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Chitin and chitosan derived from crustacean waste valorization streams can support food systems and the UN Sustainable Development Goals

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Crustacean waste, consisting of shells and other inedible fractions, represents an underutilized source of chitin. Here, we explore developments in the field of crustacean-waste-derived chitin and chitosan extraction and utilization, evaluating emerging food systems and biotechnological applications associated with this globally abundant waste stream. We consider how improving the efficiency and selectivity of chitin separation from wastes, redesigning its chemical structure to improve biotechnology-derived chitosan, converting it into value-added chemicals, and developing new applications for chitin (such as the fabrication of advanced nanomaterials used in fully biobased electric devices) can contribute towards the United Nations Sustainable Development Goals. Finally, we consider how gaps in the research could be filled and future opportunities could be developed to make optimal use of this important waste stream for food systems and beyond.

Since 2015, the United Nations Sustainable Development Goals (SDGs) have been key policy drivers for supporting sustainable seafood systems[1]. In the same year, Yan and Chen highlighted the untapped benefits of crustacean waste as a reserve of chitin (15–40%), protein and minerals, calling for a multi-million-dollar investment to establish the first shell refinery processing pipeline[2].

With a 2–3% annual growth rate, the yearly global level of crustacean production reached 13.7 million metric tonnes (mmt) in 2015 (Fig. 1), resulting in 6–8 mmt of lobster, crab and shrimp wastes[1]. Five years later, crustacean production had increased to an annual rate of 16.6 mmt, with most growth seen in Asian countries (especially China, Indonesia and India, with over a 2 mmt increase) (Fig. 1). Crustaceans contain approximately 40% meat, with the remaining 60% being inedible, raising questions within the industry about the scale of crustacean waste accumulation. However, crustacean waste contains chitin, a biocompatible and biodegradable polymer covered by protein and minerals that is invaluable for producing high-tech products such as nerve conduits (for example, Reaxon, manufactured by Medovent).

Reproducible chemical conversion processes for obtaining well-defined chitosan with specific functionalities (second-generation chitosan) have been developed since the 1970s[3]. Between 2000 and 2015, European grants of nearly €15 million went towards projects exploring chitin- and chitosan-related topics[4,5], with grant values increasing after 2015, eventually reaching €55 million (Fig. 2). Topics included chitin extraction within the efficiency borders for high-value production, environmental impacts, economic feasibility and developing a microbial-enzymatic process for converting chitin into glucosamine and *N*-acetylglucosamine. The ChiBio consortium (with a grant of nearly €4 million), comprising academic and industrial experts, developed a microbial-enzymatic process starting from a two-stage fermentation by *Serratia marcescens* and *Lactobacillus plantarum* for demineralization and deproteination followed by enzymatic depolymerization of chitin into basic building blocks—that is, glucosamine and *N*-acetylglucosamine[6]. In more recent years, protein engineering based on bioinformatics, genome mining, rational design and molecular evaluation has become more prominent in chitosan research, with a move towards a multilevel circular value chain for the eco-efficient valorization of aquaculture and fishery wastes (the Nano3Bio project, with a grant of nearly €12 million)[7]. In 2021, a €19 million project was launched by Italian academics and industrialists to develop a multilevel circular value chain for the eco-efficient valorization of aquaculture wastes within the subsequent five years[8].

Here, we examine why this amount of grant funding should be invested in a waste stream, exploring the most recent developments in eco-friendly and circular utilization of crustacean waste. We also look to the future of chitin within and beyond food systems.

Emerging technologies for crustacean waste valorization

Natural materials are reliable and suitable for use both in the environment and inside the human body, with some exceptions due to their allergenic effects for some individuals[9]. Chitin, a water-insoluble polymer with a higher number of D-glucosamine monomers than *N*-acetyl-D-glucosamine monomers, and chitosan, a water-soluble polymer with a higher number of *N*-acetyl-D-glucosamine monomers,

