

Review Article

Utilization of chitinous wastes of economically important crustaceans and molluscs in Nigeria coastal water for improved fish production

Abstract

Background: Every year, about eight million tons of different species of crustaceans shells are produced, with several million tons of various mollusks shells world-wide. These shell wastes are usually disposed into the water body or mainland, and littered everywhere, with significant impact on the environment.

Aim: To provide a profitable way of reducing and possibly removing shell wastes, and harness them for a better purpose through eco-friendly and sustainable technological approach.

Main body of the abstract: This review underscores a broad list of economically important crustaceans and mollusks, harvestable in Nigeria coastal waters whose shells usually ended up as wastes. Chitin, being the primary component of these wastes can be extracted and deacetylated into chitosan, or synthesized into nanoparticles for better applications in various aspects of aquaculture. Both chemical and biological method of chitin extractions were discussed, however, bioextraction method was recommended due to its eco-friendliness, biocompatibility, and non-hazardousness. Various ways by which these shell wastes can be processed and utilized for improve aquaculture practice were also discussed. These include: fish growth enhancement, pond water treatment, as antioxidant, as immuno-stimulant, as antimicrobial, as drug carrier, and several other purposes.

Conclusion: There are much hidden wealth in these fisheries by-products (crustaceans and molluscs shells) if properly valorized. It has a great potential to transform aquaculture industry, and bring significant, and sustainable economic development in Nigeria.

Keywords: Aquaculture, Bioextraction, Chitinous shell wastes, Shell wastes valorization, Economic Development, Nanotechnology

1.0 Introduction

The global aquaculture output depicted about 50% expansion between year 2000 to 2019, which tends towards almost 180 million tons in the year 2019, showing a tremendous growth of about 55 million tons from year 2000. Out of the overall output, molluscs represent 13%, while crustaceans was 9% [1]. Every year, about 8 million tons of crustaceans shell wastes are produced, of which 60% represents crab mass [2]. Also, more than 10 million tons of mollusks shell are produced yearly; and oyster, clam, scallop and mussel shells represent 70% of this [3]. Of the total weight of Molluscs, shells constitute 65-90%; and this also depends on species [4]. Mussels produce and contribute more shells compared to other species of shellfish [5]. Abalone and other gastropod also contribute a significant ratio of their body mass as shells [6]. Therefore, Shells should be seen as major by-product, which should not be regarded as waste, but treated as a new raw material to be highly maximized. Unfortunately, Nigeria happens to be among those nations whose coastal marine resources are being over exploited with mass wastage of shell fish exoskeleton [7]. Moreover, uncontrolled disposal of shell into the sea are usually sent back to the land through upwelling and ocean cleansing which usually brought about a negative impact on the soil and water [8]. As a result of this, piles of shells were found in virtually everywhere,

causing environmental pollution and damage due to the foul odors that are being released from the decomposition of residual tissues attached to them[6]. From field observations, Many of these shells could be found either as harvest wastes or processing wastes from individuals or processing industries. Ways by which they are consumed are different from one place to another. They are either served after the removal of shell or processed with shell and served.

1.1 Historical utilization of shell wastes

Much values have always been attached to shells over the ages. Traditionally, this has been established and passed from one generation to another so that its economic and social value can be retained. From the archeological point of view, it was discovered that since Paleolithic periods shell has been in use as a valuable resources[9, 10] and have been used to make tools or ornaments. In several cultural setting, it has also been used as a legal tender, and in exchange for goods and services, such as cowries shells and shell beads[11, 12], even till date in some places [13]. This shows that value also determine the type of standard that can be put in place about any material, which also determine how long such standard can remains. Till date, some species of molluscs shell are still much in use because of their aesthetic value. Currently, over 5000 different species of mollusks are sold because of their ornamental worth, especially gastropods. Unfortunately, there is no adequate record on this [14, 15]. In addition, there are several failed attempt to reintroduce the effective use of shells, especially as marine ornamental ventures which involved millions of gastropods as clean up animals [16]. In several places, efforts have been made on sustainable use of these shell wastes as ornamental items, but this could not go far because there are more important way by which these shell wastes can be used which were not discovered. until in recent time when many industry begin to consider a new

and more profitable enterprise with respect to shell valorization.

The primary aim of this article is therefore to provide a broad picture of shell waste re-utilization or utilization possibilities apart from traditional and inadequate current uses. This paper also aim at finding solution to reduce wastes, harnessing them for a better purposes through eco-friendly and sustainable technological (Nanotechnology) approach in order to enhance economic growth, and free the environment from the current burden of this avoidable wastes (Shell wastes) in Nigeria and to serve as a template for global application.

