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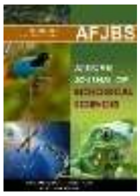

From Disposal to Asset: Comprehensive Insights into the Utilization and Management of Marine Shell Industrial Waste

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Abstract

The surge in global seafood production has led to a significant increase in marine shell waste, posing economic burdens on waste management systems worldwide. In regions heavily reliant on seafood production, such as coastal areas of India, shell waste accumulation is particularly pronounced. Understanding the composition of marine shell waste is crucial for developing effective utilization and management strategies. The current study presents insights into the utilization and management of marine shell waste across different sectors, including seafood processing, aquaculture, manufacturing, biotechnology, and construction. Bivalve shells, crustacean shells, and Mollusc shells are identified as major components of marine shell waste, with calcium carbonate, chitin, proteins, and aragonite being predominant constituents. Various potential applications of these components, such as soil amendments, animal feed additives, biodegradable plastics, and construction materials, are discussed. Utilization methods for extracting valuable components from marine shell waste are explored, including chemical and fermentation processes. Overall, this study highlights the transition of marine shell waste from a disposal burden to a valuable asset. By adopting innovative technologies and sustainable practices, industries can maximize the value and utility of shell waste, contributing to both economic prosperity and environmental conservation in coastal regions.

***Keywords*:** Shell waste, Chitin, Sustainability, Molluscs, Crustacean.

1. Introduction

The exploitation of innovative environmental and ecological materials obtained from marine wastes has been the subject of fundamental investigations in the past several years. The exponential growth of global seafood production, driven by increasing consumer demand, has resulted in a substantial surge in marine shell waste. This waste poses a considerable economic burden on waste management systems, particularly in regions heavily reliant on seafood production. India ranks as one of the major seafood processing industries in the world (Sasidharan *et al*., 2013). Coastal cities and regions with a robust seafood export and processing infrastructure also contribute significantly to the generation of sea shell waste. Statistical analysis reveals that millions of metric tons of discarded shells, primarily from crustaceans and molluscs, are generated annually. The shell wastes consist of many commercially valuable products, such as, chitin, calcium carbonate, proteins, and carotenoids. Processing of shell wastes is a source of wealth (Suryawanshi *et al*., 2019). Geographical disparities accentuate the localized impact, with coastal areas experiencing disproportionate waste accumulation.

Improper disposal practices result in habitat destruction and ecosystem degradation, as accumulated shells alter coastal environments and disrupt marine biodiversity (Peceño *et al*., 2021). Addressing the environmental impacts requires holistic approaches that prioritize sustainable resource utilization, pollution prevention, and ecosystem preservation. Moreover, the utilization of marine shell waste for sustainable material development offers a promising avenue for addressing both environmental concerns and economic challenges. Researchers and industries alike are exploring innovative techniques to harness the potential of these discarded shells, thereby mitigating the adverse effects of their accumulation while simultaneously creating value-added products.(Islam *et al*., 2004) Through various extraction and processing methods, valuable components such as chitin, calcium carbonate, proteins, and carotenoids can be recovered from the waste stream.

The versatile nature of these components opens up a plethora of applications across multiple sectors. Chitin, for instance, has gained attention for its diverse range of uses in fields such as biomedical engineering, agriculture, food packaging, and wastewater treatment (Peceño *et al*., 2020). Similarly, calcium carbonate derived from marine shells exhibits properties suitable for applications in construction materials, paper production, and pharmaceuticals. Furthermore, proteins and carotenoids present in the waste stream offer potential avenues for the development of functional foods, nutraceuticals, and cosmetic formulations. However, despite the significant potential benefits, challenges persist in the effective utilization of marine shell waste. Technical hurdles related to extraction efficiency, scalability, and product quality require careful consideration. Moreover, logistical and regulatory barriers may impede the adoption of sustainable practices, particularly in regions with inadequate waste management infrastructure (Mathew *et al*., 2020).

Collaborative efforts involving academia, industry, government agencies, and local communities are essential for overcoming these challenges and unlocking the full potential of marine shell waste. By fostering innovation, promoting knowledge exchange, and implementing supportive policies, stakeholders can work towards creating a circular economy model where waste is viewed as a valuable resource rather than a burden. Additionally, public awareness and education campaigns can play a crucial role in encouraging responsible consumption and waste management practices, thereby reducing the environmental footprint of seafood production and processing industries. In conclusion, the sustainable utilization of marine shell waste represents a multifaceted solution to environmental, economic, and social challenges. By harnessing the inherent value of these discarded shells, we can not only alleviate the strain on waste management systems but also contribute to the development of eco-friendly materials and products. However, realizing this potential requires concerted efforts and a collective commitment to embracing innovation and sustainability principles.

