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Lobster Shells: A Sustainable Source of Biogenic Materials and Their Extractions and Applications

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Lobster shell derivatives have the potential to be a valuable resource for sustainable development and innovation. This article outlines the methods and research advancements for isolating minerals and chitosan from lobster shells and converting them into functional materials. The different types of methods of extraction of major components are discussed in detail Additionally, it discusses their applications in diverse fields. This article gives a comprehensive summary of the present state of research in this field. Also, it presents a future research outlook, highlighting areas for further investigation and advancements in the field.

Keywords: Lobster shell; biogenic material; chitosan; hydroxyapatite; extraction; shell waste.

Key Points:

- Lobster shells, a waste product from the seafood industry, can be a valuable resource for sustainable development.
- Extracting minerals and chitosan from lobster shells offers a way to create new functional materials.
- This article offers a thorough overview of the current state of research utilizing lobster shell derivatives.

1. INTRODUCTION

Crustaceans are a class of segmented marine invertebrates, predominantly composed of lobsters, shrimps, and crabs. These creatures are extensively caught for their succulent meat, which is subsequently processed on a large scale for worldwide export as popular seafood dishes [1]. The lobster food industry, a global enterprise, is primarily concentrated in three countries: Canada, the United States, and Australia [2]. The four major commercial lobster species are the American lobster (Homarus americanus), rock lobster (Jasus sp), tropical or spiny lobster (Panulirus sp), and European lobster (Homarus Gammarus [2]. India's northwest coast is highly abundant in lobster resources, contributing to approximately three-quarters of the country's entire lobster landing. The Panulirus homarus spiny lobster, Panulirus polyphagous (Herbst), and scyllarid Thenus orientalis (Lund) are the dominant species in the region [3,4,5]. In recent years, there has been a notable surge in interest among researchers to explore innovative methods for converting marine resources into highly valuable chemicals and minerals. This can be attributed to the fact that such resources are found to be rich in minerals, chitosan, and other similar components. As a result, there is a growing need to develop effective and efficient techniques to leverage these resources and extract their full potential. This article aims to discuss the extraction of major lobster shell components and their various applications.

2. COMPONENTS

Lobster shells are made up of three major components: minerals (36%), proteins (29%), and commercial chitin or chitin derivatives (23-25%), with trace amounts of lipids, Pigments, and other minerals [6]. While the percentage of each ingredient changes according to species, seasons, ages, and origins, the structures are consistent.

2.1 Chitin and Its Derivatives

Chitin is a naturally occurring polymer made up of poly [(1! 4)-linked N-acetyl-b-D-glucosamine], the second most prevalent after cellulose. It has an estimated annual production of around 100 billion tons and three crystalline polymorphic forms: a-chitin, b-chitin, and g-chitin, in declining order of abundance. A-chitin's chain orientation is antiparallel, which promotes stronger inter-chain hydrogen bonding, resulting in excellent crystallinity and thermodynamic stability while making it difficult to dissolve in most solvents. Chitin derivatives, such as chitosan, have a large economic potential in food, agriculture, water treatment, healthcare items, the environment, medicines, biomedicine etc. Chitin and chitin derivatives are in high demand globally, with estimated quantities of 11,400 tons for chitin and 33,400 tons for chitin derivatives [7,8].

The method for extracting chitin involves.

2.2 Chemical Extraction

It consists of the following steps Grinding into a fine powder, demineralization (DM), deproteinization (DP), depigmentation, and

