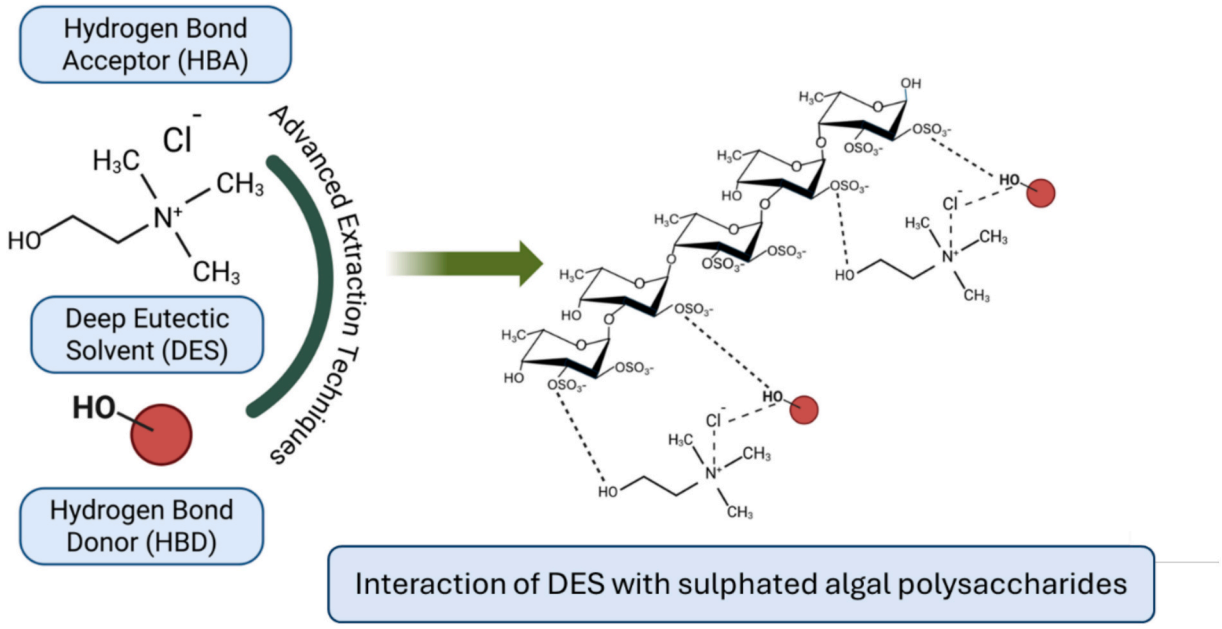


Fig. 2. Proposed interactions between deep eutectic solvents (DES) and sulphated algal polysaccharide, illustrated using fucoidan as a representative example. The chemical structure of fucoidan from *Ascophyllum nodosum* was redrawn using previously published structural data reported by (Ale & Meyer, 2013).

sulphate esters and bioactivity (Cunha & Grenha, 2016). Unlike alginate extraction, which principally depends on the fragmentation of calcium-mediated ionic linkages, DES-assisted fucoidan extraction aims to break hydrogen bonds and ionic interactions specific to its branched, sulphated molecular structure. This specificity allows for competent extraction of fucoidan with the least contamination from other polysaccharides, proteins or cellular remains. Also, adding water to DES can improve solubilization, modulate polarity, and extract fucoidan in a sustainable, single-step method (Ale et al., 2011; Jayawardena et al., 2022). The competence and efficiency of DES extraction can further be considerably enhanced through combining advanced extraction technologies, specifically MAE and UAE, which effectively increase extraction yield, purity, and preservation of bioactivity.

3.2.2. Recent advances in fucoidan extraction from seaweed using DES/ DES-combined with advanced technologies

Recently, (Guerrero-Higareda & Carrillo-Nieves, 2025) used a sequential extraction approach for fucoidan extraction from *Sargassum* seaweed biomass, using glycerol, urea, and acetic acid-based DES combined with UAE. Among the tested solvents, ChCl:Glycerol (1:2) arose as the most effective, producing a crude fucoidan yield of 0.4103 ± 0.0042 g/ g of dry biomass. This fucoidan yield was higher than those attained using other DES-UAE combinations as well as conventional extraction methods in this study, thus demonstrating the augmented proficiency of the glycerol-based DES-UAE method. This excellent performance of ChCl: Glycerol can be rationalised with the aid of KT parameters (α, β, and π*). Glycerol, being an HBD, exhibits a greater β value, forming multiple hydrogen bonds with fucoidans' (-OH) and ($-OSO_3^-$) groups (Towey, Soper, & Dougan, 2011). The three hydroxyl groups of glycerol produce a compact hydrogen-bond association, refining the association with both chloride anions and substrate, which decreases side reactions and enables more effective fucoidan solubilization compared with urea- or acetate-based DES. Nevertheless, this interpretation is largely inferred from solvent properties and extraction yield, as direct spectroscopic or molecular-level validation of these specific DES-fucoidan interactions remains limited in current studies. Unlike glycerol, urea contains ($-NH_2$) and (-C=O) groups, which, regardless of an increased β, develop hardly any directional hydrogen linkages with the (-OH) and ($-OSO_3^-$) groups of fucoidan owing to steric hindrance, restricting solubilization (Sun, Li, Wu, & Li, 2013). Similarly, acetate, through its ($-COO^-$) group, displays a lower β and predominantly leads to ionic interactions instead of broad hydrogen-bonding networks, causing a weaker interaction with fucoidan (Triolo et al., 2021). Further, ChCl, acting as the HBA, possess moderate α, which permits it to network electrostatically with the negatively charged ($-OSO_3^-$) groups with no over-stabilising the polymer sequences. This α-β synergy present in ChCl-Glycerol promotes polymer solubilization and improves its diffusion into the solvent phase. However, excessively strong DES-polysaccharide interactions may also pose challenges during downstream recovery, particularly during anti-solvent precipitation, where tightly bound systems can reduce separation efficiency. Additionally, notable π* of the ChCl:Glycerol system enhances penetration of the solvent to the seaweed cell wall matrix, further encouraging effective solvent-polysaccharide interactions. Henceforth, the better performance of the ChCl:Glycerol system in this research can be attributed to the interplay of increased β, moderate α, along with robust electrostatic stabilisation. (James et al., 2024) carried out a comparative study assessing four extraction methods: UAE, MAE, subcritical water extraction (SWE), and thermochemical extraction, utilising a ChCl: Glycerol based DES as solvent to extract fucoidan from *A. nodosum*. Consistent with the results of (Guerrero-Higareda & Carrillo-Nieves, 2025), MAE coupled with ChCl:Glycerol displayed the highest fucoidan yield, which could be credited to the identical KT-driven solvent-fucoidan interactions. Further, the instant heating and boosted mass transfer stipulated by microwaves synergistically might have decreased viscosity and ruptured the seaweed cell wall, further accelerating the solubilization and diffusion of fucoidan into the DES phase. Another research work done by (Saravana et al., 2018) examined the fucoidan extraction from *Saccharina japonica* by means of SWE combined with a DES mixture of ChCl:Glycerol, obtaining a crude fucoidan yield of 13.56% under optimised conditions (127 °C, 80 bar, 0.04 g/mL solid-liquid ratio, 300 rpm, 12 min). The remarkable performance of the selected DES mixture in this study can similarly be rationalised using KT, in line with the aforementioned explanations. Furthermore, (Guerrero-Higareda & Carrillo-Nieves, 2025) identified that ChCl:Glycerol coupled with UAE resulted in fucoidan yield of 0.4103 ± 0.0042 g/g dry biomass from *Sargassum* spp., considerably greater than conventional methods and other DES mixtures, showing the importance of mechanical