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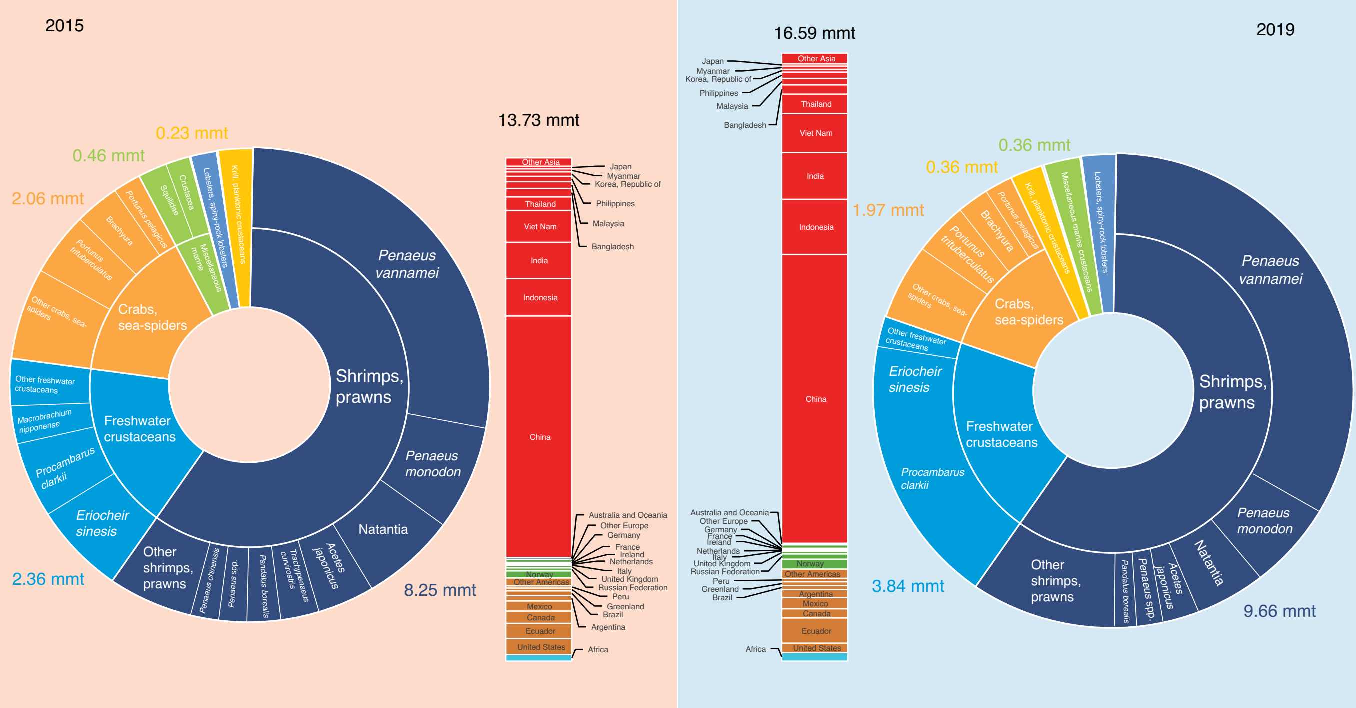

Fig. 1 | The global production of crustaceans in 2015 and 2019. The production of shrimps and prawns (dark blue), freshwater crustaceans (light blue), and crabs and sea-spiders (orange) in Africa (blue), America (brown), Europe (green), Australia and Oceania (light blue), and Asia (red) in 2015 (left) and 2019 (right). The data were obtained from the Fishery Statistical Collections, Food and Agriculture Organization of the United Nations (https://www.fao.org/fishery/statistics/global-production).

are two important polymers derived from crustacean waste. The combination of chitin, proteins and calcite crystals can give tissues superior rigidity, flexibility and transparency[10]. Chitin's acetylation pattern can be adjusted at the molecular level to optimize its properties for various applications[11]. However, without appropriate extraction technologies, the accumulated crustacean wastes derived from different species may not reflect the intrinsic value that can be derived from their composition[12]. Additionally, crustacean waste may be received from different stages of seafood processing in the form of either raw or cooked waste material, where cooking exerts positive effects on the extraction of chitin and its quality[13]. During the past few decades, the chemical processes commercialized (including deproteinization, demineralization, discoloration and even deacetylation) have provided chemically derived chitosan with known and reproducible properties (second-generation chitosan). Besides the unacceptable environmental footprint of the processes involved[14], the resulting chitosan fails to meet the requirements of high-tech applications with chitin-based products, as its molecular structure and its properties are not tuned to the needs of high-tech applications[15].