deacetylation to provide chitosan, Acid treatment (HCl, HCOOH, HNO_3, CH_3COOH, and H_2SO_4) is the primary method for demineralizing shells, eliminating minerals such as calcium carbonate and calcium phosphate by raising the extraction temperature above 100°C for an extended period [9]. Harsh acid treatment may cause chitin depolymerization and deacetylation. Mild acids such as formic acid, acetic acid, citric acid, and sulfuric acid are effective remedies to these issues, although the recovered chitins produced a significant residual ash content [10]. Demineralized shells are deproteinized using readily accessible alkalis such as NaOH, KOH, Na_2CO_3, $NaHCO_3$, Na_2SO_4, $NaHSO_4$, Na_3PO_4, etc. to eliminate pigments, particularly carotenoids, various chemical solvents, including acetone, ethanol, as well as potent oxidants such as H_2O_2, NaOCl, and $KMnO_4$, are routinely utilized for durations of 10 to 20 minutes, before being dried at ambient temperature for two hours. The conventional chemical procedure for transforming chitin into chitosan, which involves concentrated NaOH, and elevated temperatures, and is commonly employed for mass production due to its low cost and short processing time, has been noted to pose significant environmental concerns, poor reproducibility, and high energy consumption. The use of glycerol as a reaction solvent for the conversion of chitin to chitosan, however, offers certain advantages, such as the recycling of glycerol as well as the reduction of the alkali concentration necessary for the deacetylation reaction, thereby mitigating the environmental impact [11].

2.3 Fermentation Processing Method

The process of extracting chitin has evolved, with new and innovative techniques emerging as alternatives to conventional chemical procedures. Microorganism-based fermentation is one such method that offers a promising and environmentally friendly solution. This method involves using carefully selected bacterial strains that produce lactic acid and proteases to carry out the fermentation process. During this process, the generated lactic acid combines with calcium carbonate in the chitinous fraction to form calcium lactate, which can be eliminated through precipitation [12,13]. Additionally, the low pH environment created during fermentation restricts the growth of spoiling microbes. The extracellular proteases produced by the added lactic acid bacteria are primarily responsible for lobster shell deproteination, further contributing to the efficiency of the process.

2.4 Enzymatic Extraction

An enzymatic extraction is a novel approach to chitin extraction that uses proteolytic organisms or commercial proteases such as alcalase, papain, pepsin, pancreatin, and trypsin. Alcalase is the most widely used commercial protease for removing proteins from lobster shells. Enzymatic extraction is a quicker and more convenient method than previous ones. However, highly purified chitin still requires demineralization with organic or inorganic acid. It should be noted that if enzymatic deproteination is performed first, the effectiveness of proteases may be limited by minerals found in lobster shells. Therefore, demineralization should be conducted before enzymatic extraction [14].

2.5 Microwave-Assisted Extraction

Microwave-assisted extraction (MAE) is a green, cost-effective, and long-term solution that can assist in the demineralization of chemical and enzymatic chitin extractions. Microwave heating primarily occurs through dipolar polarization and ionic conduction mechanisms. In particular, MAE with the lactic acid demineralization method has been found to yield high quantities of chitin with minimal mineral residue (0.2%). Microwave-intensified lobster shell protein hydrolysate has good solubility, emulsification, bubbling, water and oil absorption, and nutrient content for food applications [15]. Overall, these innovative techniques offer promising solutions for extracting chitin sustainably and efficiently.

2.6 Ultrasound-Assisted Extraction

Ultrasound-assisted extraction (UAE) is a physical extraction technology that utilizes ultrasonic waves to disrupt the cells of the material and release the desired components more quickly and efficiently. The cavitation impact of ultrasound increases the solubility of protein linked with chitin by depolymerizing macromolecules, dissociating covalent bonds in polymer chains, and dispersing aggregates.

2.7 HOW-CA (Hot Water and Carbonic Acid) Approach

An alternative method of obtaining chitin is the HOW-CA method, which is an acronym for Hot Water and Carbonic Acid. The HOW-CA technique employs only water and CO_2 as reagents, along with hot water-treated proteins and carbonic acid-solubilized minerals, to

minimize costs and waste [16]. The HOW-CA process yields high-quality chitin (90%) with minimum deacetylation, making it suitable for large-scale production.

2.8 Ionic Liquids

Ionic liquids (ILs) have superior selectivity, lesser environmental impact, strong thermal and chemical stability, excellent conductivity, and better solubilizing capacity than standard organic solvents. However, ILs are controversial due to their toxicity and non-biodegradability [17].