energy in disturbing the seaweed matrix and increasing mass transfer. Correspondingly, (James et al., 2024) highlighted that MAE with ChCl: Glycerol accomplished the superior yield of fucoidan from *A. nodosum,* compared to the other three extraction methods used, where quick volumetric heating helps lower viscosity and progresses DES penetration into the biomass. These observations collectively suggest that process conditions, rather than DES composition alone, play a dominant role in determining extraction efficiency, highlighting the need for integrated optimisation of both solvent design and extraction technology. Notably, even without advanced extraction technologies, the effectiveness of DES alone for fucoidan extraction from seaweed has been explored. In a study by (Reynaga-Navarro et al., 2024), numerous ChCl-based DESs such as ChCl:Ethyleneglycol, ChCl:Urea, ChCl:Glycerol, ChCl:Sorbitol, ChCl:Xylitol, ChCl:Propyleneglycol, and ChCl:Glucose were used for the extraction of fucoidan from *A. nodosum*. Though the accurate fucoidan yield was not described, the authors reported that ChCl:Glycerol mixture resulted in increased yields compared to the other DES mixtures. In disparity, other DESs, namely, ChCl:Urea, ChCl:Ethylene glycol, and ChCl:Propyleneglycol, hold either reduced β, higher viscosity, or weak balanced α-β associations, resulting in frailer hydrogen bonding and electrostatic stabilisation, subsequently reducing extraction efficiencies. However, when comparing all the above studies, it is evident that introducing supplementary energy input significantly elevated the fucoidan solubilization in DES, suggesting that advanced extraction technologies can significantly increase the competence of a well-designed DES mixture. Nevertheless, out of all three research works, the stable success of ChCl:Glycerol DES can be ascribed to the consolidation of (β) from glycerol, modest (α) from ChCl, and moderate π*, which together aid in strong interactions with (-OSO_3^-) groups, ensuing in considerable fucoidan diffusion (James et al., 2024). It could be envisaged that the introduction of energy-assisted techniques such as UAE or MAE significantly increases extraction yields afar what DES alone can accomplish, even though SWE itself remains energy-intensive owing to the elevated temperatures and pressures essential to sustain water in a sub-critical state.

Overall, ChCl:Glycerol outweighs other DESs for fucoidan extraction in all studied seaweed species, both in DES alone and energy-aided DES extractions. The coupling of high β from glycerol, moderate α from ChCl, and moderate π* supports durable interactions with sulphate groups, best solubilization, and effective diffusion. Energy-assisted extraction, such as MAE and UAE, further advances yield by dropping viscosity, increasing mass transfer, and breaking cell walls (Guerrero-Higareda & Carrillo-Nieves, 2025). However, despite these promising outcomes, current studies predominantly emphasise extraction yield, with limited evaluation of fucoidan structural integrity, molecular weight distribution, and sulphation patterns, which are critical for its biological functionality. Moreover, the scalability and economic feasibility of combining DES with energy-intensive techniques remain insufficiently addressed, raising questions regarding their industrial applicability. Subsequently, ChCl:Glycerol, alone or paired with energy-assisted extraction, parallels a robust, sustainable, and substantially efficient approach for isolating high-value fucoidan from various brown seaweed species. Future research warrants investigating combinatorial DES formulations and pairing them with promising energy-assisted extraction technologies, such as pulsed electric field or low-intensity ultrasonication, that possess the potential to enhance fucoidan yields while reducing energy input. Prominence on DES recyclability, techno-economic assessment, and process optimisation is critical for sustainable scale-up. Furthermore, incorporating DES extraction of fucoidan into a biorefinery framework could aid in the co-recovery of other high-value compounds. Mutually, these approaches can enhance DES-based fucoidan extraction towards environmentally friendly and more sustainable industrial applications.

