GREEN CHEMISTRY TO VALORIZE SEAFOOD SIDE STREAMS: AN ECO-FRIENDLY ROADMAP TOWARDS SUSTAINABILITY

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Abstract

A major challenge facing sustainable seafood production is the voluminous amounts of nutrients-rich seafood side streams consisting of by-catch, processing discards and process effluents. There is a lack of a comprehensive model for optimal valorisation of the side streams. Upcoming green chemistry-based processing has potential to recover diverse valuable compounds from seafood side chains in an eco-friendly manner. Microbial and enzymatic bioconversions form major green processes capable of releasing biomolecules from seafood matrices under mild conditions. Novel green solvents, because of their low toxicity and recyclable nature, can extract the bioactive compounds. Non-thermal technologies such as ultrasound, supercritical fluid as well as membrane filtration can complement green extractions. The extracted proteins, bioactive peptides, polyunsaturated fatty acids, chitin, chitosan, and others function as nutraceuticals, food supplements, additives, and others in diverse industries. Green processing can also encourage bio-energy production. Multiple green processes integrated in a marine biorefinery can optimize valorisation on a zero-waste trade-off, encouraging a circular blue economy. The technology can address environmental, economic, and technological challenges of valorisation of seafood side streams thereby supporting sustainable seafood production .Green chemistry-based valorisation framework has potentials to meet the Sustainable Development Goals (SDGs) of the United Nations.

Keywords:

Seafood side streams, Green chemistry, Marine biorefinery, Valorisation, Seafood sustainability

1.0. Introduction

Commercial fishing activities and aquaculture provide a wide variety of finfish and shellfish. The finfish include herring, cod, anchovy, mullet, mackerel, salmon, tuna and others, while the shellfish includes crustaceans (shrimp, prawn, krill, crab, and lobster), bivalves (mussel, oyster, clam, and scallop), cephalopods (squid, octopus, and cuttlefish), and gastropods (abalone and snail). In the year 2020, global fisheries and aquaculture production reached a value of 214 million tons (MT), aquaculture alone producing 122.6 MT in 2020 (1). Fishery products including both finfish and shellfish provide consumers a rich and diverse array of nutrients including proteins, unsaturated lipids, carotenoids, micronutrients including vitamins A, D, and B, and minerals such as iodine, zinc, calcium, phosphorus, iron, and selenium (2, 3).

2.0. Loss and wastage of seafood

Food loss and wastage (FLW) occur throughout the food value chain including seafood. The annual loss of world fisheries is around 30%, of seafood production essentially due to the generation of significant amounts of ‘seafood side streams’, which include fishery by-catch, process discards and process effluents (1). The by-catch, consisting of undersized, damaged as well as commercial seafood caught in low amounts, is essentially due to destructive fishing practices. By-catch, because of its poor commercial value, is often dumped in the ocean, causing reduced oxygen levels at the ocean bottom leading to burial or smothering of living organisms, damaging marine ecosystem (4). A large portion of high value seafood is discarded as side streams during centralized pre-processing operations. These are generated during operations such as beheading, removal of fins, filleting, de-shelling, scaling, meat/bone separation, and washing. These side streams range from 20 to 80% of raw material, depending upon the fish/shellfish species and nature of processing. Finfish discards comprise of heads, liver, dark muscle, belly flaps, skeletal frames, backbones, skin, scales and viscera, roe and others, constituting up to 25-60% of the total raw material wet weight (5). Processing of crustaceans such as shrimp and lobster generate about 60 to 70% of the raw material as discards, which consist of heads, shells, livers and eggs (6-8). Currently, portions of the side streams find uses as raw material for fish meal, oil, ensilage, fertilizer, animal feed, etc. for use in agriculture and animal husbandry. Discarding of the seafood side streams is responsible for heavy nutritional loss, besides serious environmental and heavy financial costs. In the United States, about 47% of the seafood supply including bycatch was unavailable to consumers during the 2009 -2013 period. This amounted to a loss of about 208 billion g of proteins and 1.8 billion g of long chain omega-3 polyunsaturated fatty acids (PUFAs), particularly eicosapentaenoic acid (EPA), and docosahexaenoic acid, (DHA) (9). Seafood processing also generates voluminous amounts of effluents, which is another major reason for nutrient loss and environmental pollution. The effluents are characterized by high levels of total suspended solids (TSS) as a result of suspended myofibrillar proteins, collagen, gelatine, pigments, enzymes, soluble peptides and amino acids, as well as FOG (fats, oils, and grease). The TSS and FOG values are responsible for high biological oxygen demand (BOD) and chemical oxygen demand (COD) indices of the effluents, which indicate adverse oxygen balance favoring microbial growth. Such adverse environmental factors are particularly associated with discharges from fishmeal factories. Harvesting and processing vast quantities of fish also leads to the production of byproducts, further creating disposal challenges (10).

2.1. Compositional nature of seafood side streams

The solid discards, on a dry weight basis, contain as high as 60% proteins (including myosin and collagen, gelatine, enzymes, bioactive peptides, essential amino acids), 7 to 19% fat (rich in omega-3 PUFA), and up to 30% ash, composed of calcium, phosphorus, sodium and magnesium and other minerals. They are also sources of chitin, chitosan, glycosaminoglycans, and others (8, 11). Shellfish side streams contain up to 65% proteins, 21% ash, 15 to 20% chitin, besides small amounts of lipids and carotenoids (7). Crab discards, depending on the species, have 72, 34, and 28.5% of moisture, protein and ash contents, respectively (12). Dry crab shell, lobster shell and squid skeletal pen have chitin contents ranging from 67 to 72, 70 and 41%, respectively (13). The proteins present in seafood side streams have good bioactivities and functional properties. The proteins are sources of bioactive peptides having anticoagulant, anticancer and hypo-cholesterolemic and other activities (11, 14). Fish oils are excellent sources of omega-3 PUFA, having interesting therapeutic properties (3). Figure 1 shows the food waste recovery hierarchical pyramid and strategies to prevent food waste.

3.0. Sustainable seafood production

Sustainable production is defined as the process in which the exploitation of natural resources, the allocation of investments, the process of technological development, and organization changes are in harmony with each other for the current and future generations (15). Sustainability, in general, dwells on three pillars, namely, (i) renewable resources should not be exploited at a rate higher than their regeneration levels, (ii) non-renewable resources should not be depleted at rates higher than the development rate of renewable substitutes, and, (iii) the absorption and regeneration capacity of the natural environment should not be exceeded (15). Reducing food loss and waste is a major effort for sustainability (16) (Figure 1).

Sustainable seafood production is facing challenges due to a variety of problems, which include global warming, acidification, excessive and destructive fishing, destruction of coral reefs, pollution and others. These are causing particular concerns especially when global demand for seafood is rising due to population rise as well as increasing awareness on the nutritional value of fishery products. It has been recognized that by 2050, global food production including seafood availability need to increase roughly by 50%, when the population is expected to cross 9 billion (17). Potential demand for food from the sea in the year 2050 is projected to be about 103 MT (18). Currently, 90% of fish stocks are exploited at maximum sustainable levels (1). Availability of seafood is showing decreasing trends due to problems mentioned above. An example is the intense heat wave during 2018 to 2019 that crashed the crab industry worth US $ 200 million (19). Against this situation, the available seafood is not fully utilized for human consumption, essentially due to heavy loss and wastage in the commodity. The nutritional and environmental consequences of rising demand will depend on making better use of available resources. There is a need for responsible and equitable use of marine resources through sustainable manner to address challenges regarding the environment, climate change, economic limitations, and resource efficiency with respect to marine products (20)

The United Nations 2030 Agenda for Sustainable Development consists of 17 Sustainable Development Goals (SDGs) (21). The Agenda recognizes that the natural world must be urgently protected to fulfil the needs of 9.8 billion people by 2050. The SDG 12 aims at ensuring sustainable consumption and production patterns. The SDG 12.3 aims halving global food waste by 2030 at the retail and consumer levels, as well as the reduction of food loss along production and supply chains, including post-harvest losses. The SDG 12.5 aims at substantial reduction of waste generation through prevention reduction, recycling and reuse by the year 2030. Food waste valorisation involves management strategies by seafood processors to exploit food side streams for producing compounds that can command a high market value.