Alternative technologies include the catalytic conversion of chitin by breaking the chitin polymeric structure during an efficient solid-state reaction into mechanochemical chitosan with a low but narrow-range molecular weight, which could tune its properties[16]. A similar solvent-less process has been developed on the basis of a reactive ageing method consisting of repeating cycles of milling and ageing with chitinase and a small amount of water, leading to mechanoenzymatic chitosan[17]. However, the inherent heterogeneity of waste-derived chitosans in terms of the degree of acetylation and the acetylation pattern still considerably limits its use in highly sophisticated applications, which might instead be addressed by using a recombinant fungal chitin decarboxylase[18].

To address these challenges, a biotechnological solution is presented in the Nano3Bio project, granted by the European Union[7]. The natural chitin was enzymatically degraded into its building blocks (*N*-acetylglucosamine and glucosamine), which were used to reconstruct a customized biotechnology-derived chitosan structure with an engineered microbial cell. The cell was developed using either *Escherichia coli* or *Corynebacterium glutamicum* as the host[7]. Nanotechnology-based bottom-up approaches can turn the chitin–chitosan structure into chitosan nanocomposites, where the properties of the heterogenic chitosan can then be tuned. Chitosan nanocomposites engineered by adding starch and lignin to chitosan and adjusting their concentrations were successfully utilized as triboelectric nanogenerators for self-powered nanosystems in biomedical and environmental applications[19]. A hydrophobization-induced interfacial-assembly approach has been developed for converting marine chitin into two-dimensional soft nanomaterials for their application as fully biobased electric devices[20]. The ethoxylation of chitin followed by deacetylation produced glycol chitosan with improved water solubility at a wide pH range while maintaining chitosan's amine groups. These amine groups facilitated the introduction of various hydrophobic moieties, including positively charged nanoparticles (through self-assembly) or targeting moieties with high affinity for cancer-specific receptors, offering promising applications for drug delivery and as nanomedicine for tumour cells, respectively[21].

The potential of crustacean waste

Economic potentials. In early research, crustacean shells were utilized whole and without fractionating their ingredients, primarily for environmental remediation purposes. Between 2003 and 2008, JRW Bioremediation LLC was assigned a patent family to utilize the crustacean shell as an electron donor to eliminate contaminants in groundwater[22,23] and mine-influenced water[23].

The shift from first-generation chitosan (that is, a poorly defined blend of chitosans with large batch-to-batch variations) to second-generation chitosan provided important opportunities for crustacean wastes in commodity markets such as agrochemicals