3.3. Laminarin

Laminarin is a water-soluble β-glucan stored in brown seaweed vacuoles, serving as an easily accessible carbon and energy source. Structurally, laminarin is a low molecular mass β-glucan containing mostly β-(1, 3)-D-glucopyranose bonds with intermittent β-(1, 6) side units, yielding rise to both linear or slightly branched structures (Cunha & Grenha, 2016). The molar mass, polymer chain length, and level of branching vary significantly with seaweed species, growth periods, and surrounding ecological factors, thus influencing its physicochemical properties and extraction performance. Unlike alginate and fucoidan, laminarin is a neutral polysaccharide that does not contain sulphate groups and has minimal ionic interactions. Beyond, its structure is primarily stabilised through a solid arrangement of hydrogen bonds constructed involving (-OH) groups on adjacent glucose units (Kadam, Tiwari, & O'Donnell, 2015). These interactions produce compact, semi-crystalline configurations aiding in laminarin's solubility, molecular stability, and viscosity in aqueous media. Moreover, laminarin in seaweed exists in two main forms: soluble and insoluble parts that can exist in variable fractions within the seaweed cell matrix, differing in hydroxyl groups and β-1, 6 glycosidic linkages, combining a supplementary level of complexity to its extraction. Structurally, laminarin can also be categorised into G-type and M-type, based on the terminal sugar moiety, with mannitol for M-type and glucose for G-type. This structural variability not only affects its biological properties but also the performance in diverse extraction media and physicochemical environments (Cunha & Grenha, 2016). Extraction processes, whether using technology, hot water or common solvents, can moderately trigger depolymerisation in laminarin due to its unstable glycosidic linkages. This has led to increasing concern about mild methods that preserve the native molecular configuration and enhance recovery. In this context, DES have developed as a favourable green solvent for the competent and selective laminarin extraction from brown seaweeds. Due to DES's tunable hydrogen-bonding groups and polarity, DES can improve the solubilization of β-glucan units while lowering the degree of degradation.

3.3.1. Mode of action of DES in laminarin extraction

DES isolates laminarin via an association of hydrogen-bonding linkages that target the dissolution of the polysaccharide while maintaining its indigenous structure. The HBA, normally ChCl, networks ionic interactions with laminarins (-OH) groups, attenuating internal hydrogen bonding and partially breaking interactions with other matrix constituents (Yan, Guan, Liang, & Zhao, 2025). In the interim, the HBD, including ethylene glycol, glycerol or urea, establishes robust hydrogen bonds with the laminarin hydroxyls, increasing solvation, thus enabling easy extraction of laminarin from the seaweed matrix. The adjustable properties of DES permit the solvent to infiltrate the seaweed matrix efficiently, creating a gentle chemical environment that reduces laminarin's structural changes or depolymerisation (Li, Dai, Wang, & Row, 2019). Contrasting other polysaccharides such as alginate or fucoidan, which depend on interrupting sulphate or ionic associated interactions, the extraction of laminarin is predominantly aided through hydrogen-bond rupturing and solubilization of the glucan backbone. This steered DES extraction mechanism allows competent laminarin recovery with the least contamination from other polysaccharides or proteins, emphasising DES as a green and selective solvent for this marine β-glucan.

3.3.2. Recent advances in laminarin extraction from seaweed using DES/DES-combined with advanced technologies

Zhang et al. (Zhang et al., 2022) studied the application of DES-grounded magnetic molecularly imprinted polymer (MIP) for the targeted isolation of laminarin from the species L. *japonica*. The DES was made of 4-vinylbenzyltrimethylammonium chloride as the HBA and 4-vinylbenzoic acid as the HBD. This combination led to a modified

extraction environment that resulted in good solubility with clear polymerisation properties. It further enables notable laminarin solubilization and selective identification, resulting in the extraction of a total of 4762.67 μg laminarin with 93.7% purity. However, it should be noted that such high selectivity and purity are achieved within a specialised MIP-assisted system and may not be directly transferable to conventional DES extraction processes, thereby limiting broader applicability. The increased extraction execution can be justified using KT factors. The quaternary ammonium cation of VBTAC might have participated in the electrostatic associations with the negatively charged (-OH) and ($-COO^-$) of laminarin, facilitating the stable integration of polysaccharide in solution. Concurrently, the ($-COO^-$) group of HBD in this research establishes several hydrogen linkages with laminarin hydroxyls, thus boosting solubilization along with molecular mobility. Nevertheless, these mechanistic interpretations are largely inferred, as direct experimental validation of DES-polysaccharide interactions at the molecular level remains limited in current studies. DESs with fragile hydrogen-bonding ability or limited functional groups would be anticipated to display decreased laminarin solubilization and gradual liberation during extraction. In another study, (Li et al., 2019) investigated laminarin extraction from marine kelp using DES composed of ChCl and urea, working as a green solvent that improved the interfaces among reactive monomers and target template molecules throughout polymerisation. The resulting DES-aided extraction efficiencies of 87.6% for laminarin. In the ChCl:Urea based DES, ChCl acts as the HBA, where the quaternary ammonium cation undertakes hydrogen bonds from (-OH) groups of laminarin, and the reasonable π* value permits the DES to ooze out into the laminarin present in the seaweed cell matrix (Shete, 2024). Urea acts as the HBD, with ($-NH_2$) and ($-COO^-$) providing hydrogen bonds to laminarin's hydroxyl groups, whereas an increased β value allows strong associations with electronegative -OH and $-COO^-$ units. Mutually, these linkages enable hydrogen bonding that releases laminarin's structure, and efficient matrix penetration, jointly progressing competent solubilization and laminarin extraction. The above studies emphasise the potential of DESs to enhance solubility and foster the specificity of polymer-associated extraction systems. Upcoming study could emphasise optimising DES composition to boost extraction efficiency and selectivity, scaling up the extraction method for industrial use, DES coupling with an advanced extraction technology and examining its stability under various conditions.