There is an urgent need to make the seafood system resilient to make competent to provide food and nutrition security in a way that does not deprive future generations of their benefits. The SDG 14 aims protection of life below water (21). This requires a robust oceanic health through a blue transformation of aquatic supply chains. This could be achieved by science based policies and new technologies for both wild caught and aquacultured seafood. This demands total utilization of available seafood resources including high-potential waste, which can support seafood sustainability. Such solutions also address major challenges like climate change, disaster risk reduction, food and water security, biodiversity loss and human health.

The demand for a healthy ocean has encouraged interests in ‘blue economy’, defined as sustainable productive, service, and all other related activities using and protecting marine and coastal resources (21).

There are other international efforts also to protect health of the oceans. These include ‘The Ocean Decade of the UN to deliver science-based solutions to achieve the 2030 Agenda (https://oceandecade.org/ (accessed March 5, 2023), and the World Economic Forum (WEF) presents an action-oriented roadmap for estimated benefits in terms of reduced food waste, water usage, lower greenhouse gas (GHG) emissions and increased productivity to promote sustainability, inclusivity, nutrition, and health It has been anticipated that transforming the world’s food systems could generate $1.0 trillion in economic return and help to create a net-zero, nature-positive world, while also ensuring social justice and food security (22; https://oceandecade.org/ accessed March 5, 2023), Other international efforts include the ‘Nature 2030’of the International Union for Conservation of Nature (IUCN) (https://www.iucn.org/nature-2030, accessed Septemner 12, 2023), the Future of Sustainable fisheries of the World Wildlife Fund (WWF) (https://seafoodsustainability.org/, accessed September 12, 2023), and the Ocean Panel (https://oceanpanel.org/), accessed September 12, 2023). The large amount of seafood side streams need to be profitably utilized through effective eco-friendly strategies to support sustainability and food security (11, 23). Recent challenges in finding value to seafood processing discards are demanding sustainable options for their utilization. This article examines the advantages of green chemistry based transformation of seafood side streams to improve seafood sustainability.

4.0. Green chemistry to valorise seafood side streams

4.1. Principles of green chemistry

Green chemistry (also known as sustainable chemistry) emerged in the 1990s as an environmentally benign alternative to conventional valorisation methods. It aims at design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal (24, 25). It is defined as ‘a scientific concept that seeks to improve the efficiency with which natural resources are used to meet human needs for chemical products and services’ (26). Recently, sustainable chemistry has evolved as a closely related, yet more holistic approach. Its concept includes design and use of benign chemicals, development and use of alternative solutions for problematic applications, reduction of impacts, conservation of natural resources, promotion of reuse and recycling, increase of market opportunities and application of corporate social responsibility (27). The Framework Manual of the UNEP introduces various facets of green and sustainable chemistry. The framework seeks to promote chemistry innovation that is compatible with and supports the implementation of the 2030 Sustainable Development Agenda of the United Nations (21, 24). The twelve objectives of green and sustainable chemistry encompass minimizing chemical hazards, sustainable sourcing of resources and feed stocks, advancing sustainability of products, enabling non-toxic circularity, advancing circularity of production processes, avoiding regrettable substitutions and alternatives, minimizing chemical releases, and maximizing social benefits and protecting consumers and vulnerable populations developing solutions for sustainability challenges (28). Green extraction is a major practice in green chemistry to protect both the environment and consumers. Green extraction deals with the use of alternative solvents, reduction of unit operations as well as energy, production of co-products, and development of materials without loss of their functionality (29). Green and sustainable chemistry innovation can play an important role in advancing a circular economy. It stimulates design of molecules, materials and products that can be more easily recycled and up-cycled than those currently on the market. Innovative green technologies to tackle food loss in the supply chain are a vibrant field with large potential (16). Green process engineering based on green chemistry tools, ideally through a biorefinery, provides a sustainable route for the recovery of valuable products from waste biomass (30).

4.2. Advantages of green processing of seafood side streams

Green processing has several advantages over conventional processes for valorisation of seafood side streams. In conventional processes, neutralizations of hydrochloric acid (HCl) and alkali (NaOH) have a high insidious impact on the environment. Other disadvantages are high energy consumption as well as possible thermal degradation of target compounds. During hydrolysis of proteins, the amino acids bound to polypeptide bonds are likely to undergo racemisation. Amino acids such as tryptophan, cysteine, tyrosine, serine, and threonine may also undergo partial or complete destruction. Conventionally, chitin is extracted from crustacean shells by initial demineralization with strong HCl followed by removal of protein by NaOH extraction. These may affect molecular size of the biopolymer. Traditionally fish oil is extracted by wet reduction involving cooking, pressing and filtration. The extracted oil is refined by carbon treatment, degumming, and alkali refining. The process can cause oxidation of unsaturated fatty acids and hence loss of their functionality. Furthermore, conventional processes require vessels which are resistant to acids and alkali, which increases treatment costs. The limitations of conventional chemical processing on components of seafood side streams are shown in Table 1.

Innovative green processing, on the other hand, has high potentials for safe transformation of seafood side streams through extraction of novel products at higher efficiencies and possibly at lower costs, protecting the environment and therefore satisfying a green economy, which require optimization of intervention strategies (31, 32). The biotransformation of food discards is generally on a zero-waste strategy and the recovered products can retain their functionality and therefore can have multiple uses. (33). Therefore, suitable bio-transformations of global biomass have potentials to satisfy a green economy (34, 35). The choice of the green process and the extent of product recovery are dependent on the nature and type of raw material, food matrices, the chemistry of the targeted compounds and environmental and economic challenges (**24**, 36, 37). The multiple uses of the extracted ingredients in agriculture, health, and other industries enhance the value of the seafood materials (38, 39).Table 2 gives advantages of green chemistry-based technologies.over traditional methods

Eco-friendly extraction is the salient feature of green chemistry based processing of seafood side streams, which involve initial bioconversions of components present in seafood side chains. The bioconversions make use of microbial fermentations, ideally with appropriate microbial strains and/or enzymatic processes. Eco-friendly non-thermal processes can enhance bioconversion and extractability of compounds. The released components are recovered by downstream processing, making use of the principles of biotechnology (39, 40).

4.3. Microbial bioconversions

Microbial biotechnology offers 'green' innovations, to improve sustainability and resilience of agri-food systems while meeting the needs of future generations (41). The microbe-mediated bioconversion, generally termed as fermentation, is an efficient low-cost green process for bio-refining of food side streams including seafood resources. Fermentation, which results in modification and release components attached to food matrices, can be of different types, namely, solid state, submerged or liquid state, anaerobic, batch, continuous, or fed batch. Fermentation employs aerobic, anaerobic, or facultative microorganisms including bacteria, fungi, microalgae and protozoa to degrade organic matter. The process is safe, environmental, and energy-friendly. Its efficiency is influenced by the nature of the starter culture, time, pH, and substrate composition (42). A robust microbial strain is critical in the fermentation process. Lactic acid bacteria (LAB) are popularly used in fermentation systems. Lactic acid (LA) is the most predominant industrial product obtained from LAB. LAB fermentations may be performed in solid (SSF) or in the fed-batch mode. SSF has good scope for the synthesis of microbial products such as food, feed, enzymes, fuel, industrial chemicals, and pharmaceutical products.

Some of the advantages of SSF are low sterility requirement, less water demand and high volume production. The advantages of SSF over conventional submerged fermentations could push the technology towards a future bioeconomy (43). Lactic acid (LA) bacteria are used to produce a wide variety of chemicals of high commercial interests. These organisms are used to produce a wide variety of chemicals of high commercial interest such as bacteriocins, lipoteichoic acid, and probiotics. Hence, the creation of new ways to revalorize LA production processes is of high interest and could further enhance economic value of the process (44). The fed-batch fermentation targets isolation of microbial biomass, organic acids (mainly lactic acid), ethanol, bioactive peptides, organic acids, antibiotics, vitamins, enzymes, and other compounds (45). Since the 1980s biomass fermentation has emerged in the food industry for the production of cell mass for further use as sources of enzymes, flavours, food, biomaterials, therapeutics, fuels and in recent times, as sources of alternative proteins to develop cultivated seafood formulations (46). Precision fermentation is intended to produce specific functional ingredients using tailor-made microbial hosts. The global fermentation industry focused on animal-free alternatives to conventional proteins. Scientific advances, new products and prototypes, manufacturing facilities, and partnerships brought the world more meat, seafood, eggs, and dairy made via microorganisms—a nature-inspired technology primed to transform the future of food (47).