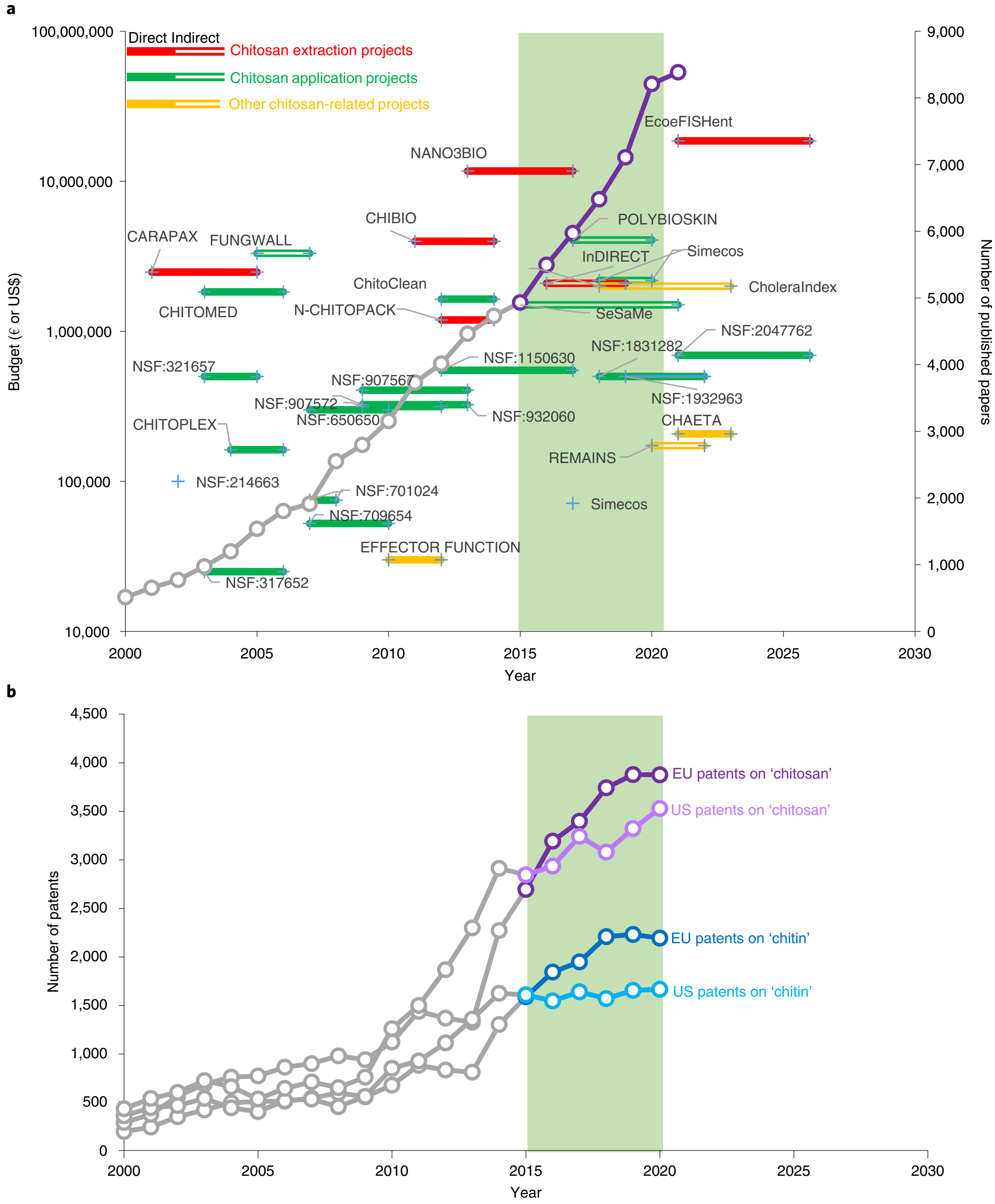

Fig. 2 | Growth in chitin and chitosan research projects, publications and patents from 2000 to 2022. a, The global landscape of chitin- and chitosan-based publications (Scopus database) (right *y* axis) and research grants (CORDIS, European Commission and US National Science Foundation) (left *y* axis). **b**, European Patent Office (EU) and United States Patent and Trademark Office (US) patents. The green shading represents the five-year period predicted by Yan and Chen[2] to witness a multi-million-dollar investment in the first shell refinery processing pipeline.

(>US$60 billion market value[24]) and water treatment agents (>US$30 billion market value[25]). Chitosan is a natural antimicrobial polycation used in pesticide formulations (for example, as an encapsulating agent[26]), ending up as soil-enriching derivatives through natural biodegradation. In August 2019, the US Environmental Protection Agency published a scientific analysis supporting the addition of chitosan to the list of minimum-risk ingredients of pesticides[27], promoting chitosan-based pesticides and broadening their opportunities in the agricultural market. As a polycation, chitosan can be utilized to formulate chitosan–lignosulfonates as a biocide enhancer[28]. Moreover, the chelating properties of chitosan make it a potential biodegradable coagulant/flocculant to be used in wastewater treatment processes instead of metallic salts and synthetic polyelectrolytes[29], with environmental benefits such as non-toxicity, biodegradability and ecological acceptability[29]. Agratech International Inc. also utilized/valorized and patented the hydrophobic potential of chitosan in developing chitosan-coated hydrophobic glass[30,31].