2. Environmental impacts of seashell waste

Seashells are part of the almost 7 million tons of "nuisance waste" that the seafood sector discards annually, the majority of which is disposed of in landfills or the ocean(Tsai *et al*., 2021). Such debris can be recycled and reused as a great substitute for disposal. The environmental impact of marine shell industrial waste is profound and encompasses various interconnected factors. Improper disposal practices result in habitat destruction and ecosystem degradation, as accumulated shells alter coastal environments and disrupt marine biodiversity (Branigan *et al*., 2020). Moreover, the decomposition of marine shells releases organic matter and nutrients into water bodies, leading to eutrophication and the subsequent disruption of aquatic ecosystems. The transportation and disposal of this waste contribute to carbon emissions, exacerbating climate change. Additionally, the loss of valuable resources like calcium carbonate, inherent in marine shells, perpetuates resource depletion and intensifies the strain on natural mineral reserves. As marine shell waste occupies landfill space, it exacerbates the challenges of waste management, furthering the urgency for sustainable solutions. Furthermore, marine pollution ensues when waste is improperly discarded, posing threats to marine life and exacerbating the global issue of ocean pollution.

3. Seashell composition and its potency

Approximately 50–60% of the total weight is trash, which is produced during the industrial processing of shellfish for human consumption, such as shrimp, crab, and krill (Islam, 2004). These shells are of different kinds and are used for the extraction of valuable products, for human use and supplements. The shell wastes consist of many commercially valuable products, such as, chitin, calcium carbonate, proteins, and carotenoids.

Different types of shell wastes are dealt. Bivalve shells are among the most abundant types of marine shell waste belonging to mollusc with two hinged shells, such as oysters, mussels, clams, and scallops (Hart, 2020). After the edible meat is harvested for consumption, the shells are typically discarded. Bivalve shells are composed primarily of calcium carbonate and may vary in size, shape, and thickness depending on the species. Another type is the Crustacean shells, also known as exoskeletons found in crustaceans such as shrimp, crab, lobster, and crayfish. After the edible meat is extracted during processing, the shells are often discarded which contains chitin, calcium carbonate and protein (Hayes et al., 2008). Mollusc shells, exemplified by those of abalone and mussels, are abundant biogenic materials boasting unique properties like nacre's toughness. Beyond their aesthetic value in jewellery, these shells inspire biomimetic materials research. Additionally, their composition, rich in calcium carbonate, offers potential for eco-friendly applications in fields ranging from construction to water purification, demonstrating their versatility and environmental significance. The composition of the shells and their potency are given underneath in brief:

a. ***Calcium Carbonate ($CaCO3$):*** Predominant component in marine shells, comprising a substantial portion of their structure (Miron *et al*., 2022) . The seashell material attracts attention due to high calcium carbonate content, low-cost and availability provided by the fast developing seafood industry (Barros *et al*., 2009). The mussel shell constitutes approximately 31-33% of the total mussel weight in the cannery and processing facilities (Azarian & Sutapun, 2022). This shell is a composite biomaterial, with the mineral phase, primarily calcium carbonate, making up 95-99% of its weight. The remaining 1-5% comprises an organic matrix. (M.C. Barros *et al*., 2007). Valuable for the production of calcium-based products, such as calcium supplements, and as a substrate for the synthesis of biomaterials through biotechnological fermentation processes.

b. ***Chitin:*** Chitin is a biopolymer that occurs naturally and is composed of 2-acetamido 2-deoxy-b-D-glucose linked by a b (1,4) bond. Similar to cellulose, it is the second most prevalent polymer on Earth and serves as a structural polysaccharide. Abundant in the exoskeletons of fish (silver and pang scales), some mollusks (oyster shell and mussels), and crustaceans (prawn and crab), The entire yearly output of chitin in aquatic habitats was calculated to be 1.3~1012 kg for marine ecosystems and 2.8~1010 kg for freshwater environments, respectively (Owuamanam & Cree, 2020). Extracted chitin can be enzymatically converted into chitosan, a versatile biopolymer with applications in pharmaceuticals, agriculture, and water treatment, contributing to sustainable waste utilization.

c. ***Proteins:*** Found in varying proportions in different types of marine shells, such as abalone shells and sea urchin shells. The shell matrix proteins of the mollusc start to reveal their secrets after more than 20 proteins or protein families have been identified (C. Zhang & Zhang, 2006). The protein component of marine shells can be explored for the production of bioactive peptides or as a substrate for enzymatic processes in biotechnological fermentation, offering potential applications in medicine and industry.