Fermentation, which is traditionally used to increase the shelf-life of fishery products, results into the formation of bacteria metabolites of interest. Fermentation of seafood by-products results in protein hydrolysates and production of oil and antioxidant compounds. Fermentation is safe, environmental-friendly and low energy consuming (48). Seaweed associated bacteria; namely, *Bacillus* spp., *Brevibacterium* spp. and *Vibrio* spp. degraded crustacean shells as well as fish scales in a seawater-based broth (49). Microorganisms can treat seafood industry process effluents in reaction systems such as activated sludge, aerobic lagoons, trickling filters, and rotating disc contactors. Anaerobic digestion (AD) has been identified as a potential green technology for treatment of high-strength industrial wastewaters including aquaculture and fishery wastes. Studies have indicated that AD of freshwater, brackish, and saline wastewater has shown promising results (10, 45).

Microalgae such as Chlorella spp., Spirulina spp., Dunaliella spp., diatoms, and cyanobacteria (commonly referred to as blue green algae), are promising agents for the bioconversion of biomass including seafood discards. These organisms can be grown in nutrient medium under appropriate phototrophic (light and CO_2) conditions. Algal cultivation can be in open ponds or in closed photo-bioreactors, or heterotrophically in closed systems. Heterotrophic cultivation in closed systems eliminates the requirement of light, but the culture can be prone to contamination by other microbial species (50). The algal biomass, ideally grown in medium supplemented with food discard biomass, is known as single cell proteins (SCP), which is a promising alternative to conventional food and feed. Enzymatically hydrolyzed fishery products can support growth of algae. The dried pellet of rainbow trout supported the growth of the red alga, Galdieria sulphuraria. No pathogens such as *Salmonella* sp. could be detected under the non-sterile conditions (51). The SCP contains high amounts of protein and oil, besides being a good source of polysaccharides, minerals, and pigments including chlorophylls, carotenoids, and phycobiliproteins. Stringent nitrogen limitations stimulate algae to synthesize lipids, as high as 75%, with high contents of n-3 PUFA (52). The ingredients from SCP can be extracted by suitable downstreFam green processes including enzyme, supercritical-fluid, microwave-assisted and pressurized-liquid-based extractions or by the novel impinging jet mixers. The proteins isolated from SCP can be used for food purposes, while the oil can be a PUFA-rich nutrient. It can also serve as raw material for biofuel. The extraction efficiency of nutrients from SCP can vary highly depending on the methods used and the target compounds (36, 53).

4.4. Enzyme-based bioconversions

Enzymatic processes have significant importance in food waste management. Enzymes, because of their specificity, catalytic properties and appreciable activities at moderate temperatures, could enhance reaction rates, offering reduction in process cost, time and energy. Compared to synthetic catalysts, enzymes have higher specificity and improved environmental sustainability in performing chemical transformations, Therefore, enzymatic bioconversions are favorable over chemical processes, and are promising and emerging field in green chemistry practice (54, 55). Seafood side streams can provide several enzymes such as proteases, lipases, chitinase, lipases, alkaline phosphatase, transglutaminase, hyaluronidase, acetyl glycosaminidase, among others. Enzymes from organisms from colder habitats such as fish and shellfish are particularly useful since they can function comparatively at lower temperatures thereby saving energy and protecting the food products. Recovery of these enzymes from various fishery sources serves additional benefit of waste disposal. Methodologies for isolation of enzymes from seafood side streams have been summarized (56). Hydrolases, which include proteases, carbohydrases, chitinases and lipases, are popular enzymes for bio-refining. Protease treatment can help preparation of protein hydrolysates, tenderization of fish meat and squid, extraction of flavourings from marine products, scaling of fish, removal of viscera from clam, ripening of salted fish, among others (56).Immobized enzymes can have different applications for transforming food components. These include hydrolysis of complex molecules, debittering, removal of allergens, flavour modification, and others (57). Valorisation of food processing waste streams using immobilized enzyme systems, particularly hydrolases, presents a unique technological approach to increase the environmental and economic sustainability of food production. For commercial applications, inexpensive carriers, carrier-free immobilized enzyme systems as well as multi-enzyme systems need to be explored (57).

4.5. Extractions by green solvents

'Green solvents' have received considerable attention and wide applications in different research fields, such as chemistry, biology, catalysis, energy, and environmental sciences. This is attributed to a growing awareness on the adverse impacts of conventional solvents on the environment, energy usage, air quality and climate change. Most prominent green or sustainable solvents include ionic liquids (ILs), deep eutectic solvents (FESs), switchable solvents, supercritical fluids and others (58). Ionic liquids (ILs) represent liquids that exist in only ionic form, fused salt, molten salt, liquids organic salt, and others. ILs possess a very low viscosity and vapor pressure or non-volatility under ambient conditions, thermal stability, and low corrosivity relative to mineral acids and bases. ILs can be recycled, recovered, and easily separated after use. A typical example of ILs is the ethyl ammonium nitrate (59, 60). Deep eutectic solvents (DESs) are nontoxic, recyclable and biodegradable. They share the solvent characteristics of ILs, such as thermal and chemical stability and low vapor pressure. The DES system is made up of essentially two, or occasionally more than two, components: a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). When HBD and HBA combine, they create a new eutectic phase whose melting point is lower than that of individual components, which are usually below 100 °C. Their renewability, low toxicity, biodegradability, and most significantly low cost make these solvents distinctive and viable sources for extraction of bioactive compounds. A classic example of DES is the eutectic mixture formed when choline chloride (ChCl) and urea having melting points of 302° and 133°C, respectively, are mixed in the ratio 1:2 at room temperature. Some of the other eutectic solvents are choline chloride–lactic acid (CCLA), choline chloride–malonic acid (CCMA), choline chloride–urea (CCUR), and choline chloride–citric acid (CCCA). DESs have been proposed as potential solvents to dissolve and extract valuable compounds such as proteins, lipids, and carbohydrates such as chitin from food discards. They can be used for waste water treatment. DESs are generally less expensive and easier to prepare (61, 62, 63).

Pressurized liquid extraction (PLE) is a promising green technology to extract various added-value compounds from marine biomass. Supercritical CO_2 extraction is based on the pressurization of water with CO_2, which has a moderate critical temperature and pressure (31.1° C and 7.4 MPa). It gives an acidic, hot, and pressurized environment to extract ingredients including lipids and pigments from seafood and plant side streams and also algae (58). The PLE technique at pressures typically 5 to 20MPa and at high temperatures as high as 200°C, allows appreciable extraction of intracellular compounds in a short time. Subcritical water (SCW) has attracted interest as a green solvent for waste and biomass conversion. SCW extraction uses water at 100−300 °C and pressure above saturation value but less than critical, just to maintain water as liquid. Pressurized extractions are highly beneficial to extract components from marine biomass and others, generated by bio-transformations. The technique dramatically reduces solvent consumption compared to conventional extraction processes (64). Table 3 indicates some potential green solvents for extraction of components from seafood side streams.

4.6. Non-thermal technologies

Eco-friendly non-thermal processes such as ultrasound, pulsed electric field, pulsed light, high pressure are recent technologies. These can be used either alone or in conjunction with bioconversion processes to enhance the efficiency of extraction processes. They have minimum effects on color, flavor and nutrients of the resources. Interests in non-thermal technologies are essentially due to their short duration of treatment and lower environmental impacts. Ultrasound-assisted extraction (UAE), pulsed electric field (PEF), high hydrostatic pressure (HHP) and membrane technology offer green techniques that can assist extraction. Microwaves are non-ionizing electromagnetic radiation with frequencies in the range of 300 MHz to 300 GHz. The use of short microwave pulses can reduce heat and benefit extraction. High-intensity ultrasounds have low frequency (20 kHz-100 kHz) and high power $>1 W/cm^2$ and are used for extraction purposes either in pulse or continuous mode. UAE allows the extraction of labile bioactive compounds without losing their functional quality and stability. The impact of ultrasound offers greater penetration of solvents into the sample matrix for better extraction of compounds. UAE has a great potential to recover products such as oil, polysaccharides, fatty acids, organic acids, proteins, lipids, and enzymes from food waste and can also assist production of bioenergy. UAE can be merged with other innovative methods such as SFE or vacuum-based or enzymatic extractions (65, 66, 67, 68). PEF involves applying an external electric field on living or non-living cells for a short duration of time, which results in the formation of pores on the cell membrane of the living cells. The electroporation process does not cause changes in the organoleptic and nutritional properties of the treated products (69). The advantages of microwave-assisted extraction (MAE), which is a thermal process over conventional thermal protein extraction, are uniform flow of heat, faster extraction rate, reduced solvent consumption, as well as short extraction time (70). With challenges in recovering intracellular bioactive compounds, these methodologies are being relooked continuously in the quest for sustainable production practice (66).