3.4. Carrageenan

Carrageenan is a large macromolecule, a linear, sulphate-rich polysaccharide found mostly in red seaweed cell walls, where it functions as an essential structural support as well as an intermediary of osmotic stability. Structurally, carrageenan is composed of successive groups of D-galactose and 3, 6-anhydro-D-galactose connected through alternating β-(1, 3) and α-(1, 4) glycosidic bonds (Usov, 1998). Further, with regard to the degree and location of sulphation, carrageenan is organizationally categorised into three types mainly: κ-carrageenan (sulphation at C-4 of the β-D-galactose unit), ι-carrageenan (supplementary sulphation at C-2 of 3, 6-anhydro-D-galactose), and λ-carrageenan (more wide-ranging sulphation without the 3, 6-anhydro bridge) (Istini, OHNo, & Kusunose, 1994; Shafie et al., 2022). This flexibility in sulphation severely changes carrageenan's physicochemical characteristics, predominantly its competence to develop into gels in the presence of peculiar cations, say, K^+, Ca^{2+}, along with its rheology, solubility, and firmness. The seaweed carrageenan backbone is also rich in (-OH) and ($-OSO_3^-$) functional groups, which govern both ionic cross-link formation and hydrogen bonding, as well as impact solvent-polymer interactions. The conventional method of extraction for carrageenan frequently uses alkaline solvents or high temperatures, and this could aid in degradation of carrageenan, desulphation, and decrease of gel strength (Das, Sharma, Mondal, & Prasad, 2016). In this situation, DES propose a gentle and ecologically safe replacement, permitting selective solubilization of sulphated galactans whilst sustaining their structural integrity as well as sulphate swap pattern.

3.4.1. Mode of action of DES in carrageenan extraction

The carrageenan extraction with DES requires a coupled mechanism of hydrogen-bond and ionic interference, enhanced solvent diffusion, and loosening of the seaweed cellular network. In distinctive DES systems, the HBA generally ChCl networks electrostatically with negatively charged ($-OSO_3^-$) with carrageenan chain. This association matches with the indigenous ionic cross-links among carrageenan and cations (K^+, Ca^{2+}), successfully weakening the gel-comparable network and advancing the release of polysaccharide. At the same time, the HBD used develops hydrogen bonds with ($-OH^-$) groups located at C-2, C-3, and C-6 of galactose and 3, 6-anhydrogalactose units (Ramli, Rosli, Hamdan, & Adam, 2024). These connections reduce the structural organisation of the matrix, thereby enhancing the solubility of carrageenan into the DES medium. In addition, the occurrence of ($-OSO_3^-$) and ($-OH^-$) groups along the polymer leads to the formation of several binding sites for DES, which facilitates extraction under gentle conditions, eliminating the need for elevated temperature and alkaline exposure, thus preventing depolymerisation and preserving sulphation patterns. After carrageenan extraction, carrageenan can be removed from DES medium through cooling or precipitation, as DES go through phase alteration under specific environments, permitting streamlined extraction and recovery of the targeted molecule. To date, few studies have investigated the application of DES for the carrageenan extraction from seaweeds, aiming to develop more resource-efficient methods with respect to conventional solvent extraction.

3.4.2. Recent advances in carrageenan extraction from seaweed using DES/DES-combined with advanced technologies

In a research study by (Das et al., 2016), κ-carrageenan extraction from *K. alvarezii* employing DES exhibited the ability of these solvents for effective recovery of polysaccharides. The authors compared two DESs, ChCl-Glycerol and ChCl-Urea and revealed that the urea-based solvent produced the highest yield (~43.4%), outperforming the (~36.8%) obtained with glycerol-based solvent. This superior performance is attributed to urea's robust hydrogen-bonding potential and enhanced polarity, which enabled the rupture of ionic linkages and intermolecular hydrogen bonds inside the seaweed matrix (Shukla, Isaacs, Hamann, & Platzman, 2001). Also, during the process of extraction, the choline cation in the used DES would have networked electrostatically to the negatively charged sulphate groups in the κ-carrageenan, swapping native cations (Das et al., 2016). In contrast, the urea molecule would have developed several hydrogen bonds with ($-OSO_3^-$) and ($-OH^-$) groups, weakening the targeted compounds' interaction with seaweed matrix, thus boosting solubilization. Based on KT parameters, the ChCl:Urea mixture displays elevated α and β values, compared to the ChCl-Glycerol mixture, demonstrating an effective potential to network with polar functional groups. In a recent study (Ramli et al., 2024), the use of DES was discussed not just as an extraction solvent but also as a plasticising and modifying agent in the preparation of carrageenan-based films, thus widening the functional application of DES ahead of polysaccharide isolation. In this study, several ChCl-assisted DES, chiefly ChCl-Glycerol and ChCl-Lactic acid, were used to κ-carrageenan matrices to enhance elasticity, moisture resistance, and tensile strength. The research findings indicated that the ChCl:Lactic acid DES displayed higher performance as a plasticizer, generating films with elevated extension at break (41%) and increased tensile strength (32 MPa) compared to DES with ChCl-Glycerol. Authors credited this enhancement to the powerful hydrogen-bond donor ability as well as the reasonable polarity of lactic acid, as mirrored through its enhanced α and β values, which permitted further wide-ranging hydrogen bonding with ($-OSO_3^-$) and ($-OH^-$) groups present along the carrageenan main chain. These interfaces would have disturbed the rigid polymer-polymer connections and augmented free space inside the

matrix, producing better elastic and consistent films with improved mechanical properties (Gong, Xiang, Zhang, Chen, & Zeng, 2019).

In summary, the two research studies discussed above mutually confirm that DES not only facilitate effective and green extraction of carrageenan but also aids post-processing properties for preparing biodegradable films. Upcoming investigations warrant attention on coupling DES-based extraction through in situ biodegradable film development, optimising recovery of solvent, as well as modifying DES polarisation and hydrogen-bonding properties to attain a greater extraction yield and required material strength. Furthermore, increasing research on natural deep eutectic solvents (NADES) obtained from bio-based elements could further increase biocompatibility, lower environmental footprint, and assist a completely circular making model for carrageenan-related biopolymers. Table 2 compiles the studies performed to extract alginate, fucoidan, laminarin, and carrageenan from seaweeds, summarising critical process parameters, solvent systems (including DES formulations), and the corresponding extraction efficiencies reported across green extraction technologies.