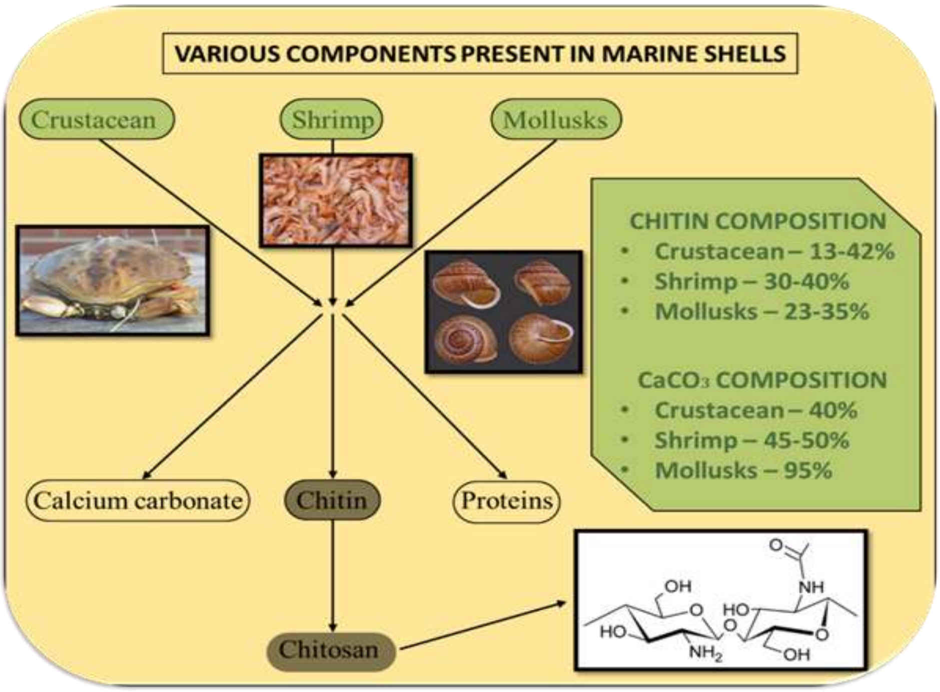

Figure 1. Representation of components of marine shell

d. ***Aragonite:*** Commonly found in the cuttlefish bones, providing structural integrity (Suryawanshi & Eswari, 2022). Aragonite is a crystalline form of calcium carbonate with applications in materials science. Additionally, the chitin derived from cuttlefish bones can be explored for various biotechnological applications, contributing to the development of novel materials and processes.

4. Utilization and methodology

One important source of valuable minerals, including chitin, calcium, protein, and carotenoids, is the use of marine industrial food-processing waste, including the shells of shrimp, crabs, and krill (Nguyen *et al.*, 2020). These shells include varying amounts of chitin, usually between 15% and 40%, depending on species and culture circumstances (D. H. Lee *et al.*, 2021). However, the problem of firmly bound proteins and calcium must be overcome in order to extract chitin effectively, requiring a series of pre-treatment steps. Proteins and calcium carbonate are frequently extracted from these shells using chemical and fermentation processes. However, using conventional chemical processes frequently results in waste, excessive expenses, and damage of the environment. Shells—mollusc shells in particular—have drawn attention in recent decades due to their distinctive morphological and biological characteristics. Interestingly, nacre—the aragonite layer found in mollusc shells—has the remarkable ability to withstand fractures and has demonstrated potential for promoting bone growth. Water treatment, medicine, and pharmaceuticals are just a few of the industries that use chitin, a biopolymer that is often found in the shells of marine crustaceans. One viable option for the long-term use of marine shell debris is biotechnological fermentation processes.