4.7. Isoelectric solubilization precipitation (ISP)

Isoelectric solubilization precipitation (ISP) is a technique valuable to recover proteins from protein-rich feedstock. The process involves homogenization of the protein-rich material with either dilute acid (pH 2.5 to 3.5) or alkali (pH 10.8 to 11.5). Raising the pH of the homogenate to their isoelectric pH of pH 5.2 to 6.0, results in precipitation of up to 90% of the dissolved proteins. The precipitated proteins are then concentrated by centrifugation or membrane filtration. The technique has been applied to recover proteins from several types of seafood discards including bycatch. In general, the ISP recovered proteins have good functionalities including gelation and textural properties and viscosities, whiteness and color. They also retain good nutritive value and digestibility (71).

4.8. Membrane processes

Membrane filtration has emerged as novel environment-friendly method to efficiently to concentrate, separate, or fractionate bioactive compounds from the downstream processing streams of the agro-food chains. Depending on the types of membranes used, the major membrane processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO). Membrane processes are cost-effective essentially due to their low energy requirement. They have potentials for commercial treatments of food process effluents and also seawater and groundwater. Membrane bioreactors integrate bioreactor vessel with a membrane separation unit for isolation of bioactive materials, which include peptides, chito-oligosaccharides and polyunsaturated fatty acids from seafood side streams (72).

The advantages of membrane technology, non-thermal processing methods, and enzyme-assisted methods are they are highly environmentally savvy. They can recover compounds, for example bioactive peptides from marine protein hydrolyzates, without loss of their functionality (45, 72). From an industrial perspective, the reusability of immobilized enzymes and membrane separation techniques offer viable, cost-effective. Nevertheless, further research is needed to overcome the challenges related to large-scale production of bioactive molecules (73).

5.0. Green extractions of ingredients of seafood side streams

5.1 Proteins

Protein is an essential nutrient for healthy living. The demand for protein is expected to increase due to several reasons. These include rise in global population, depletion of natural resources, climate change and delete (current) inefficiencies in current food systems. The situation demands development of healthy, sustainable, and innovative proteins from diverse and novel sources. Aquatic proteins, in comparison with plant sources, are nutritionally superior with a better balance of dietary essential amino acids. Currently, fish, crustaceans and molluscs provide only 17% of edible meat, globally. In 2018 fishery products contributed a total of 13, 950 Kt proteins (7,13Kt and 6,815 Kt contributed by capture fisheries and aquaculture, respectively). This amounted to15.3% of total animal proteins (74). There is good scope in using seafood side streams as substantial source of marine proteins (75, 76). There is interesting scope for the recovery of proteins from food discards to include them as an important component of food supply chains (77).

Proteins from diverse seafood side streams belonging to both finfish and shellfish have been recovered by the ISP process. The pH modulation associated with the process removes insoluble impurities such as bone, skin, oil, and membranes, separating the proteins (71). The separated proteins can be extracted by DES or ILs solvents, due to their unique physicochemical and solubilisation properties (59). The DES-based methods exhibit high efficiency in extracting proteins, and also amino acids, and enzymes without loss of functional properties. Non-thermal processes like microwave irradiation in conjunction with ISP and also DESs have potentials to enhance extraction of seafood proteins.

Some specific examples of uses of green solvents for protein recovery can be cited. The DES systems for protein extraction include choline chloride-glycerol, choline chloride-oxalic acid, choline chloride-urea ethanol (62, 79). Betaine/polyol-based deep eutectic systems extracted proteins from sardine biomass. The extracted proteins retained bioactive functions. Most DES extracts obtained at 80 °C surpassed the antioxidant and antimicrobial potential of water extracts, with an increase in activity of up to 3-fold and more than 250-fold, respectively (80). In another study, sequential fractionation of sardine discards was carried out using subcritical

CO_2 (SC-CO_2) and subcritical water (SCW). Initial removal of fat of the feedstock enhanced protein recovery and its purity (81). DES solvent composed of citric acid, xylitol and water at a molar ratio of 1:1:10 extracted type I collagen from blue shark fins having good biocompatibility. The green method required much lower extraction time, gave a yield 2.5 times higher than the conventional method (82). A greener approach for collagen extraction involving multiple processes including fermentation, high shear mechanical homogenisation, and non-thermal methods avoided use of chemicals and shortened processing time (83). Collagen type I from codfish skin was extracted by an aqueous DES solution containing urea and lactic acid in a 1: 2 molar ratio (84). An integrated process of UAE for 5 min at a pH of 13.0 in presence of 250 mg of chitosan as flocculant recovered up to 90% proteins from lobster heads (85). Pepsin isolated from rainbow trout stomach was used for collagen extraction from wasted yellowfin skin supported by ultrasound cavitation for 15 min, which recovered 24% collagen having highest imino acid content of 18%. The protein had superior functionality in acidic environments and lower salt concentrations, suggesting a green technology for collagen recovery (86). Several novel green technologies have been suggested for extraction of gelatin. These encompass ultrasound-assisted extraction (UAE), subcritical water extraction, high-pressure processing, and microwave-assisted extraction (MAE). These processes safeguard the environment as they reduce solvent usage and carbon footprint along the way (87). Hydrothermal pre-treatment at 159 °C for 2 min, followed by heating at 121 °C for a period of 70 min optimally extracted fish bone proteins (88). UF using food grade polysaccharides such as carrageenan, alginate and carboxy methylcellulose followed by dewatering by filtration, sedimentation and centrifugation recovered up to 77 to 80% proteins from shrimp boiling waters (89). Membrane processes such as UF have been successful in recovering functionally active proteins from cuttlefish waste water, shrimp shell wastewater, snow crab cooking effluents, surimi wash water and. pre-salting brine used for marination of herring (72).

Development of animal/plant-based protein hydrolysates and their application in food, feed and nutraceutical industries have been discussed (90). Fish proteins, protein hydrolysates and bioactive peptides offer opportunities as nutraceuticals, fortificants, and texturizers in food and pharmaceutical industries. They can also function as milk replacers, bakery substitutes, soups, and infant formulas. Marine bioactive peptides function as antimicrobial, antiviral, antitumor, antioxidant, antihypertensive, cardio-protective, anti-amnesiac, immune modulatory, analgesic, anti-diabetic, anti-aging, appetite-suppressing, and neuro-protective activities (39, 85). Protein-rich edible products can be prepared from seafood by-catch. The general methodology involves isolation of meat from the eviscerated fish as mince. The mince can be converted into secondary products such as surimi and surimi-based restructured products, extrusion-cooked products, sausages, and fermented products (46, 91). Fermentation technology has been used to develop edible paste of jellyfish, having unique sensory characteristics in terms of umami, smoked, dried fruit, spices odours, besides desirable nutritional traits (92). The microbial protein market, however, will mostly depend on a favourable legislation, public acceptance, and acceptable costs (42).