Originating from the food processing chain, crustacean wastes have high potential to be utilized as food packaging films or fruit preservatives, as well as food additives and dietary supplements. Owing to its film-forming properties, chitosan was first suggested as a biocompatible, biodegradable and non-toxic raw material for food packaging. However, due to the poor mechanical and UV protection properties of chitosan, chitin in the form of nanocrystals or nanofibres has taken center stage as a biocompatible food packaging raw material[4]. Supplementing chitin nanostructures with sensitive additives such as konjac glucomannan[32] or curcuma oil[33] could play an important role in the future of "smart food packaging films"[34]. Chitosan is a potential edible preservative coating for fruit and vegetables owing to its antimicrobial properties. However, its application should be limited because of the health side effects when included in daily diets[35,36].

The use of chitosan as a dietary supplement for bodyweight reduction is the most important human exposure to chitosan. In 2005, the US Food and Drug Administration (GRN 170) noted that "chitosan was non-toxic to humans and other test animals", but using chitosan as a regular diet ingredient is questionable due to the doubt on "whether or not chitosan would interfere with fat-soluble vitamin and mineral status in humans, when the substance was consumed on a chronic basis as part of a general diet"[35]. In 2017, a six-month feeding study conducted by the US National Toxicology Program revealed that the lowest observed effect level for chitosan exposure is 1% (approximately equivalent to 450 $\mathrm{mg\,kg^{-1}}$ or 31.5 $\mathrm{g\,d^{-1}}$ for a 70 kg individual) in males and 9% (approximately equivalent to 6,000 $\mathrm{mg\,kg^{-1}}$) in females[36]. With the Food and Drug Administration's approval and the relatively high lowest observed effect level, chitosan has great potential to be used in dietary supplements (with a market value of >US$220 billion[37]).

The biotechnologically derived chitosan termed as 'third-generation' may pave the way for high-tech applications of chitosan, mostly in biomedical engineering (with an approximate market value of US$250 billion[38]) and tissue engineering. For example, bridging peripheral nerve defects (an issue for around 300,000 people per year in Europe) could be achieved with engineered chitosan with a degree of acetylation of 5%[39]. Nanotechnology-derived chitosan and derivatives also promise highly sophisticated biomedical and environmental applications such as self-powered nanosystems[19], fully biobased electric devices[20] and tumour-targeting nanoparticles[21] (Fig. 3).

SDG realization. Farmed crustaceans account for nearly 10% of aquaculture production by volume and over 24% by value globally[40], generating 8 mmt of waste annually. Emerging technologies for the valorization of crustacean wastes could therefore align well with the ambitions of SDG-12 (responsible consumption and production) and several targets categorized within different goals, including SDG-2 (food security, improved nutrition and promotion of sustainable agriculture), targets 2.2, 2.3 and 2.4; SDG-3 (good health and well-being), targets 3.1, 3.2, 3.3 and 3.9 (crustacean-waste-based medical and pharmaceutical products); SDG-6 (crustacean-waste-based flocculating agents for clean water and wastewater treatment); SDG-7 (sustainable energy), targets 7.2 and 7.b (crustacean waste as energy resources for small island developing states); SDG-11 (sustainable cities and communities), target 11.6 (crustacean-waste-based preservatives, coagulation agents and dietary supplements); SDG-13 (climate action—crustacean-waste-based agrochemicals and fertilizers), target 13.1; SDG-14 (life below water), target 14.3 (crustacean-waste-based marine oil spill treatment agents); and SDG-15, target 15.3 (life on earth—crustacean-waste-based biostimulants, biofungicides and biopesticides).