Lactic fermentation bioprocesses, for example, can efficiently condition the medium by utilizing certain bacterial strains to produce lactic acid and proteases, which facilitate the extraction of chitin (Suryawanshi *et al*., 2019). Additional fermentation techniques, including enzymatic hydrolysis or the use of fungi, have the potential to produce useful products from shell waste. Moreover, waste from the industrial processing of marine shells, which makes up around 50–60% of the total weight, offers potential for the production of minerals like hydroxyapatite (HAP), which has potential use in bone tissue engineering (Suresh & Chandrasekaran, 2020). To sum up, trash from marine shells is a rich source of important minerals and compounds. Through the implementation of inventive techniques for extraction and exploitation in conjunction with sustainable biotechnological processes, we can efficiently convert this waste stream into valuable resources that support economic viability and environmental sustainability.

4.1. Pre-treatment

Dense chitin fibres seen in the shells of crustaceans and molluscs are connected by protein covalent connections. Calcium carbonate, in particular, is the mineral salt that is deposited to further fortify the chitin-protein matrix. According to (Sini *et al*., 2007), the complexity of the shell structure has risen due to the inclusion of proteins in the shell wastes. Over the course of the subsequent pre-treatment procedures, the proteins and calcium were carefully eliminated in order to extract pure chitin from such a complicated structure. The pre-treatment procedure included a combination of physical, chemical, and fermentation methods. Alkaline or enzymatic hydrolysis of the proteins within the shell was accomplished by the process of deproteinization. Using either inorganic or organic acids from fermentation processes, calcium carbonate deposits were eliminated throughout the demineralization process.

Depending on the situation, pigment removal may be required as an extra step. This can be done with an appropriate organic solvent mixture (Younes and Rinaudo 2015). Remarkably, the pre-treatment process's yield and pace have been greatly impacted by the size of the particles (Hou *et al*., 2016). As a result, before beginning the pre-treatment procedure, shell wastes must be reduced in size. Several techniques, including demineralization (treatment with hydrochloric acid) and deproteinization (treatment with sodium hydroxide), have been used to remove these contaminants from chitin shell waste, and numerous studies have reported great results.

4.2. Chemical extraction method

The traditional chemical extraction process for chitin involves various steps, such as demineralization (DM), deproteination (DP), bleaching/discoloration and deacetylation to form CTS. Concentrated acid and alkali solutions are used in these procedures, which are run at high temperatures for an extended period of incubation(Lagat *et al*., 2021). The stages involved in chemical extraction use more energy, take longer, and use more solvents. Strong acids and bases that remove chitin have a number of detrimental effects, including: (A) destroying the physico-chemical characteristics of chitin; (B) producing wastewater effluent that contains chemicals; and (C) raising the expense of the chitin purification process (Dhillon *et al*., 2012). For this reason, a safe and affordable extraction method for chitin is needed. Additionally, the use of microorganisms (MOs) for chitin extraction is becoming increasingly popular as green extraction methods based on the idea of "Green Chemistry" gain ground (Janković *et al*., 2020). High repeatability in less time, easier manipulation, less solvent usage, and less energy input are all benefits of the biological extraction of chitin. The biological extraction approach has the potential to replace chemical procedures, which have several drawbacks when used to a commercial scale. However, it is presently restricted to laboratory size experiments.

Chitin extraction is a crucial step in obtaining chitin from marine wastes, affecting its purity, degree of acetylation (DA), molecular weight (MW), and polydispersity index. Chemical methods are currently used on a commercial scale, while bio-extraction has gained interest. Chemical extraction involves removing non-edible materials from shellfish, such as shrimp, crab, and krill, which are considered a major environmental pollution due to uncontrolled dumping (Dhillon *et al*., 2012). However, shrimp waste is often used as a substrate for chitin and CTS production due to its chemical composition and availability in the seafood industries. Traditional chemical methods, such as demineralization treatment with HCl, HNO_3, H_2SO_4, CH_3COOH, and HCOOH, are used to extract chitin from crustacean shell waste (CSW) (Sandford, 2003). However, these methods have negative implications, such as harming the physico-chemical properties of chitin and causing detrimental effects.

Biological extraction methods, on the other hand, remove pigments like melanin and carotenoids from crushed shells using various methods. These methods can result in effluent wastewater containing chemicals and increase the cost of chitin purification processes. The quality of extracted chitin is affected by the extraction method and the nature of the chitin (Kjartansson *et al*., 2006).