4. Unlocking the full potential of DES in seaweed polysaccharide extraction - bridging the gap between alginates and other seaweed polysaccharides

This review has methodically delved into the transformative capabilities of DES as a sustainable, eco-friendly approach to polysaccharides extraction from seaweed, exhibiting their potential to deliver an efficient and sustainable substitute to solvent extraction methods. DES, prepared using HBA and HBD, focuses on unique physicochemical attributes, covering tunable viscosity, high polarity, and increased solubility, which confirm them as best suited for breaking the tough cell structure of seaweed. In addition to summarising past studies, Table 3 provides guidance on choosing DES combinations for the extraction of seaweed polysaccharides according to definite objectives. The recommendations presented in Table 3 are based on insights acquired from the interactions of DES with polysaccharide functional groups, as understood during the preparation of this review.

Further, DES's potential to specifically dissolve polysaccharides using safe, less-energy processes is associated with the assumptions of green chemistry. Fig. 3 illustrates the basic factors influencing the extraction of seaweed polysaccharides using DES.

The alginate extraction, a substantial polysaccharide present in brown seaweeds, has been exceptionally aided by DES application for extraction owing to particular connections that DES solvents develop among the ionic bonds of seaweed alginate molecules. As alginate entails units of guluronic acid and mannuronic acid associated with calcium ions, DES design, chiefly choline chloride-associated mixtures, can competently disrupt these ionic relations, although conserving the molecular veracity of polysaccharide, resulting in significant purity and yield (Saravana, Cho, et al., 2018). Additionally, merging DES with emerging extraction technologies such as UAE and MAE encourages sustainable green chemistry initiatives through reducing the necessity for high temperatures or harsh chemicals, ultimately improving extraction effectiveness and decreasing the specific energy requirement. These non-thermal technologies lower the time of extraction while increasing the DES solubilization to the seaweed cellular matrix, leading to enhanced alginate recovery along with other polysaccharides through insignificant deprivation or adulteration from undesirable compounds.

Though the alginates extraction has achieved important attention owing to their marketable reputation and structural characteristics, other prominent polysaccharides discussed in this review, namely fucoidan, laminarin, and carrageenan, continue to be under-explored, in spite of their increasing demand in industries such as food, nutraceuticals, biotechnology, and pharmaceutical sectors. The challenge resides in the structural intricacy of the mentioned polysaccharides: fucoidan encompasses exceedingly branched structures comprising sulphate ester clusters, laminarin is made of glucan, which needs to be solubilised with cautious hydrogen-bond associations, and carrageenan is another sulphate galactan that depends on complex hydrogen bonding and ionic links (Cunha & Grenha, 2016; Li et al., 2008). These structural challenges obscure the extraction step, making it complicated to distinctly

Table 2
Summary of recent studies on the extraction of seaweed-derived polysaccharides using deep eutectic solvents (DES) combined with advanced extraction technologies.

Targeted polysaccharide	Seaweed species	DES composition (HBA: HBD)	Extraction technology	Salient findings	Reference
Alginate	*Ascophyllum nodosum*	ChCl: Urea (1:2)	Conventional	Alginate yield: 74% (DES) vs 10–24.5% (conventional alkali)	Hiemstra et al. (2024)
Alginate	*Ascophyllum nodosum*	ChCl-based DES	Ethanol, $CaCl_2$, acid precipitation	Alginate yield: Ethanol: 51.2 ± 1.3%, $CaCl_2$: 45.7 ± 1.2%, Acid: 9.6 ± 1.3%	(Reynaga-Navarro et al., 2024)
Alginate & Fucoidan	*Laminaria japonica*	ChCl: Glycerol (1:2)	Subcritical Water Extraction	Alginate yield with DES was 28.1% higher than that of HCl extraction	(Saravana, Cho, et al., 2018)
Alginate	*Sargassum horneri*	ChCl:1, 2-Propanediol (1:2)	Ultrasound-Assisted Extraction	DES extracted alginate yield was 11.31% (*w/w*) with higher purity, lower protein/mineral contamination	(Nie et al., 2020)
Alginate & Fucoidan	*Ascophyllum nodosum*	ChCl: Glycerol	Microwave- Assisted Extraction	Alginate yield: 46.2%, Purity: 33.43%	(James et al., 2024)
Alginate	*Fucus vesiculosus*	ChCl:1, 4-Butanediol (1:5)	Microwave-Assisted Extraction	Alginate yield: 116.33 mg/g at 168 °C, 32% water	(Wu et al., 2021)
Alginate	*Ganoderma lucidum* (non-seaweed)	o-Cresol: Ethanolamine	Thermal Reuse Study	Maintained extraction over 5 cycles, showing reusability	(Cai et al., 2020)
Fucoidan	*Sargassum* species	ChCl: Glycerol	Ultrasound-Assisted Extraction (UAE)	Fucoidan yield: 0.4103 ± 0.0042 g/g dry basis	(Guerrero-Higareda & Carrillo-Nieves, 2025)
Fucoidan	*Saccharina latissima*	Water-rich DES	UAE + MAE (Ultrasound + Microwave)	Single-step green extraction; enhanced selectivity	(Zeb, Gerhardt, Johannesen, Underhaug, & Jordheim, 2024)
Fucoidan	General (Multiple species)	ChCl + various HBDs	UAE/MAE	Enhanced yield & bioactivity	(Kyriakoudi et al., 2024)
Laminarin	*Kelp* (brown algae)	DES-modified MIPs & ILs	Solid Phase Extraction (SPE)	Extraction efficiency: 87.6%	(Li et al., 2019)
Carrageenan	*Kappaphycus alvarezii*	ChCl: Urea, ChCl: Glycerol, ChCl: Ethylene Glycol	Conventional Extraction	ChCl: Urea gave the best extraction efficiency	(Das et al., 2016)
Carrageenan	Not specified	Various DESs	Composite Formation	DES enhanced the flexibility & mechanical strength of bio-composites	(Ramli et al., 2024)

Table 3
Recommendation on selecting DES combinations for the extraction of seaweed polysaccharides based on insights acquired from the DES interaction with polysaccharides, as understood during the organisation of this review.