Although several chitosan-based medical products are commercially available (such as hydrogels and wound-healing bandages), more products are expected soon, contributing to the development of safer technologies to achieve good health and well-being (SDG-3). Chitosan-covered gauze can be used as an inexpensive uterine packing material for more effective control of postpartum haemorrhage through reducing the risk of infection[41], directly contributing to the realization of target 3.1 ("reduce the global maternal mortality ratio"). Chitosan oligosaccharides have been investigated in trials using rats for their neuroprotective effects on hypoxic–ischemic brain damage, a major cause of newborn morbidity and mortality in recent years[42]. Extending these findings to develop new products is expected to contribute to the realization of target 3.2 ("end preventable deaths of newborns"). Furthermore, the immunostimulatory properties of chitosan reported since the 1980s[43], along with its ability to efficiently penetrate through mucosal surfaces, have been applied in vaccine delivery nanoparticles against infection with hepatitis B[44] and SARS-CoV-2[45]. Developing chitosan-based vaccines with improved immunization against communicable diseases directly contributes to the realization of target 3.3 ("end the epidemics of AIDS, tuberculosis, malaria and neglected tropical diseases and combat hepatitis, water-borne diseases and other communicable diseases")[46]. Iron-loaded chitosan pectin microparticles have recently been suggested as an iron delivery system, where chitosan as a cationic structure in conjunction with pectin as an anionic counterpart forms a unique polyelectrolyte complex for efficient iron delivery[47]. Such evidence marks the high potential of chitosan to play key roles in the future of iron delivery and food supplementation systems, addressing the ambition of target 2.2 (addressing global nutrition gaps).

As a nitrogen-containing renewable organic resource with over 10^5 mmt of annual production in the aquatic biosphere, chitin has great potential to be used as eco-friendly fertilizer to partially replace ammonia produced by the Haber–Bosch process (150 mmt per year)[48]. Chitin-derived nitrogen-containing platform chemicals, especially 3-acetamido-5-acetylfuran, have great potential for addressing SDG-13. Besides nitrogen fixation, the catalytic conversion of crustacean shells into some platform chemicals such as levulinic acid[49], acetic acid and pyrrole[50] could be a sustainable route for reducing the carbon footprints of commodity products. Chitosan is also an advantageous biopolymer for controlled-release formulations for agricultural purposes, especially in the case of pest control. The electrostatic interaction of the amine groups of chitosan with other polymers provides the possibility of obtaining stable hydrogel beads for controlled-release formulations of pesticides, such as pH-responsive chitosan-modified cenosphere/alginate composite hydrogel encapsulating Imidacloprid[51], an important role played by chitosan in realizing SDG-2 (zero hunger) environmental target 2.4.

About one third of the current global chitosan market is devoted to its application in water and wastewater treatment. Chitosan-based flocculants are commercially available, but chitosan-based adsorbents for water treatment (especially for removing micropollutants) are still under development. Owing to their hydroxyl, amine and amide functional groups, chitin and chitosan are efficient adsorbents for heavy metals and organic micropollutants[52]. In this context, chitosan has been evaluated in the forms of wet chitosan microspheres with immobilized laccase[53], cross-linked chitosan/zeolite[54], tri-functional chitosan-EDTA-β-cyclodextrin polymer[55] and ethylene diamine tetra acetic acid-functionalized β-cyclodextrin-chitosan[56]. The challenge of cost-effective removal of a wide range of micropollutants may therefore be addressed by developing specific chitin- or chitosan-based adsorbents, which would be in line with the ambitions of SDG-6.

Chitin's potential. Future research is required to expand the role of chitin in achieving the SDGs. The environmental impacts of the large-scale utilization of crustacean waste for bulk products, especially packaging and agrochemical materials, can be quantified on the basis of its effects on carbon and nitrogen cycles. Chemically