2.0 Methodology

Data were sought from research articles, books, book chapters, review papers, yearbook, booklets, and conference proceedings from high impact factor journals in Scopus, schimago, google, and semantic scholars' database. Moreover, articles from 1990 to 2023 were used. Articles, starting from the year 1990 to 2000 are just 6.2 %, from 2001 till 2009, 15.38 %, from 2010 till 2014, 22.31 %, while publications dating from year 2015 till January 2023 are 51.54 %. Thus, about 74 % of all articles used were published within a short period of about 12 years. Some articles were added after cross-citation analysis of the selected materials. The key terms or phrases used for internet search include: shell waste, chitinous exoskeleton, shell waste re-utilization, mollusc waste, crustacean shell waste etc. This were use without adding values in between Boolean searching tools. The results were streamlined based on titles and abstracts, in order to ensure appropriate selection. During the search, various fields in Applied Sciences were focused on, such as Fisheries, Aquaculture, Agriculture, Food Sciences, etc. while Fisheries and Aquaculture application was the centre focus. However, so many recent literature discussed more on biomedical, general agricultural, and cosmetics applications while few discussed on Fisheries

and Aquacultural applications, which is the main focus of this paper, with the aim of making relevant documents available to the researcher, academics, and industrialist on the current state of chitinous wastes (a byproduct of fisheries and aquaculture), and thus provide modern economic solution most especially to improve fisheries and aquaculture practice, training and research.

3.0 Economically important crustaceans and molluscs in Nigeria coastal waters

3.1 Crustaceans

Crustaceans are a large and diverse groups of invertebrate, which fall under the Arthropoda phylum, with about 45,000 species. One of the defining features of crustaceans is their hard exoskeleton, made primarily of chitin, which protects their body and provides structural support. Crustaceans can be aquatic, semi-aquatic or terrestrial. They include well-known animals such as crabs, lobsters, shrimps, crayfish, barnacles, and woodlice. As they grow, crustaceans undergo a process called molting, where they shed their old exoskeleton and form a new one. Crustaceans typically have segmented bodies that are bilaterally symmetrical, with each segment potentially carrying a pair of appendages [17, 18].

3.2 Mollusks

Mollusks are the second largest phylum of invertebrate after Arthropoda. Members are known as molluscs or mollusks. Around 76,000 extant species of molluscs are recognized. Molluscs are any soft – bodied invertebrates of the phylum Mollusca, usually wholly or partly enclosed in a calcium carbonate shell secreted by a soft mantle covering the body and live in aquatic or damp habitats. They are grouped into three major classes such as **gastropods**; which includes slugs and

snails; **bivalves** such as oysters, clam, scallops, seas mussels; and **cephalopods** such as squids, cuttle fish and octopus [17].

3.3 Coastal waters

Coastal waters are those parts of the ocean closest to the land. They start where the breakers hit the beach and then stretch seaward as far as 100 nautical miles [19]. Coastal biotope include lagoon, coastal wetlands, delta, coral reefs, mangrove forests, kelp forests, and upwelling areas. Any bays, inlets, coves, harbors or sounds in this range are also considered part of the coastal waters. [20, 21]

Nigeria has a coastline of 853 km, a maritime area of 46,500 km² and an exclusive economic zone (EEZ) of 210,900 km². This territorial waters lies from latitude 4⁰ 10' to 6⁰ 20' N and longitude 2⁰ 45' to 8⁰ 35' E. It is characterized with high temperature during the day, and up to 34⁰C in the dry season. It could also be highly humid, especially in the evening periods, or during high rainfall. The mean annual rainfall is about 1200mm which occurs mostly between late March to late October, and sometimes till early November. Sometimes it may rain for a continuous periods of about 24 hrs which sometimes result in floods [22, 18]. Figure 1 represent the Map of Nigeria showing the coastal areas. The blue colour symbolizes water body.