Chitin is the raw material used in commercial production of CTS and glucosamine, with an estimated annual production of 2000 and 4000 tons, respectively material (Sandford, 2003). Chitin can be deacetylated to create CTS, a more flexible and soluble polymer. The process involves hydrolysis of acetamide groups of chitin by severe alkaline hydrolysis treatment, which releases amine groups (NH_2) and imparts a cationic characteristic to CTS (Janković *et al*., 2020). Deacetylation can be performed at room temperature or elevated temperature depending on the final product desired. The quality of the extracted chitin depends on the molecular weight, polydispersity, and deacetylation (DA) of the polymer (Jung *et al*., 2007). Harsh acid treatments during the DM stage may result in hydrolysis, inconsistent physical properties, and environmental hazards. High NaOH concentrations and high temperatures during DP steps can cause undesirable deacetylation and depolymerisation, limiting its use in various applications (Kjartansson *et al*., 2006; Yang et al., 2000). Environmental concerns arise from chemical extraction, which is energy-intensive and causes environmental pollution. Chemical treatments also create disposal problems for wastes, as neutralization and decontamination may be necessary due to strict government legislations (El-Saied & Ibrahim, 2020). Additionally, valuable protein components are damaged during chemical extraction, making them unsuitable for animal feed. Biological techniques, such as living microorganisms (MOs), have been proposed as an environmentally safe extraction method for chitin and CTS (Gagne & Simpson, 1993). MOs secrete proteolytic enzymes with various properties, such as wide substrate specificities and stability towards temperature, pH, and organic solvents (Zou *et al*., 2021). However, MOs-mediated extraction processes can be made economical by optimizing process parameters and recovering valuable by-products like proteins, free amino acids, carotenoids, and mineral salts, with higher economic and environmental impacts.

4.3. Biological extraction process

Bio-based products, such as food, alcoholic beverages, and biochemicals, are increasingly being developed and used due to their eco-friendliness, safety, and flexibility compared to chemical synthesis methods (Kaur & Dhillon, 2015). Fermentation is considered one of the most eco-friendly, safe, and economically feasible alternatives. Solid-state fermentation (SSF) reproduces natural microbiological processes, such as composting and ensiling, and offers numerous advantages for producing bulk chemicals and enzymes. Bacterial strains like Lactobacillus sp. and Clostridium sp. are widely used for ensiling (Atalla *et al*., 2020). Biological silage, which uses MOs to produce LA in situ, can be used for waste bioconversion, while shrimp waste ensilation can be carried out biologically or chemically. Ensilation of crustacean shells can be done in situ using by-products like whey, lignocellulosic biomass, and starch. Ensilation also provides advantages as a preservation method and allows recovery of value-added by-products, such as chitin, proteins, and pigments, with a broader market (Lagat *et al*., 2021).

MOs-mediated dewatering and dewatering (DP) and dewatering (DM) of bio-waste produce a liquor fraction rich in proteins, minerals, and carotenoids, including astaxanthin, and a chitin-rich solid fraction (Balitaan *et al*., 2020). This liquor fraction can be used as animal feed or as a protein-mineral supplement for human consumption. Dewatering of bio-waste mainly occurs by proteolytic enzymes produced by Lactobacillus, resulting in clean chitin fraction and liquor with high content of soluble peptides and free amino acids (Lin *et al*., 2021). Proteases and LA bacteria are used for DP and DM of crustacean shells, reducing the use of concentrated alkali and acid treatment (Hou *et al*., 2016). Biological DM has been used for chitin production from crustacean shells with enzyme-catalysed reactions or microbial processes involving species. DP and DM steps can be integrated, and co-fermentation using different MOs known for LA and protease producing capability can be employed (Jung et al., 2007). Researchers have explored LA fermentation combined with chemical treatments as an alternative to chemical extraction for chitin recovery, reducing the need for alkali and acid. This process removes protein and calcium through enzymatic action on tissues and solubilization of calcium by organic acids, using lactose and protease-producing bacterial strains (Kjartansson *et al*., 2006).

5. Applications of Marine shell wastes

5.1. Chitin:

5.1.1. Biomedical Materials: Chitosan, a derivative of chitin found in marine shells, has diverse biomedical applications (Baharlouei & Rahman, 2022). It can be used to create wound dressings, sutures, and scaffolds for tissue engineering due to its biocompatibility and antimicrobial properties.

5.1.2. Biodegradable Packaging: Chitin-based materials obtained from marine shells can be used to produce biodegradable and compostable packaging products. These eco-friendly alternatives to conventional plastics help reduce plastic pollution and contribute to sustainable packaging solutions.