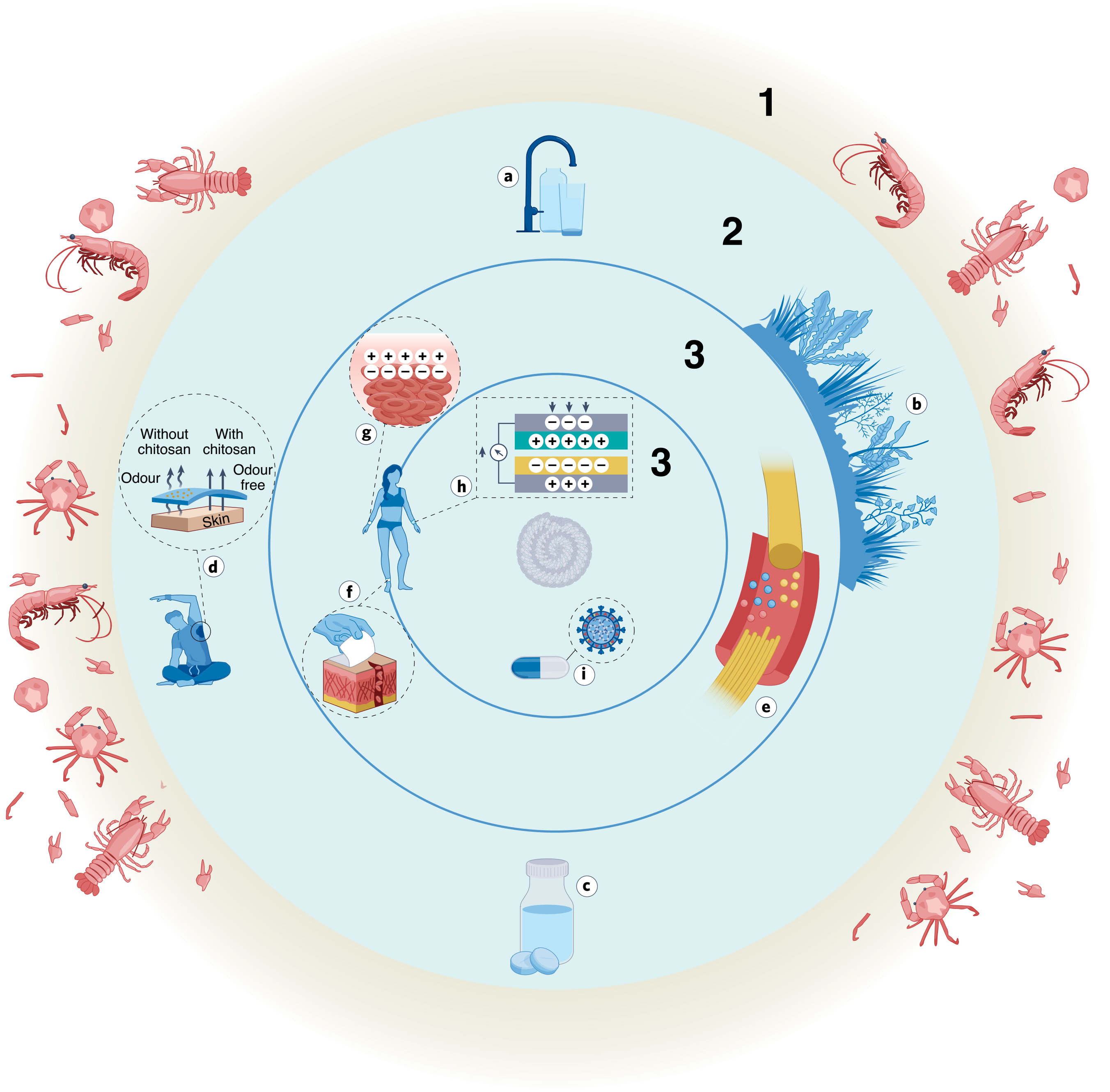

Fig. 3 | The evolutionary cascade of chitin–chitosan applications. a–d, (1) The outmost layer represents first-generation chitin–chitosan, also referred to as un- or less-processed chitin–chitosan. (2) The second layer represents the applications of second-generation chitosan, including in water treatment (as a bioflocculating agent) (**a**), agriculture (as a biofertilizer and biopesticide) (**b**), biodegradable packaging (**c**) and the textile industry (**d**). **e–h**, (3) Two layers are designated by 3, representing the applications of third-generation chitosan. The outer 3 illustrates the applications of biotechnologically derived chitosan, including in composites for nerve conduits (**e**), haemostatic dressings (**f**) and wound gauzes (**g**). The inner 3 represents the applications of nanotechnology-derived chitosan, including laser-processed chitosan for triboelectric power generation and two-dimensional soft nanomaterials for fully biobased electric devices (**h**), and tumour-targeting glycol chitosan nanoparticles for drug delivery (cancer nanomedicine) (**i**). The innermost circle presents the structure of chitin–protein fibrils and represents the future potentials for more advanced generations of chitosan and their applications.