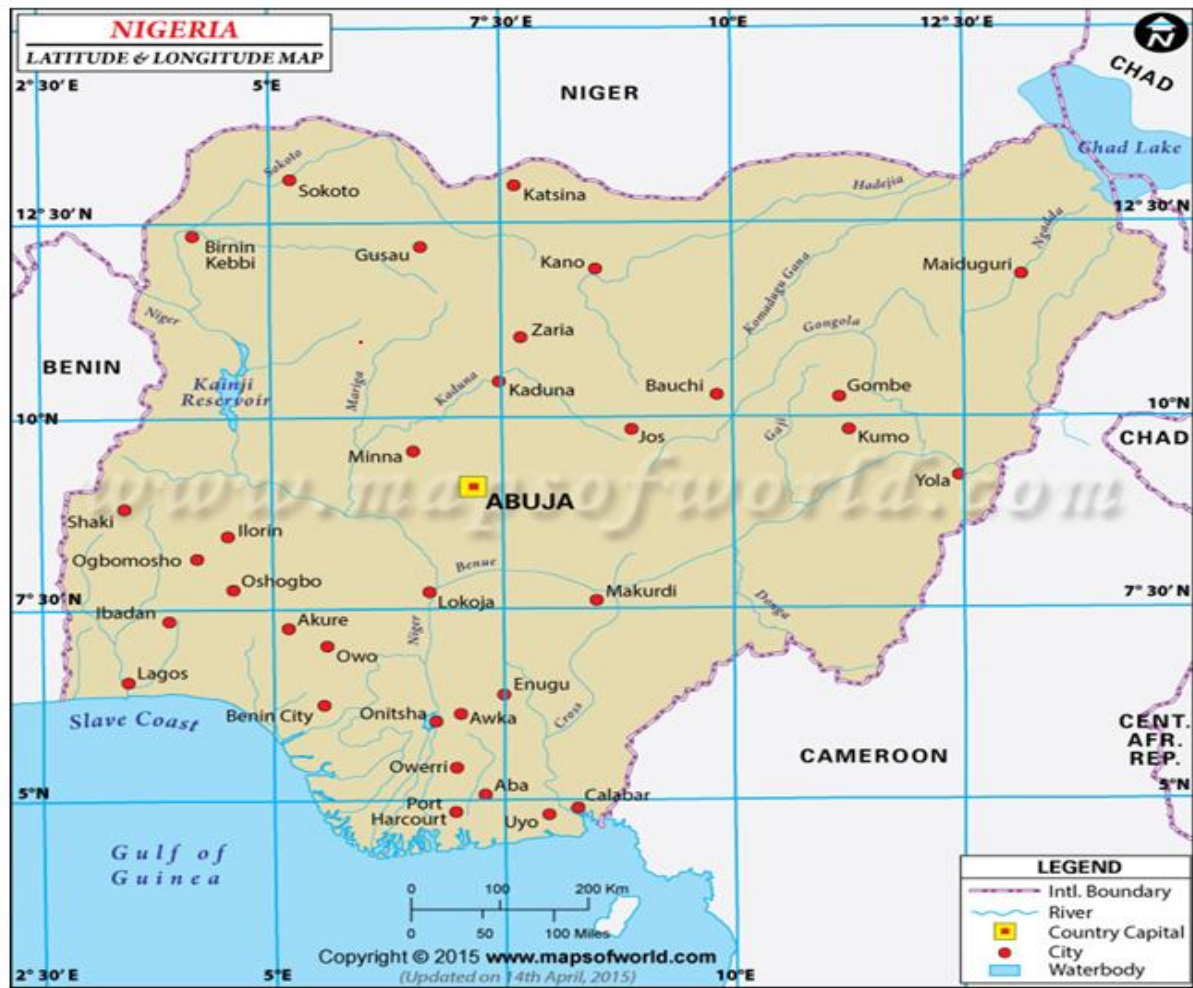


Figure 1: Nigeria Map showing the coastal area. Ateme [20].

The predominant mean of livelihood in the coastal communities is capture fisheries in which different types of nets are use for fishing. The fishing activities are usually carried out in the creeks, offshore, inshore, mudflats and lagoon. Commercial fishing are also engaged with government license, using ocean going fishing vessels such as trawlers.

Moreover, the coastal biotope is blessed with varieties of fishes resources. A total of 46 economically important species of crustaceans, belonging to 33 genera (Table 1) found in the Nigeria coastal water includes decapods (Crabs, Lobsters, and shrimps), isopods (land based crustaceans), amphipods (sandhoppers), stomatopods (mantis shrimps) and euphausiids (krill). Different species of Prawn, shrimp and crabs were also included in high abundance, and dominate most of the catches. They are found in the lagoons and the adjacent rivers. The most economically important family of crab in the Nigeria coastal water is Portunidae (*Callinectes* sp. and *Portunus* sp.).[21, 6]. Table 1 shows the various classifications of crustaceans available in the Nigeria coastal waters.

Table1: List of economically important Crustaceans in Nigeriacoastal Waters

S/N	Family	General	Species
1	Hippolytidae	1	1
2	Nematocarinidae	1	1
3	Palaemonidae	1	7
4	Pandalidae	3	3
5	Pasiphaeidae	1	1
6	Palinuridae	1	1
7	Scyllaridae	1	1
8	Aristeidae	2	2
9	Penaeidae	3	4
10	Sicyonidae	1	1
11	Solenoceridae	1	1
12	Calappidae	1	3

13	Gecarcinidae	1	1
14	Geryonidae	1	1
15	Graspsidae	4	4
16	Homolidae	1	1
17	Majidae	1	1
18	Ocypodidae	2	3
19	Portunidae	4	7
20	Xanthidae	2	2
	Total	33	46

In Nigeria, molluscs can be located in various substrata, within the fresh/brackish water, and estuaries/marine environments. The following are the list of economically important molluscs in a taxonomic form: Bivalves (Table 2a), Gastropods (Table 2b) and Cephalopods (Table 2c).