5.2. Lipids

The livers of albacore, cod, salmon, haddock, tuna and others are good sources of PUFA-rich oil, which could be recovered by natural, thermal, solvent, enzyme extractions or microbial fermentation. The drawbacks of conventional solvent extraction are low efficiency, longer time and higher temperature, which can cause oxidation of the extracted lipids. In this regard, the applications of green chemistry based processes are much vital for better recovery, product quality, lower investment and sustainable production. Enzymatic processes disrupt the tissue and membranes under mild conditions to release oil from liver, roe and other fish products (93, 94). SC-CO_2 is a promising technology for extracting high-quality lipids from fishery discards including liver, viscera and heads.(23). The lipid fraction of sardine waste was isolated through SFE with SC-CO_2 at 250 bar and 40 °C, yielding 20 g oil per 100 g waste with up to 17.2 % wt. of PUFAs (81). Ultrasonic coupled technologies normally extract lipids more efficiently due to the synergistic effect. The UAE assisted lipid extraction has been discussed details with respect to its mechanism, solvent, feedstock, quality evaluation and coupled technologies (95). UAE combined with enzymes or SFE improved oil extraction from fish meal (36, 68). MAE could extract high-quality oil from fish by-products without loss of functionality of PUFA. Under optimal MAE conditions 60 and 100% of oil could be recovered in about 19 min with less solvent consumption (96). As high 20% oil was isolated from sardine waste with SC-CO_2 (81). The high price of the extracted fish oils makes the various technologies viable for the process. The market value of EPA and DHA in 2020 was US $1.41 billion (https://goedomega3.com/, accessed Dec.1, 2021).

5.3. Carotenoids

The major carotenoids present in seafood by-products are astaxanthin, cantaxanthin and zeaxanthin. Marine carotenoids are used in food products, pharmaceuticals, and cosmetics. The SC-CO_2 method extracts carotenoids in high yield at lower temperature without the use of harmful organic solvents. Solvents, which are generally recognized as safe (GRAS), can also be used to stimulate extraction of carotenoids (97). Fermentation of shrimp waste by *Lactobacillus plantaram* has given good yield of astaxanthin, along with chitin. The alternative microbial process displayed advantage over existing hazardous, non-economical chemical process (98). Cultivation of the microalga, *H.*

pluvialis, for both single cell proteins (SCP) and astaxanthin has been economically sustainable (99).

54. Chitin, chitosan and their oligosaccharides

Chitin is the most abundant polysaccharide in the marine ecosystem,and second in nature, after cellulose. It is made up of N-acetylglucosamine units, joined by 1,4 covalent linkages. Crustacean (crab, shrimp, lobsters and krill) shell discards contain chitin up to 70% on dry weight basis. Chitosan is a linear polysaccharide comprising of deacetylated and acetylated units of D-glucosamine, linked by β-(1, 4) glycosidic bonds. The ratio of glucosamine and *N*-acetyl glucosamine generally defines the degree of deacetylation in chitosan. Chitin, chitosan and their derivatives have been explored as sustainable safe, biodegradable, materials for various applications such as agriculture, textiles, cosmetics, food processing, packaging, and others. Seafood discards have a promising benefit for the development of environmentally friendly food packaging systems. Therefore, the green packaging from seafood leftover can be better exploited and replace the synthetic counterparts. Their nanomaterials in different forms such as fibres, hydrogels, beads, sponges, and membranes have interesting applications in biomedical fields such as urgical sutures, artificial skin, rebuilding of bone, controlled drug delivery, and others (100, 101, 102, 103).

Conventionally, chemical extraction is employed for chitin and chitosan recovery from crustacean shells (104). In view of the limitations of these processes, in recent years, **environmentally** safe green routes are finding uses for chitin/chitosan extraction. These include enzymatic hydrolysis, microbial fermentation, ultrasonic or microwave-assisted processes and extraction by ionic liquids, and deep eutectic solvents (13, 23, 105,106). The microbe-enabled chitin production probably offers the highest potential for commercial application. The dominant status of microbial approach as the preferred valorisation strategy for chitin production from crab waste has been recognized (12, 105). Deproteinization and demineralization of chitin at 68% and 96%, respectively, were achieved by solid state fermentation by *L. brevis* and *R. oligosporus*. The isolated chitin retained about 94% acetylation. Protein hydrolysate and astaxanthin were the other products of fermentation (107). Fermentation of shrimp waste by *Lactobacillus plantaram* could recover chitin (98). The use of proteolytic enzymes for chitin and chitosan from shrimp and crab shells has been studied (108). In a combination process, protease was used to remove Ca^{2+} and protein, followed by fermentation by *B. coagulants* to recover chitin from crayfish shell waste (109).

Chitin could be dissolved in DESs such as choline chloride-thiourea in a ratio of 1:2(CCT 1:2), choline chloride-urea (CCU 1:2), choline bromide-urea (CBU 1:2), and betaine hydrochloride-urea (BHCU 1:4), betaine hydrochloride -urea, ChCl-ethylene glycol, and ChCl-glycerol. The dissolution can be assisted by conventional, microwave or ultrasound-assisted heating. Almost 90% chitin was extracted from shrimp shell, with a purity of 98%, using choline chloride-lactic acid CCLA). It is possible to recycle the DES several times without loss of capacity to fractionate shrimp shell (110)). A sustainable strategy for chitin extraction involves dissolution in choline chloride–malic acid as DES along with microwave treatment. The treatent removed most proteins and minerals from crustacean shells and the isolated chitin had 76% crystallinity (60). Ammonium-based ILs are promising green solvents to extract chitin from shrimp shells (111). Table 3 gives some examples of green solvents for chitin extraction.

Nano-chitin can be made from chitin by using acid hydrolysis, ultrasonication, grinding, microwave irradiation, and electro-spinning. Chitin microfibrils were produced using DESs prepared from choline chloride and organic acids such as lactic, oxalic, citric, malonic and malic acids. DESs were useful for shape-controlled synthesis of nanoparticle (102). Nano-chitin finds wide application in the food industry due to its unique characteristics, including its smaller size, solubility, low density, high surface area, superior chemical reactivity, low toxicity, biodegradability, biocompatibility, antioxidant activity, antimicrobial properties, and excellent mechanical strength. It can be used to stabilize emulsions, as a reinforcing agent in food films, inhibition of starch retrogradation, and others (102).

(Para) Enzymatic preparation of chitosan uses chitinolytic enzymes belong to the glycosyl hydrolase family, which hydrolyse the β-1, 4-glycosidic bonds between N- acetyl- D- glucosamine residues in the chitin chain. Another green process for chitosan preparation involves hydrolysis of N-acetyl amide linkage of chitin by fungal chitin deacetylases isolated from *Mucor rouxii, M. mechei*, or *Aspergillus Niger*. To enhance the accessibility of the enzyme to acetyl groups of natural crystalline chitin, pre-treatment by ultrasonication and microwave radiation were beneficial (101).

Green processes are emerging for the production of degraded products of chitin or chitosan, namely, chito-oligoosaccharides (COSs), N-acetylglucosamine (GlcNAc) or glucosamine (GlcN), and also hetero-oligosaccharides composed of GlcNAc and GlcN with enhanced biological activities such as anti-microbial, anti-inflammatory, anti-oxidant and anti-tumor activities. Bacterial chitinases play a fundamental role in the degradation of chitin (112). To date, various green-chemical strategies involving enzymatic synthesis of COS with designed sequences and desired biological activities are available. In recent years, chitinolytic enzyme-mediated hydrolysis of chitin into N-acetyl glucosamine (GlcNAc) is a more attractive and greener approach due to its high yields under mild condition.The enzymatic strategies involve transglycosylation or glycosynthase reactions using reducing end-activated sugars as the donor substrates (113, 114). Immobilized microbial α-amylase could convert 73% of the chitosan to COSs using continuous stirred tank reactor before flowing through a packed bed reactor (57). Another green process to hydrolyze chitin into its monomer employed acidified lithium halide molten salt hydrate (AMSH) systems to convert native chitin into *N*-acetyl glucosamine (NAG). Kinetic investigations indicated the superacidic property of LiBr and LiCl AMSHs to be the key for the fast cleavage of β-1,4-glycosidic linkages, leading to NAG formation. The critical role of Li^+ in the disruption of the hydrogen bonding network of chitin on the acetamido group was indicated which promoted chitin swelling and dissolution (114). Because of their biocompatible, biodegradable and nontoxic nature, COSs find applications in biomedical, food, pharmaceutical, agricultural, and cosmetic industries (115).