5.1.3. Water Treatment Solutions: Chitin and chitosan derivatives can be used in water treatment applications for heavy metal removal, wastewater purification, and environmental remediation (Tsai *et al.*, 2021). Their adsorption properties make them effective agents for removing pollutants from industrial effluents and contaminated water sources.

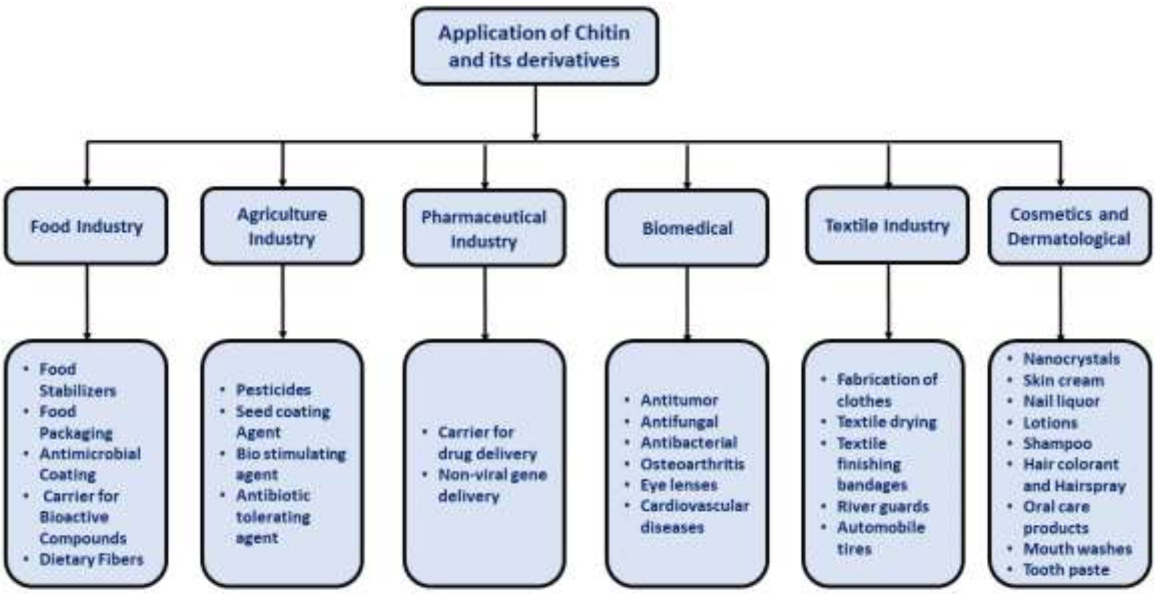

Figure 2. Applications of chitin derivatives

5.2. Calcium Carbonate

5.2.1. Construction Materials: Calcium carbonate is used as a building material in the form of limestone and marble. It is employed in the production of cement, concrete, mortar, and stucco. Its high calcium content makes it ideal for use as a filler and extender in these materials. Calcium carbonate extracted from marine shells can be used as a filler in various construction materials such as concrete, asphalt, and plaster (Barros *et al*., 2009). It improves durability, reduces costs, and provides environmental benefits by utilizing a renewable resource.

5.2.2. Calcium Supplements for Pharmaceuticals: Calcium carbonate is used as a dietary supplement to provide calcium, which is essential for bone health. It is also employed as an antacid to relieve heartburn, indigestion, and acid reflux. Calcium carbonate extracted from marine shells can be purified and used as a source of calcium in pharmaceutical formulations such as antacids and calcium supplements. This natural source of calcium offers a bioavailable and cost-effective alternative to synthetic sources.