Polysaccharide	Effective DES combination(s)	Recommended focus/notes
Alginate	ChCl:Urea (1:2)	Excellent for solubilization; however, it may restrict precipitation. Apply if a moderate yield with the highest polymer relations is required
	ChCl:Glycerol (1:2)	Best for significant yield and competent precipitation, appropriate when high recovery is significant
	ChCl:1, 2-Propanediol (1:2)	Deliver moderate yield but greater purity; supreme when extract purity is more important than extract yield
	ChCl:1, 4-Butanediol (1:5)	Suitable for speedy extraction and better polymer diffusion
	o-Cresol: Ethanolamine	Best when stable polysaccharide recovery is required
Fucoidan	ChCl:Glycerol (1:2)	Competent for high yield and efficient extraction.
	Other ChCl-based DES (urea, acetate, ethylene glycol, propyleneglycol)	Lower yield, but can be used when mild extraction conditions or selective solubilization are desired
Laminarin	VBTAC +4-vinylbenzoic acid	Excellent when high purity and selectivity are significant; suitable for targeted extraction
	ChCl:Urea	Applicable when a significant yield and moderate purity are of target
Carrageenan	ChCl:Urea	Suitable when a high extraction yield is needed
	ChCl:Lactic acid	Suitable for post-processing and film applications
	ChCl:Glycerol	Moderate yield; develops mechanical properties of films; appropriate when functional properties are emphasised

separate these polysaccharides without a detrimental effect on their structural stability. Nonetheless, the green chemistry perspective of DES in overcoming these tasks is enormous. Latest research investigations have established that tailoring the DES composition, altering HBD and HBA components, can augment this polysaccharide extraction through disintegrating precise hydrogen or ionic bonds that alleviate their structure in the seaweed matrix (de Souza Mesquita, 2024). Fig. 4 provides a schematic illustration of DES-mediated extraction of seaweed polysaccharides, highlighting solvent design, targeted seaweed polysaccharides, key interaction mechanisms and challenges associated with the extraction of algal polysaccharides.

While ChCl has been the main HBA explored for DES-related extractions, alternative HBAs such as betaine, choline acetate, and proline could provide improved extraction efficiency. Moreover, research has principally focused on binary DES formulations; however, ternary DES systems could enhance selectivity and solubilization of seaweed polysaccharides. When considering sulphated polysaccharides, DES containing metal ions could aid chelation interactions with sulphate groups, possibly enhancing recovery yields and providing structural integrity (Al-Akayleh et al., 2025). Likewise, merging DES with non-thermal technologies presents a convincing solution to maximise recovery yields, increasing purity, and reducing the extraction of detrimental co-products completely, while lowering ecological influence (James et al., 2024). Forthcoming studies should focus on modified DES designs to improve the extraction of fucoidan, laminarin, carrageenan, and other polysaccharides from seaweeds. Additionally, optimising process parameters of extraction, such as time, temperature, molar ratio of DES and solvent-to-feed ratios, will be necessary to obtain great yields of these polysaccharides whilst sustaining their bioactivity. The expandability and sustainability of DES for commercial applications could also be adopted to warrant the environmental application of these solvents. Through harnessing the complete possibility of DES and advanced extraction technologies, it is conceivable to generate more sustainable, green progressions for polysaccharide retrieval from seaweeds, meaningfully decreasing the ecological footprint of conventional extraction methods. Eventually, linking the gap in research among alginate as well as other seaweed polysaccharides via the incorporation of green chemistry values can reveal innovative and competent approaches for polysaccharide extraction, driving novelty in both industrial and research applications.

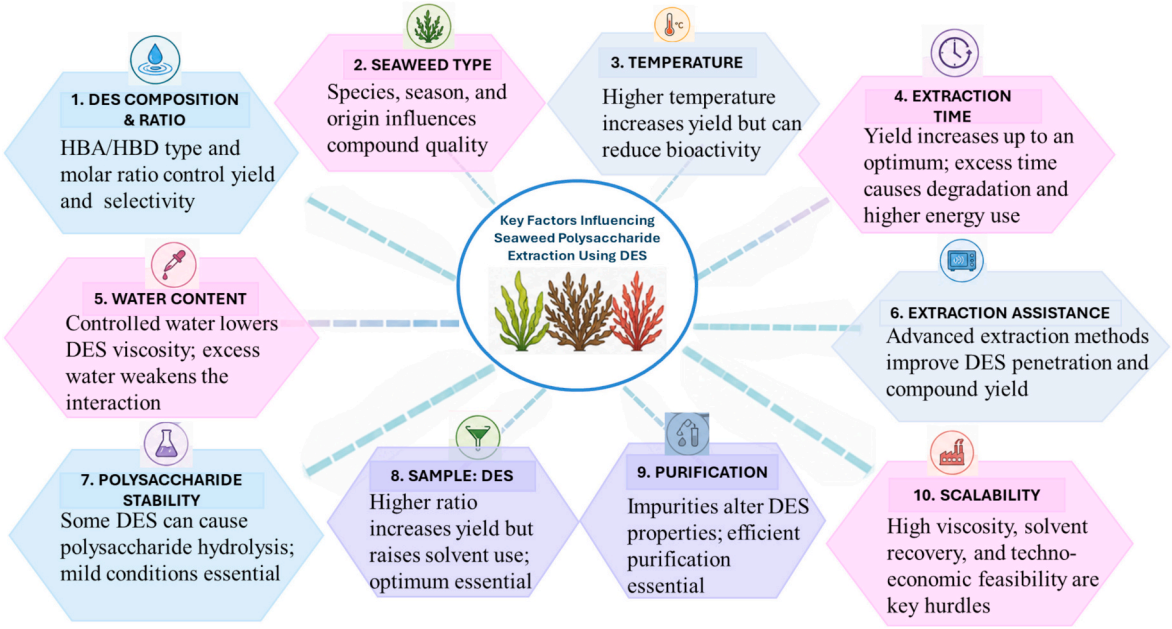


Fig. 3. Key factors influencing the extraction of seaweed polysaccharides using deep eutectic solvents.