Chitin has has remarkable potential for as raw material the production of renewable, value-added platform chemicals, especially N-containing compounds. In this respect, the Diels–Alder (DA) cyclo-addition of furans has been the subject of extensive research, in particular, usage of biomass derived furans such as furfural and 5-hydroxymethylfurfural (HMF).The direct conversion of chitin, chitosan and (NAG) into the less explored chitin derived furan, namely, 3-acetamido-5-acetylfuran (3A5AF) through the DA reaction is a green process. The 3A5AF is an important platform compound that can be utilised for synthesising value-added N-containing fine chemicals. So far, nineteen new products have been obtained from 3A5AF in high yields that can have interesting applications in areas such as materials, energy and drug discovery. Future applications of this chemistry can lead to considerable advances in sustainability and carbon neutral economy (116). An integrated engineered fermentative process was developed for upcycling chitin into tyrosine and and L-3,4-dihydroxy phenylalanine (L-DOPA) (117). Another chemo-enzymatic process to convert chitin into 3A5AF has been reported. It involves initial enzymatic chitinolysis of chitin to NAG, which is then converted to 3A5AF using ammonium thiocyanate as catalyst. The protocol provided a good option to convert chitin resources into 3A5AF (118). Future opportunities include improving the efficiency and selectivity of chitin separation from wastes, redesigning its chemical structure, converting it into value-added chemicals, and developing new chitin and chitosan applications, all of which can contribute towards the UN SDGs (119). In summary, fermentation, enzymatic processes and extractions by green solvents are ideal for chitin extraction. Chitin and chitosan can be subjected to hydrolysis by chitinases for oligraphenegosaccharides. These have high value for use as feedstock for platform chemicals.

5.5. Glycosaminoglycans (GAGs)

Glycosaminoglycans (GAGs) are linear polysaccharides consisting of repeating disaccharide units. They include chondroitin sulfate (CS), hualuronic acid, (HA), heparan sulfate, dermatan sulfate, among others. Eco-friendly processes for their isolation have been discussed. The methodologies include combination of microbial, enzymatic and other strategies to produce CS, HA, and also chitin and chitosan (120).

5.6. Mineral compounds

Fish bones are rich in calcium and other minerals. Calcium from fish bones has received attention as a natural supplement for individuals having calcium deficiency. Several traditional methods have been pointed out for mineral extraction (23). Treatment by flavourzyme followed by fermentation with *Leuconostoc mesenteroides* of fish bones gave a preparation rich in soluble calcium lactate, calcium acetate and also small amounts of calcium peptides. The calcium is bioavailable and can promote growth, suggesting its use as a calcium supplement (121). The high calcium contents of mollusc shells make it an alternative to natural limestone. Eco-friendly cement has been produced by incorporating crushed oyster shell at 10 to 20%. This can also partially mitigate CO_2 emission (122). Fish industry waste has also potentials for the development of sustainable materials for energy storage devices including lithium-ion batteries. These materials present advantages including high conductivity, high tensile strength, low density, and the possibility to obtain different structures by a careful selection of the starting material (123).

5.7. Biofuel

Biofuel can be defined as the energy (work, heat or electrical) derived from biomass and its refined products such as bioethanol, biodiesel, bio-kerosene, natural gas, etc. Global concerns on energy and also food security along with escalating challenges of biowaste disposal have attracted interests in biological materials as feedstock for the production of sustainable and renewable energy. Seafood discards offer valuable options in this respect. The crustacean shell waste, which is composed of 20 to 50 % calcium carbonate ($CaCO_3$), 15 to 40 % chitin, and 20 to 40 % protein is an interesting raw material (119). Chitin has potential to be a potential cheap and renewable source for bioethanol. In a recent study, chitin was hydrolyzed to oligosaccharides by chitinase from a marine bacterium, *Bacillus haynesii*. The COS was used as an effective renewable substrate by *Mucor circinelloides* to produce bioethanol. The authors reported production of 7.4 g/L of ethanol from 30 g/L of COS (124). Seaweed associated bacteria; namely, *Bacillus* spp., *Brevibacterium* spp. and *Vibrio* spp degraded crustacean shells as well as fish scales within a few days in a seawater-based broth. The sugars released are fermented to give bioethanol by *Saccharomyces cerevisiae* (49). Oil-rich fish discards are promising feedstocks for energy. The oil can be purified followed by methanol esterification at 60°C for 1 hr initially under acidic followed by alkaline conditions. The preparation satisfied viscosity, flash point and other required standards (125, 126). The oil was transesterified in presence of methanol. The reaction was catalyzed by calcium oxide generated by calcination of shrimp shell itself A maximum biodiesel yield was obtained from the oil at an oil to methanol molar ratio of 1:12, at a catalyst concentration of 5 wt% of oil, reaction temperature of 65 °C, and reaction time of 120 min. The biodiesel production was scaled up to a 50 L oil volume batch and achieved a good yield of 88.7 wt%. The physicochemical properties and cold flow property of the biodiesel suggested its as fuel (127). Lipases from Candida antarctica B were used to hydrolyse and then esterify cooking oil to produce biodiesel. Over 90% conversion was achieved after 10 hr hydrolysis and 10 hr esterification (57).

Microalgae have the key advantage to produce third generation biofuel. Cultivation of microalgae and other organisms in fish discards medium including process effluents under appropriate conditions can yield oil-rich single cell proteins. The algae use primary carbon recovered from food side streams. The productivity of algal biomass is generally 40–50% higher than that of terrestrial crops with a high atmospheric carbon fixation rate (128). The various methods of both biomass harvesting and lipid extraction for biofuel production from microalgae have been discussed (129). There has been a growing focus on biodiesel production from various recalcitrant wastes for cultivation of oleaginous yeasts. The metabolic pathways that facilitate the conversion of the recalcitrant wastes into single-cell oil (SCO) have been pointed out. Emphasis has been provided on the application of Ohmic techniques to increase waste bioconversion into lipids for the process commercialization (130).

A number of green processes for seafood process effluents are available. The process of dissolved air flotation (DAF) reduces BOD and COD of the effluents. Anaerobic digestion of seafood industry effluents in a dissolved air flotation (DAF) system removed organic contents. (10). Suitable membrane processes including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO) can remove proteins, lipids, etc. Electro-chemical oxidation reduces organic matter from aquaculture effluents. Electro-flocculation or flocculation by chitosan, carrageenan, alginate, carboxymethyl cellulose, and other flocculants can sediment proteins and other components (72).

6.0. Integrated green processing: Perspectives of a marine refinery

A biorefinery integrates biomass conversion processes and equipment to produce value-added materials chemicals (food, feed, chemicals and fuel) from biomass. The biorefinery approaches involving multiple processes on a circular economy protocol aim at total utilization of the raw material at higher efficiency and at reduced production costs. This ensures sustainability and economic benefits besides protecting the environment (35, 131, 132). The bioconversion of feedstock on a zero-waste strategy involves essentially three steps, known as ‘3R’, namely, ‘reuse-remake-recycle’ (22). A marine biorefinery envisages integration of green methods for recovery of various ingredients present in marine resources, essentially through a circular blue economy framework (131).

Integrated green chemistry-based tools to manufacture ocean-based resources provide a sustainable route to a range of products including minerals, fuels, polymers, and nutritional supplements. The innovative biochemical, thermo-chemical and hybrid methods can convert aquatic biomass into valuable materials. The products include proteins, lipids, polysaccharides, biofuels, minerals, and others, which are recovered from oceanic resources in the format of petroleum refinery. Their implementation, however, requires expertise in all stages of manufacturing, in addition to a clear vision of all raw materials, residues, and products. Ocean-based industries are adopting new sustainable production models, particularly biorefineries, which are effective for converting low-value biomass into commercially relevant by-products (132.133. 134, 135).