derived chitin or chitosan (second-generation) is still the only commercially available source used in bulk products[57]. The industrial bottlenecks of using waste-derived chitin nanocrystals, known as chitin-nanofibrils, for producing food packaging have been assessed in a European Union project (the n-CHITOPACK project was funded for approximately €1 million), which reported that replacing non-renewable materials used in food packaging with chitin-based films could lead to a 12 mmt CO_2 emission reduction per year[4]. Such a reduction can satisfy nearly 2% of the decarbonization rate (0.6 Gt $CO_2\,yr^{-1}$) required to achieve the ambitious mitigation scenario that would limit 2100 warming to 1.5 °C (RCP 2.6—2017 scenario)[58]. Chitin has the potential to provide a nitrogen-containing agrochemical that can be used instead of petrochemically derived ammonia to address concerns about the effects of fossil-fuel-derived ammonia on global nitrogen cycles. Crustacean waste with an annual production rate of 8 mmt could provide about 0.7 mmt of nitrogen that could replace 0.85 mmt of ammonia, nearly 0.5% of the global ammonia demand. Nevertheless, its role in reducing carbon and nitrogen footprints does not represent the totality of chitin's beneficial sustainable value or its sustainable impact, especially when economic, environmental and social (health) issues are considered together.

While allergenicity concerns would need to be addressed, the shift from polypropylene- to chitin-based films in the food packaging industry would exert a positive effect on the 'carcinogens' impact category, even with the current 'non-environmentally-optimized' extraction methods[59]. The carcinogenic impacts of chitin-based films (defined as the annual number of deaths caused by the substance) are stated as being 72% lower than those of polypropylene films[59]. Moreover, a considerable amount of toxic pesticides, 1,000 times the amount reaching target pests, are currently released into the ecosystem, threatening human health on a global scale[60], which could be largely prevented through commercializing chitosan-based formulations to enhance the targeted and controlled release of pesticides.

Conclusions and future directions

It has been predicted that global seafood consumption will increase during the next 30 years by 36–74%[61]. Despite there being eight years remaining to address the SDGs, only 15% of the intended progress has been made on target 12.3 regarding food loss and waste[62]. Given the levels of research funding highlighted in this paper, crustacean waste valorization should see accelerated progression in the near future.

Current technologies for chitosan production suffer from delivering a lack of quality in terms of achievable purity and reproducibility, sustainability issues through emitting heavy pollution during the production process, or high production and storage costs. The biological properties of extracted chitin and its derivatives already form important components of advanced biomaterials. This area merits further investments in developing technologies based on protein engineering and cell factories to harness the full potential of this waste stream. The production of third-generation chitin or chitosan polymers may address these challenges in the future. The ambition of producing a homogeneous and application-specific chitosan structure with a predetermined acetylation pattern could pave the way for the highly sophisticated use of chitosan, particularly as a biodegradable cationic polyelectrolyte in advanced biomaterials. Knowledge creation on the relationships between the acetylation pattern and different properties of chitosan at the molecular level is thus an important aspect for future studies in the field.

If industry and public awareness were increased, the demand for chitin-derived products such as smart food packaging materials would expand, acting as a driver for technological developments in crustacean waste valorization. However, life sciences researchers need to explore mitigation options for products of animal origin and address challenges such as allergenic or viral contaminations of waste-derived chitosan. Without these advances, the ability to fabricate highly sophisticated biomaterials for special applications in the pharmaceutical and medical industries will be limited.

It is time to reimagine the value of crustacean-waste-based products to support future food systems through shell biorefineries, not only from an economic resilience perspective but also to mitigate sustainability and human health concerns. Such attention will ensure that this important food system waste product can become a resource that is utilized in line with the ambitions of the United Nations SDGs.

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Author contributions

H.A. conceptualized the project, analysed the data and wrote the original draft. M.S., L.M. and J.F.K. analysed the data and reviewed and edited the original draft. J.G. collected and analysed the industrial data. S.M.M.B. studied the applications of chitosan and developed the illustrations. M.A., V.K.G. and M.T. contributed to this work throughout its conceptualization, including obtaining resources and funding, supervision, writing and editing.

Competing interests

The authors declare no competing interests.

Additional information

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