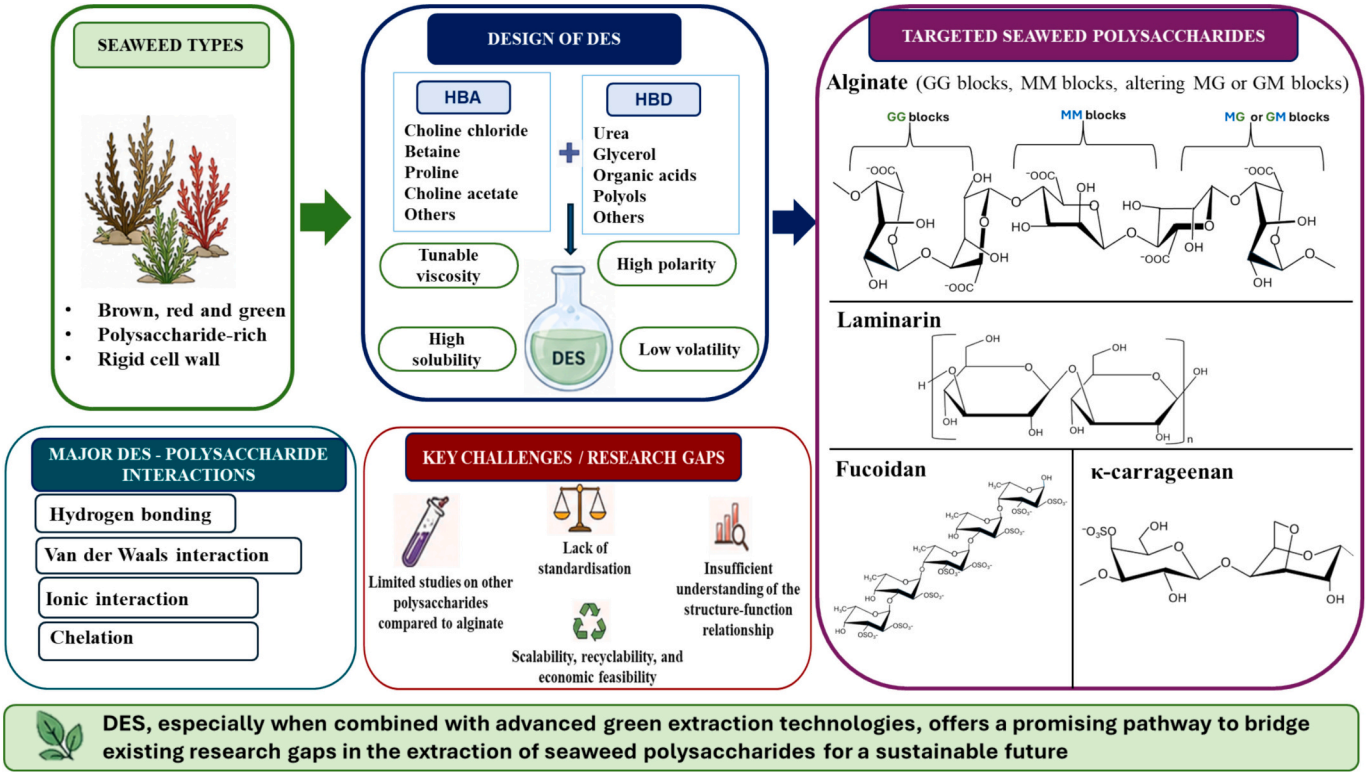


Fig. 4. Overview of DES-driven extraction of seaweed polysaccharides, illustrating solvent design, targeted seaweed polysaccharides, major interaction mechanisms, and challenges associated with the extraction of algal polysaccharides. The chemical structures of alginate, laminarin, fucoidan and κ-carrageenan were redrawn from (Abka-Khajouei et al., 2022); (Pradhan & Ki, 2025); (Ale & Meyer, 2013); (Campo, Kawano, da Silva Jr, B., & Carvalho, 2009), respectively.

5. Conclusions, challenges and future perspective

The application of DES in polysaccharide separation and isolation from seaweeds advances a stimulating transformation towards better sustainable alternatives to conventional solvent methods. After investigating an extensive selection of research studies, it is evident that DES depicts distinctive benefits for recovering not only alginate but also other seaweed polysaccharides, such as fucoidan, laminarin, and carrageenan. Conversely, while considerable developments have been completed, challenges endure in maximising the extraction steps for several polysaccharides. Interestingly, amid the varied DES mixtures studied, choline chloride-design systems appeared as the most effective for the extraction of polysaccharides, especially in the case of alginate separation. The mixture of choline chloride-urea has greatly explained significant extraction yields and insignificant polysaccharide degradation. After the relative evaluation of carried out research studies, it can be understood that ChCl:Glycerol and ChCl:Urea, prove to be the best extensively investigated and efficient DES systems for the extraction of seaweed polysaccharides. ChCl:Glycerol steadily validates higher extraction performance, resulting in enhanced recovery rates and considerable precipitation across numerous polysaccharides owing to its stable hydrogen-bonding ability, modest viscosity, and various hydroxyl attributes. On the contrary, ChCl:Urea displays robust solubilization power owing to its elevated basicity value, making it valuable when improved polysaccharide-DES interactions are needed. Therefore, ChCl: Glycerol can be considered as the favoured DES for reaching significant extraction yields, whilst ChCl:Urea, continues to be important for selected or structure-conserving isolations. Furthermore, decreased harmfulness, biodegradability, and adjustable properties of choline chloride-based DES enhance its suitability as a robust candidate for expanding to industrial scales without compromising ecological sustainability.