A typical marine biorefinery is the shell bioreinery, intended for sequential treatments of crustacean waste to recover chitin, proteins, lipids, carotenoids, calcium carbonate and chitin monomers (136). The shell refinery can isolate products from the crustacean shell waste on an environmentally safe manner, on a zero-waste perspective (137). Another shrimp shell biorefinery produced commercially important biomolecules such as astaxanthin-rich oil, protein, chitin, and chitosan. SC- CO_2 extraction was performed for the recovery of astaxanthin and oil. Astaxanthin yield was about 30 mg per kg dry shell weight. The extracted oil was rich in PUFA, in particular, PUFA, particularly, EPA and DHA. The remaining waste was used for protein extraction at a yield of about 22%. The left over residue provided 224 g chitin per kg, which was then deacetylated to give chitosan at 57 g per kg (138). A maximum of 44% protein and 37.4 g per kg oil were recovered from snow crab discards using proteolysis of shells with entrails along with 24 mg carotenoids and 100 g chitin per kg of waste. The protein and oil could be extracted in scalable processes in a profitable way (19). In another process, two recombinant aspartic proteases were used for protein hydrolysis, recombinant chitinase for chitin hydrolysis, and ethyl acetate for astaxanthin extraction. The process recovered 91.4% protein and 89% chitin, without loss of functional properties (139). An integrated biorefinery process to develop two aromatic nitrogen containing chemicals, namely tyrosine and L-3,4-dihydroxy phenylalanine (L-DOPA) was developed. The process involved pretreatment of chitin-containing shell waste followed by an enzymatic/fermentative process using metabolically engineered *Escherichia coli*. The process gave 0.91g/L or 0.41 g DOPA from 22.5 per per liter unpurified shrimp shell waste (119). The valorisation of wastes generated in the processing of farmed fish is currently an issue of extreme relevance for the industry, aiming to accomplish the objectives of circular bioeconomy (44).An integral process based on enzyme proteolysis for the production and recovery of fish protein hydrolysates (FPHs), oils, bioactive peptides and fish peptones has been reported. The procedure was initially applied to ten fish discards to lab scale. FPHs of high quality in terms of soluble protein and amino acid contents, digestibility and bioactivities were obtained. Pilot plant trials confirmed the results of FPHs production obtained at lab scale (140)

Microalgae can be an interesting component of seafood biorefineries (10, 72). Cultivation of microalgae in nutrient rich medium from seafood sources under appropriate conditions can single cell proteins (SCP) rich in oil, which can be used for biofuel production. Techno-economic studies on commercial production of biofuel along with other SCP components including pigments and animal feed have suggested economic viability of microalgae-based biorefineries. The technology can promote a circular bio-economy (141). The current state-of-the-art on marine biorefineries and the sources and applications of their by-products have been provided. The economic viability of individual biorefineries needs to be evaluated for their successful commercialization (99). Suggestions have been put forward to integrate green chemistry and blue economy principles into ocean-based industries towards a more sustainable, profitable, and conscious ocean-based economy (142**).** Table 4 shows a few examples of seafood waste bio-refinery for multiple products,

7.0. Factors favouring green processing

7.1. Life cycle assessment

LCA is defined as a product oriented environmental tool, which provides a systematic way to quantify the environmental effects of individual products or services from ‘cradle to grave’ (37). LCA studies throw light on environmental impacts of processing of seafood and other food side stream systems. These impacts include ozone depletion, climate change, terrestrial acidification, freshwater eutrophication, toxicological stress, water depletion, land use and fossil depletion. These occur while extracting resources, producing materials, manufacturing, during their consumption/use, and at end-of-life of the products. LCA analysis of food waste as a bioenergy source can significantly contribute to closing the carbon cycle by reintroducing energy into the food supply chain. The LCA data of bioconversion and valorisation have been provided for more than 60 seafood items (143). LCA studies suggested economic viability of chitin extraction using hot water and carbonic acid (144).

7.2. Availability of functionally active novel compounds

Innovative processing presents prospects for industries for novel compounds and hence significant additional revenue. The beneficial factors that favor green processing of seafood side streams include low cost of the raw material, general lower cost of processing compared to conventional processes, lower environmental hazards due to processing, high market values of the recovered ingredients and therefore increased profitability. Unlike most agro-waste, the seafood side streams can be transformed into high value items, which can command significant commercial values because of their diverse functionalities as well as interesting applications Green processing of seafood side streams employing novel technologies have scope to isolate these ingredients thereby generating more value for the ocean biomass (38, 39,134) .

7.3 Commercial potentials

Green chemistry-based processing of seafood side streams into ingredients presents an opportunity for novel industries and prospects for additional revenue (146). Considering invariably the huge gap between cost of raw material and products, these technologies can offer viable processes, which can ultimately support seafood security. The high value of the recovered products makes the generally low value seafood side streams a valuable feedstock that benefits the global economy. In view of the advantages, novel green chemistry related processes are evolving in recent times. There are indications that the ocean-based industries are adopting new sustainable production models, similar to biorefineries, which are effective for waste valorization (142).

Some interesting green processes have evolved during the last few years. Processes such as ISP, green solvent extraction, fermentation and non-thermal technologies can favor economically viable protein extractions from the seafood side streams. A recent cost analysis of the chemical-only, enzymatic–chemical, and microbial fermentation based chitin extraction suggested that the microbial chitin production pathway constituted the most appropriate technology for future (12). The polysaccharide released by the bioconversion process can be extracted by DESs. The extracted chitin offers interesting scope for several novel products including bio-energy, as discussed in this article. A method for mild extraction of chitin using hot water and carbonic acid was economically beneficial (144). There are potentials for green extractions of glycosaminoglycans and minerals from seafood discards. Microbial fermentation, enzymatic processes particularly proteases and chitinases, ISP extraction, green solvents, and others may be integrated in a marine refinery.

Currently several marine products are available in the market for diverse applications (3). The demand for seafood-based innovative products is likely to reach new realms the near future making theme part of expanding global green chemical market, which stood at US$9413 million in 2020 and is expected to reach to US$ 22,039 million in 2030. (https://www.psmarketresearch.com/market-analysis/green-chemicals-market-outlook, accessed September 15, 2023). Products recovered from seafood side streams through green processing can significantly contribute to the market in the near future. Consumers in general favourably respond to efforts to protect the environment. It is important to increase consumer awareness of the valuable products and their production routes, which protect the environment.

. The crustacean and bivalve side streams have been recognized raw materials complying with specific EU regulations (6). The Bio-based Industries Joint Undertaking (BBIJU) has promoted bio-based platform chemicals and materials. The up-scaled technologies can be catalysts for a green transition under the European Green Deal (147). Partnerships, collaboration and a genuinely trans-disciplinary approach based on green processing can favor management of seafood side streams in a way that can meet sustainability goals (21).

7.4. Challenges facing green processing

In spite of ample scope, green processing faces some challenges. Many of the novel technologies employed in recent times are at the laboratory or pilot plant scale; sufficient data on commercial as well as economic aspects are lacking, particularly with respect to valorization through a marine biorefinery. Although eco-friendly, they have limitations in the up-scaling process (13). Anaerobic digestion of seafood effluents although is promising, it faces considerable operational and process stability issues due to low solid concentrations, salinity, low carbon/nitrogen ratio, and high lipid content in the waste streams (10). Success in green processing of seafood side streams depends on regular availability of sufficient quantity of seafood side streams, technical feasibility of the processes at industrial scale, techno-economic potential, and life cycle assessment to evaluate environmental benefits of the processes. It is recommended that the green processing plants may be located at a centralized location near the coast where seafood plants will be located. There is much scope for research and investments in developing green technologies to harness the full potential of utilizing seafood side streams to address seafood sustainability. Another challenge is with respect to the nature of seafood feedstock, which is generally bulky with its nature significantly varying with respect to fish/shellfish resource, their species and size and susceptibility to rapid microbial spoilage (11).. It is essential to know not only the composition of the seafood feedstock, but importantly the potential market value and application of the biomolecules, chemicals, and other by-products that can be isolated or converted from each type of waste.

Valorisation of seafood side streams through green processing into commercially viable products needs efforts to popularize the concept.

Several challenges have been recognized with respect to marine biorefinery. The crucial step in successfully designing a marine biorefinery is an in-depth knowledge of each resource, productive chain, operational limitations, and field of application. Clustering of different production chains into a single biorefinery mode is technologically demanding. Demonstration plants are necessary to evaluate commercial success in the development of sustainable technologies.The current state-of-the-art on marine biorefineries and the sources and applications of their by-products have been provided (142).