2.9 Deep Eutectic Solvents

In recent years, various experiments have been conducted to extract chitin and its derivatives using deep eutectic solvents (DESs) instead of ionic liquids (ILs). DESs have properties similar to ILs, but they are more advantageous due to their biodegradability, low cost, and simple manufacturing process [18].

2.10 Ethylenediaminetetraacetic Acid

Ethylenediaminetetraacetic acid (EDTA), a metal chelator that can demineralize chitin, can be used instead of hydrochloric acid. This chemical method has minimal impact on the chitin molecular chain and allows for easy recovery or recycling of EDTA [19].

2.11 Electrochemistry

Electrochemistry is a relatively unknown field that is gaining interest. In one investigation, shrimp shells were electrolytically treated with 1% acidic and alkaline water at 20 V for 6 hours. After removing all minerals and proteins, 19.5% of the extraction ratio was successfully recovered [20]. The extraction of chitin from lobster shells has not yet been researched.

3. PROTEIN

Lobster shells, also known as carapace, have been identified as a potential source of protein, containing approximately 25% protein, and may serve as a promising avenue for protein extraction (Venugopal V 2009). The nutritional value of lobster protein can be considerably increased by the natural combination of astaxanthin, a powerful antioxidant that creates a protein complex known as carotenoprotein. This compound is discovered in high concentrations (16%) in lobster shells (Tu et al., 1991) [21,22]. Furthermore, regardless of the pH or ionic strength of the solution used, the solubility of lobster shell protein (LSP) recovered in either aqueous extraction or enzymatic digestion exceeds 93%. Additionally, lobster protein hydrolysate (LPH) has been shown to exhibit good emulsifying properties (69.7 vs 50.3 m2/g of cow gelatin) (He et al., 2016) [23,24].

4. ASTAXANTHIN

Astaxanthin, a potent antioxidant, is present in lobster shells and is known to enhance the nutritional value of lobster protein by forming a protein complex called carotenoprotein. The astaxanthin content in crustaceans is known to vary depending on the species, season, and growing conditions. Astaxanthin can occur in both free and complex forms, including carotenoprotein. The high hydrostatic pressure technique has been shown to yield food-grade astaxanthin in the shells of American lobsters [25].

5. MINERALS

Calcium carbonate extracted from lobster shells is biodegradable and can be safely used in high-value applications, including human consumption. Lobster minerals, being a rich source of calcium, are used in the manufacturing of meals, calcium-fortified goods, and nutraceutical supplements. Lobster calcium has high solubility and bioavailability, making it an excellent ingredient for promoting healthy bone metabolism. In comparison to commercial competitors such as CCS, CCL, and casein, the lobster mineral has superior solubility and bioavailability, as well as water and oil, bind capabilities. In vitro experiments have shown that lobster mineral promotes cell proliferation in both human bone and skin cells without causing significant cytotoxicity in macrophages.

5.1 Extraction of Minerals

5.1.1 Chemical extraction

To recover minerals from raw materials, it is essential to perform demineralization. This process is typically carried out using acidification, particularly with hydrochloric acid, as the carbonate component reacts with the acidic ingredient to cause mineral precipitation. Acid demineralization can produce minerals ranging from 69.4 to 100%, depending on various reaction factors such as temperature, pH, duration, and the quantity of acid utilized [26].

Table 1. Summary of study reporting material extractions and their application of different species of lobster shell derivatives

SNO	Lobster species	Materials	Method of Extraction	Application
1.	Lobsters [28] (available in Australia)	Calcium	Microwave-intensified lactic acid demineralization	1. Nutrients in Foods and Calcium-Fortified products 2. Proliferation of Bone and Skin Cells
2.	Thenus unimaculatus [29]	Chitin	Chemical method	1. Antioxidant 2. Antidiabetic 3. Anticoagulant
3.	Panulirus Homarus [30]	Hydroxyapatite	Precipitation method	1. Application on Bone tissue engineering 2. enhance the apatite mineralization bioactivity
4.	Panulirus Homarus [31]	Bioceramic Hydroxyapatite Beta TCP (Tricalcium phosphate)	Precipitation method	Biocompatibility for human bone
5.	Homarus americanus [32]	Chitin	Microbial degradation by chitinolytic microorganisms	Antimicrobial activity
6.	*Panulirus Homarus* [33]	Hydroxyapatite Beta TCP (Tricalcium phosphate)	porogen leaching method with polyethylene oxide (PEO)	biocompatibility, bioactivity, and osteoconductivity