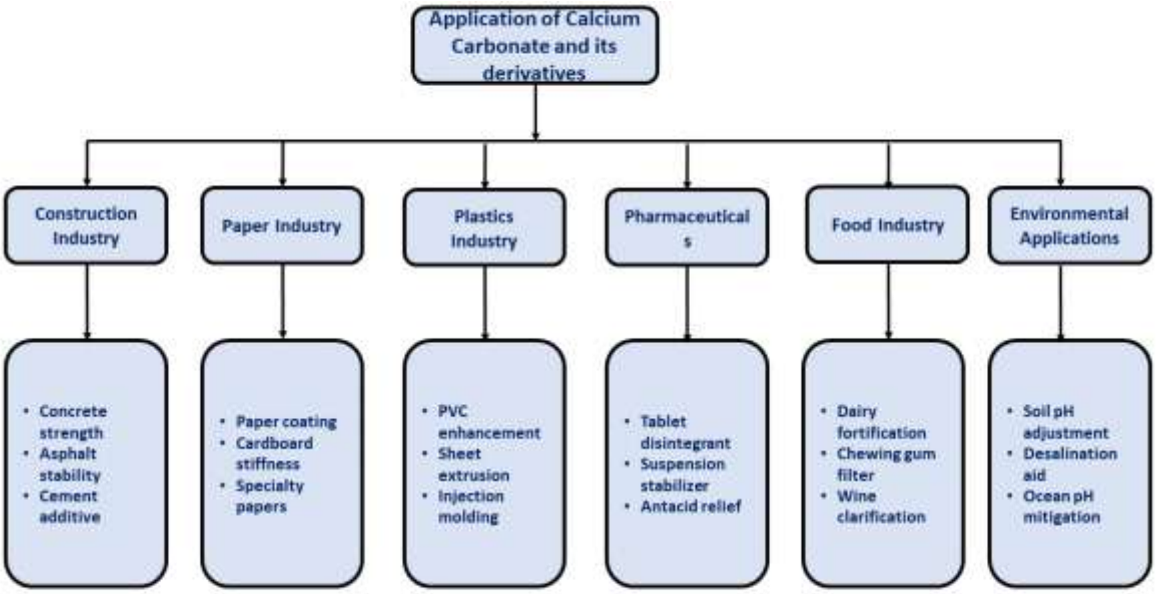

Figure 3. Applications of derivatives

5.3. Additional derivatives and its by-products

5.3.1. Protein-Rich Animal Feed: Proteins recovered from marine shell waste can be processed into high-quality animal feed supplements. These proteins are rich in essential amino acids and can enhance the nutritional value of livestock and aquaculture feeds, reducing reliance on traditional protein sources like soybean meal.

5.3.2. Carotenoid Extracts for Nutraceuticals: Carotenoids, natural pigments found in marine shells, have antioxidant properties and various health benefits (Jo *et al*., 2010). Extracts derived from shell waste can be incorporated into nutraceuticals and dietary supplements to promote eye health, skin health, and overall well-being.

5.3.3. Carotenoid Pigments in Cosmetic Formulations: Carotenoids extracted from marine shells can be incorporated into cosmetic formulations such as lipsticks, creams, and lotions for their natural colorant and antioxidant properties. These pigments provide vibrant hues and anti-aging benefits to cosmetic products.

6. Future perspectives

In light of the current research findings and practical applications, several future perspectives emerge in the realm of utilizing marine shell waste. Firstly, there is a pressing need for the advancement of extraction techniques to enhance the efficiency and yield of valuable components from these waste streams (Muthu *et al*., 2021). Research efforts could focus on exploring novel solvents, enzymatic processes, and biotechnological approaches to optimize extraction rates and purity (Aam *et al*., 2010).

Additionally, biopolymer engineering holds promise for tailoring the properties of chitin and chitosan for specific applications in biomedicine, packaging, and beyond. Circular economy initiatives are essential for integrating marine shell waste into existing industrial processes, fostering partnerships between seafood processors, waste management facilities, and product manufacturers to create closed-loop systems (Xu *et al.*, 2020). Moreover, the development of waste valorisation platforms and collaborative networks could facilitate knowledge exchange and technology transfer, accelerating the adoption of sustainable practices (Suresh Kumar *et al*., 2020). Environmental impact assessments are crucial for evaluating the sustainability of different utilization pathways, guiding decision-making and policy development. Furthermore, consumer awareness campaigns and policy support from governments can drive demand for products derived from marine shell waste, fostering a shift towards sustainable consumption choices (Muthu *et al*., 2021). By addressing these future perspectives, stakeholders can work towards unlocking the full potential of marine shell waste as a valuable resource for sustainable development.

7. Conclusion

Increased consumption of marine food had implications of their waste management a challenge as they have an impact on environment. Alternate studies are gaining interest amongst which the converting this a valuable resource is the best (Mohan et al., 2021). The industrially valuable products like chitin, calcium carbonate and proteins production from these ditch are major. This review concludes that the biological method of extraction from the shells waste is an eco-friendly and economically feasible method (Younes & Rinaudo, 2015). However, further studies can be conducted to develop an even easier for the extraction.

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