8.0. **Green processing to enhance seafood sustainability**

Scientific management of seafood side streams within the perspective of green chemistry encourages environmental friendly utilization of the biomass. Valorization of the feedstock needs to be based on the strategy of 3R, viz.,'Reduce' the waste as much as possible, 'Reuse', and after 'Recycle', and, finally if nothing else works, eliminate . An ecologically conscious valorisation approach based on the above concept is likely to minimize waste, develop valuable products, improve food security, nutrition, social benefits and provide economic profit, within the concept of a circular economy (134,135, 145). Because of the regenerative nature of the seafood biomass, its utilization is highly significant. An ecologically conscious valorisation of the biomas, ideally through a marine biorefinery using green chemistry based valoristion technologies, can reduce the seafood side streams, environmental pollution, support sustainability and encourage blue economy. Reduction of seafood discards satisfies the sustainable development goal (SDG) #12.3, which calls for halving global food waste including waste from marine sources at the production and supply chains (21). There are other benefits also on the SDG. Table 5 gives likely contributions of seafood side stream management to SDG 12. In view of its potentials, green chemistry needs to get more attention to meet seafood sustainability

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Table 1. Limitations of chemical processing on components of seafood side streams

Component	Method	Disadvantages
Proteins	Chemical extraction under elevated temperatures	Longer time, high energy consumption, possible racemization of amino acids, splitting of disulphide bonds, loss of cysteine, serine and threonine via β-elimination reactions, formations of toxic compounds such as lysin alanine. D- amino acids are not absorbed by humans
Peptides	Chemical hydrolysis and solvent extraction	Toxic compounds, residual solvents
Oil and biodiesel from oil	Acid digestion using HCl at high temperature until complete dissolution, other conventional methods	High reaction temperature, contamination of glycerol with alkali, soap formation,waste generation
Chitin, chitosan, chitin oligosaccharides	Demineralization by mineral acids, deproteinization by alkali such as sodium or potassium hydroxide	Hazardous, energy consuming, chemicals-rich effluents can cause health and safety concerns. affects intact nature of chitin, higher costs
Chitin, chitosan	Derivatization of functional groups for a wide spectrum of compounds	Chemicals used entail risks for human health and the environment
Chondroitin and hyaluronic acid	Solvent extraction	Most solvents used entail risks for human health and the environment. May also lead to compound degradation

Source: Summarized from references, 13, 24, 97,114

Table 2. Comparison of traditional processes and green processes

Parameters	Traditional processes	Green processes
General reaction conditions	Chemical treatment, likely at high temperature and pressure	Chemical reactions take place usually at ambient temperature and pressure
Nature of reagents	Reactive, persistent, or toxic Many organic solvents have adverse health effects	Green solvents are inert, recyclable and sustainable
Energy source	High energy generally from fossil feedstock	Low-energy chemical reactions
CCatalysts	Catalysts may include elements from the entire periodic system. Some may be toxic. Some processes require high heat or pressure conditions	Microorganisms and enzymes serve as low cost, stable biocatalysts.
Changes in resources	Drastic degradation Design exclusively for use phase	Degradation is part of design, ‘timed degradation’ or ‘triggered instability’.
Creation of functionality of the product	Functionality is created by the new material itself	Functionality is created by the structure. Scope for improved bioactivities
Type of processes	Linear	Circular
Management approach	Waste treatment	Waste utilization
Profitability	Maximum chemical production for minimum profitability	Maximum chemical production with minimum benign material use for increased profitability

Adapted from Ref.24

Table 3. Some green extraction systems for seafood side streams

Raw material	Green solvent	Product
Shrimp shell waste	Deep eutectic solvents (DESs) such as choline chloride and malic acid alone or in combination with non-thermal methods	Chitin
		Chitin
Shrimp shell waste	Hot water-carbonic acid	Chitin
Seafood side streams	Ionic deep eutectic solvents	Proteins
Seafood side streams	Deep eutectic solvents (DESs) choline chloride-glycerol, choline chloride-oxalic acid, choline chloride-urea ethanol	Proteins
Marine biomass	Pressurized extraction systems	Higher extraction efficiency. Reduces solvent consumption compared to conventional extraction processes
Agro-food items	SC-CO_2 extraction	Carotenoids
Different marine wastes	Cmbination of microbial, chemical, enzymatic and membranes strategies	Chondroitin Sulfate, Hyaluronic acid, chitin, chitosan

Source: References 60, 62, 63, 64, 79, 97, 120

Table 4: Some green processes used in seafood waste bio-refinery for multiple products

Green processes	Products	Reference
Lactic fermentation	Several useful products including astaxanthin, hydrolyzed protein and chitin	44
Pretreatment of shell waste and an enzymatic/fermentative process using metabolically engineered *Escherichia coli*	L-3,4-dihydroxy phenylalanine (DOPA) and tyrosine from crustacean shell waste	117
Proteolysis of shells for proteins, and conventional processes for chitin and carotenoids	Protein, oil, carotenoids and chitin from snow crab shell waste	19
Supercritical carbon dioxide extraction for the extraction of astaxanthin and oil, supercritical fluid extraction for protein extraction	Protein, chitin, chitosan, PUFA- rich oil, astaxanthin, from shrimp waste	138
Water, acetic acid, and buffers, with solid–liquid extraction, along with centrifugation, and membrane filtration	Proteins, chitin, calcium carbonate, astaxanthin from crustacean waste	137
Rcombinant aspartic proteases, recombinant chitinase and ethyl acetate	Protein, chitin and astaxanthin from shell waste	139
Microbial, enzymatic and membranes strategies	Chondroitin sulfate, hyaluronic acid and chitin/chitosan from marine waste	120
Chitin was hydrolyzed to oligosaccharides, which were used as substrate by *Mucor circinelloides* to produce bioethanol	Oligosaccharides, bioethanol from shell waste	124
Isolation of oil followed by transesterification of oil	Renewable fuels	126,127

Table 5.Potential contributions of seafood side stream management to sustainable development goal (SDG) 12

1. Sustainable management and efficient use of seafood resources (SDG 12.1)
2. Halving global production of seafood side stream (SDG 12.3)
3. Substantially reduce seafood side stream through prevention, reduction, recycling and reuse (SDG 12.5)
4. Encourage adoption of sustainable seafood side stream management practices by seafood companies (SDG 12.6)
5. Technology transfer on seafood side stream resource recovery to developing countries to aid sustainable seafood resource utilization (SDG 12a)

Source: Adapted from Ref. 21

Legends to Figures

Figure 1. (a) Food waste recovery hierarchical pyramid; (b) types of strategies to prevent food waste. Source: United States Environmental Protection Agency, with permission
(Please note that color may not be required for this figure)

TOC Graphic:
Title:
Major achievable targets through green processing of seafood side streams

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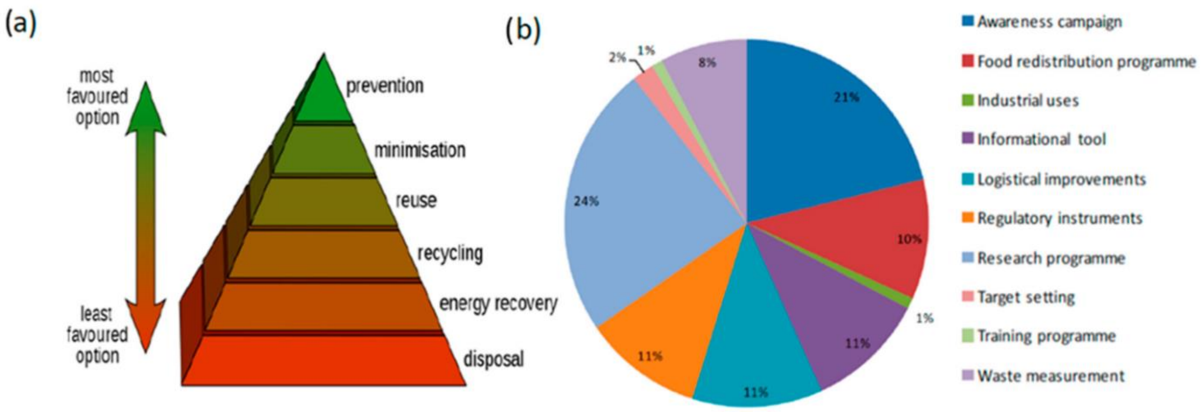
(a)
most favoured option
least favoured option
prevention
minimisation
reuse
recycling
energy recovery
disposal
(b)
21%
10%
1%
11%
11%
11%
24%
2%
1%
8%
Awareness campaign
Food redistribution programme
Industrial uses
Informational tool
Logistical improvements
Regulatory instruments
Research programme
Target setting
Training programme
Waste measurement

Figure 1.

152.

TOvC Graphic

omments