Despite the mounting interest in DES as a sustainable extraction medium for seaweed polysaccharides, numerous critical challenges persist that may control their broader industrial use. One of the most commonly stated constraints is the naturally elevated viscosity of DES systems, which substantially limits mass transfer and solvent diffusion into the dense and extremely cross-linked seaweed matrix. This lowered mobility confines the availability of solvent molecules to intracellular polysaccharides, often resulting in lower extraction yields and prolonged processing times (Dai, Van Spronsen, Witkamp, Verpoorte, & Choi, 2013b; Smith, Abbott, & Ryder, 2014). To mitigate this, the integration of water to produce hydrated DES has been extensively investigated, as it efficiently lowers viscosity, augments diffusivity, and upgrades extraction kinetics (Dai et al., 2015). However, excessive water content can interrupt the hydrogen-bonding network of DES, leading to weakened solvent-polysaccharide interactions and decreased selectivity, thereby demanding cautious optimisation of hydration levels (Van Osch et al., 2019). A second major challenge is the dependence on enormous volumes of anti-solvents, for instance, ethanol or water, for the isolation and precipitation of extracted polysaccharides. While DES accelerate competent solubilization, the downstream separation phase continues to be resource-intensive, increasing both operational rates and consumption of solvent (Bubalo, Ćurko, Tomašević, Ganić, & Redovniković, 2016; Smith et al., 2014). This necessity can also negotiate the overall process sustainability, specifically when solvent recovery and recycling are not implemented efficiently. Thirdly, the chemical nature of certain DES mixtures causes a risk to the structural arrangement of isolated polysaccharides. DES systems combining acidic or basic hydrogen bond donors may induce partial hydrolysis, depolymerisation, or desulphation of sensitive polysaccharides such as fucoidan and carrageenan (Li, Shi, Chen, & Liu, 2024). These structural variations can substantially alter functional group composition, molecular weight distribution, and eventually lower biological activity, which is remarkably important for applications in food, nutraceuticals, and pharmaceuticals.

Another notable limitation is the co-extraction of undesired

molecules, including proteins, pigments, polyphenols, and minerals (Cunha & Fernandes, 2018; Paiva et al., 2014). Even if DESs are often labelled as selective solvents, their robust solvation capability can lead to the concurrent extraction of various molecules, thereby complicating purification stages and affecting the purity of the target polysaccharide. This imposes further downstream processing, which can offset the economic and environmental advantages of DES-assisted extraction. Likewise, the recyclability and reusability of DES persist in confronting the scale. While DES are hypothetically recyclable, continual usage may outcome in accumulation of impurities, fluctuations in physicochemical properties and lowered extraction efficiency over time (Smith et al., 2014). The regeneration of DES often needs energy-consuming purification steps, such as filtration, evaporation, or adsorption, which can fade their overall sustainability profile. Scalability is another important concern that confines the conversion of DES-based extraction from laboratory to industrial scale. Challenges such as managing extremely viscous fluids, guaranteeing constant mixing, sustaining steady mass transfer, and incorporating DES systems into existing industrial infrastructure present significant engineering hurdles. Furthermore, techno-economic assessments of DES-based processes are still limited, making it difficult to assess their commercial possibility compared to established extraction technologies. In addition, the environmental impact of DES, although generally considered lower than that of conventional solvents, is not yet fully understood. While many DES components are biodegradable and derived from generally recognised as safe (GRAS) materials, the environmental fate, toxicity under long-term exposure, and the impact of large-scale disposal require further investigation (Radošević et al., 2015). This is remarkably influential when considering industrial uses where solvent losses and emissions may occur. Overall, while DES offer a promising green alternative for the extraction of seaweed polysaccharides, tackling these interconnected tasks, including viscosity limitations, hydration effects, anti-solvent dependency, structural stability of polysaccharides, co-extraction issues, recyclability constraints, and scalability barriers, is essential for their successful implementation in sustainable biorefinery systems.

Yet, when studying the polysaccharides isolation except alginates, it is obvious that a one-size-fits-all methodology does not work. Other polysaccharides present in algae, owing to their varied molecular arrangements, demand several solvent molar ratios to increase extraction efficiency. Regarding enhancing the current research findings, numerous areas warrant future consideration. First, when the seaweed alginates have been widely researched, other polysaccharides, unfortunately, have not obtained equal attention despite their increasing commercial requirement. There exists a persistent need for further comprehensive research studies into optimising DES designs for selective separation of seaweed fucoidan, laminarin, carrageenan, agar, cellulose and so forth, mainly by discovering by what means differences in the molar ratio of HBD-HBA affect the competence of polysaccharide retrieval. In addition, examining the synergistic influence of DES with emerging thermal and non-thermal methods could advance extraction efficiency with a lesser environmental footprint. Lastly, while DES shows a confirming potential for novel extraction methods, escalating these methods continues to be a challenge. The DES reusability, solvent retrieval, and the implementation of scalable extraction approaches must be directed to safeguard that this expertise is not only valuable but reasonably sustainable for large-scale industrial uses. Further, this review delivers that the prospect of seaweed polysaccharides lies in the amalgamation of DES as an adaptable, green solvent platform. With precise adaptation of DES solvents accompanied by an attentive effort on tackling the tasks of other polysaccharides apart from alginates, DES possess robust potential to transfigure polysaccharide extraction, depicting it as highly efficient, cost-effective, and sustainable for the future.

CRediT authorship contribution statement

Rifna E. Jerome: Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Conceptualization. **Nilushni Sivapragasam:** Writing – review & editing, Validation, Formal analysis, Conceptualization. **Vijai K. Gupta:** Writing – review & editing. **Brijesh K. Tiwari:** Writing – review & editing, Formal analysis. **Gaurav Rajauria:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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