5.1.2 In biotechnology extraction

Bacteria such as Lactobacillus sp are commonly utilized to ferment crustacean shells, producing lactic acid and enzymes. The lactic acid produced by these microbes reacts with the calcium carbonate in the shells to make calcium lactate, which can be eliminated by washing, which resembles the chemical demineralization process. The success of this process depends on several factors such as the number of microbes present, duration of reaction, specific species of bacteria, environmental factors like temperature and pH, and the presence of carbon sources [27] (Table 1).

6. APPLICATION OF CHITOSAN AND MINERALS DERIVATIVES

6.1 Application of Chitosan and Their Derivatives [34]

The applications of chitosan in nanotechnology are diverse and varied. Nanotechnology provides a range of possibilities for the enhancement of biological systems. Specifically, it offers the potential for the development of anticancer, antibacterial, and antimicrobial agents, tissue engineering as well as improvements in enzyme immobilization, wound dressing, cosmeceuticals, stem cell technology, drug delivery, obesity treatment, and anti-inflammatory agents [35].

Recent research has revealed promising alternatives to traditional antibiotics in light of the growing challenge of antimicrobial resistance. Researchers proposed a novel approach for modifying chitosan using salicylhydrazide, leading to the creation of two derivatives: salicylhydrazide chitosan Schiff's base (SCsSB) and salicylhydrazide chitosan (SCs. This advancement shows promising targeted activity based on microbial cell wall structures [36]. Nanocomposite materials are also used in the development of drug/gene delivery systems and nano scaffolds for tissue engineering, bone tissue regeneration, and cell scaffolds, among other applications.

6.2 Application of Minerals

The use of minerals is widespread in several industries, including pigments, fillers, soil conditioners, rubber, plastics, construction, paper, pharmaceuticals, and agriculture. Calcium carbonate and phosphates are the most commonly used minerals in these industries [26].

Calcium carbonate is also a valuable fertilizer in agriculture and aquaculture. Its nanoparticles can be employed in phytopharmaceuticals or pesticides, protein stabilizers, emulsifiers, antioxidants, texture enhancers, microbiological control agents, and laxatives.

Hydroxyapatite and tricalcium phosphate are commonly used minerals in biomedical applications, dentistry, bioimaging, separation, purification, catalysis, surface treatment, and energy [37]. The versatility of these minerals makes them valuable components in various industries where their unique properties can be harnessed to achieve a range of desired outcomes.

7. FUTURE SCOPE IN THE MEDICAL AND DENTAL FIELD

Research has shown promising potential for utilizing it as a biogenic material. However, it is imperative to carry out further research to explore and fully comprehend their applicability in this particular domain.

Some potential applications include [34,37,35] the prevention of demineralization of enamel, Enhancement of Remineralization of enamel, Bone tissue engineering, Prevention of plaque and biofilm formation, Stimulation of salivary secretion, Improvement of wound healing, Implant coating, Treatment of Dental hypersensitivity, Periodontal tissue regeneration, etc. Biomedical applications, such as tissue engineering scaffolds, and regenerative medicine, controlled drug delivery systems [36], have witnessed significant advancements. Nevertheless, challenges persist in attaining precise control over drug release kinetics, augmenting tissue regeneration capabilities, and fostering enduring biocompatibility.

8. CONCLUSION

Lobster shells have emerged as a promising topic in the realm of biogenic materials. Their potential for development and application is substantial, as they offer a cost-effective and sustainable solution for use as a biogenic material. However, the existing body of research on lobster shells and their derived functional materials remains limited, thus highlighting the need for further scientific and technical investigation to overcome the current obstacles in their application.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of this manuscript.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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