Table 2a: List of economically important molluscs Bivalves (Molluscs) in Nigeria coastal Waters

S/N	Family	General	species
1	Arcidae	4	4
2	Alonidae	4	4
3	Cardiidae	1	3
4	Carditidae	1	2
5	Chamidae	1	2
6	Donacidae	3	7
7	Dreissenidae	1	1
8	Ericinidae	1	1
9	Garidae	1	1
10	Glycymeridae	1	1
11	Hiatellidae	1	1

12	Mactridae	2	5
13	Mytilidae	4	7
14	Ostreidae	1	3
15	Pectinidae	2	2
16	Petricolidae	1	1
17	Pholadidae	3	3
18	Pinnidae	2	2
19	Pteriidae	1	3
20	Saxicavidae	1	1
21	Solecurtidae	2	2
22	Solenidae	3	3
23	Tellinidae	2	4
24	Teredinidae	1	1
25	Veneridae	4	6
26	Vulsellidae	1	1
	Total	49	71

Table 2b: List of economically important Gastropods (Molluscs) in Nigeria coastal Waters

S/N	Family	Genera	Species
1	Haliotidae	1	1
2	Fissurellidae	2	3
3	Patallidae	1	1
4	Neritidae	1	2
5	Littorinidae	2	4
6	Turritella	1	4
7	Architectoma	1	1
8	Vermetidae	2	3
9	Melanidae	1	2
10	Potamididae	1	2
11	Cerithidae	2	3
12	Calyptraeidae	1	2
13	Xenophoridae	1	1
14	Strombidae	1	1
15	Naticidae	1	8

16	Cypræidae	1	4
17	Cassididae	1	3
18	Doliidae	1	1
19	Muricea	4	15
20	Columbellidae	1	1
21	Buccinidae	1	2
22	Galeoidea	1	1
23	Nassidae	4	7
24	Olividae	1	3
25	Mitridae	1	1
26	Harpidae	1	1
27	Volutidae	1	5
28	Turridae	3	6
29	Conidae	1	5
30	Terebridae	1	2
	Total	42	94

Table 2c: List of economically important Cephalopods (Molluscs) in Nigeria coastal Waters

S/N	Family	Genera	Species
1	Sepiidae	2	6
2	Loliginidae	2	2
3	Ommastephidae	8	9
4	Octopodidae	1	2
	Total	13	19

4.0 Utilization of shell waste of Crustaceans and Mollusks of Nigeria coastal water for sustainable Economic Growth.

4.1 Cleaning of shells

For ease of processing towards reutilization of chitin, shells need to first be cleaned. However, cleaning can be undertaken through blanching with hot water to remove dirt and some organic materials clinging on it and then thoroughly wash. Moreover, since the target is to produce chitin and chitosan, for onward utilization, there are standard procedures which are required in order to obtain pure chitin and chitosan. These polymeric substances (chitin and chitosan) are the focus of this discourse, how they can be obtained from shell wastes, and be channeled towards aquaculture development (in Nigeria). After cleaning, chitin will then be extracted, and to get chitosan, further step involving de-acetylation will be required. These procedures are necessary prior to their utilization. Apart from chitin, these shells can also serve as sources of calcium and phosphorous (Minerals) for animal feeds (4, 6].

4.2 Extraction and Deacetylation of chitin from shell wastes using chemical method

Animal exoskeletons are made up of three primary components. These are proteins, chitin and calcium carbonates (CaCO_3) with pigment and salts in small quantities [23]. Extraction of chitin can be carried out in three sequential steps. The first two are fundamental, the third are mainly for shell obtained from crustaceans.

1. Removal of mineral/Decalcification using HCl (Hydrochloric Acid));
2. Removal of Protein/Deproteinization at high temperature. It is performed by NaOH (Sodium Hydroxide).
3. Removal of pigments and salts using hydrogen peroxide or oxalic acid in order to obtain a pure white powder. This is done only for crustacean shell whose colour is usually a pale-pink. Furthermore, to convert chitin to Chitosan whose uses has greater advantage than chitin, it has to

be subjected to a process known as Deacetylation, which is the removal of the acetyl group from chitin [24]

The schematic diagram in Figure 2a summarizes the chemical process of chitin extraction and its deacetylation to give rise to chitosan.

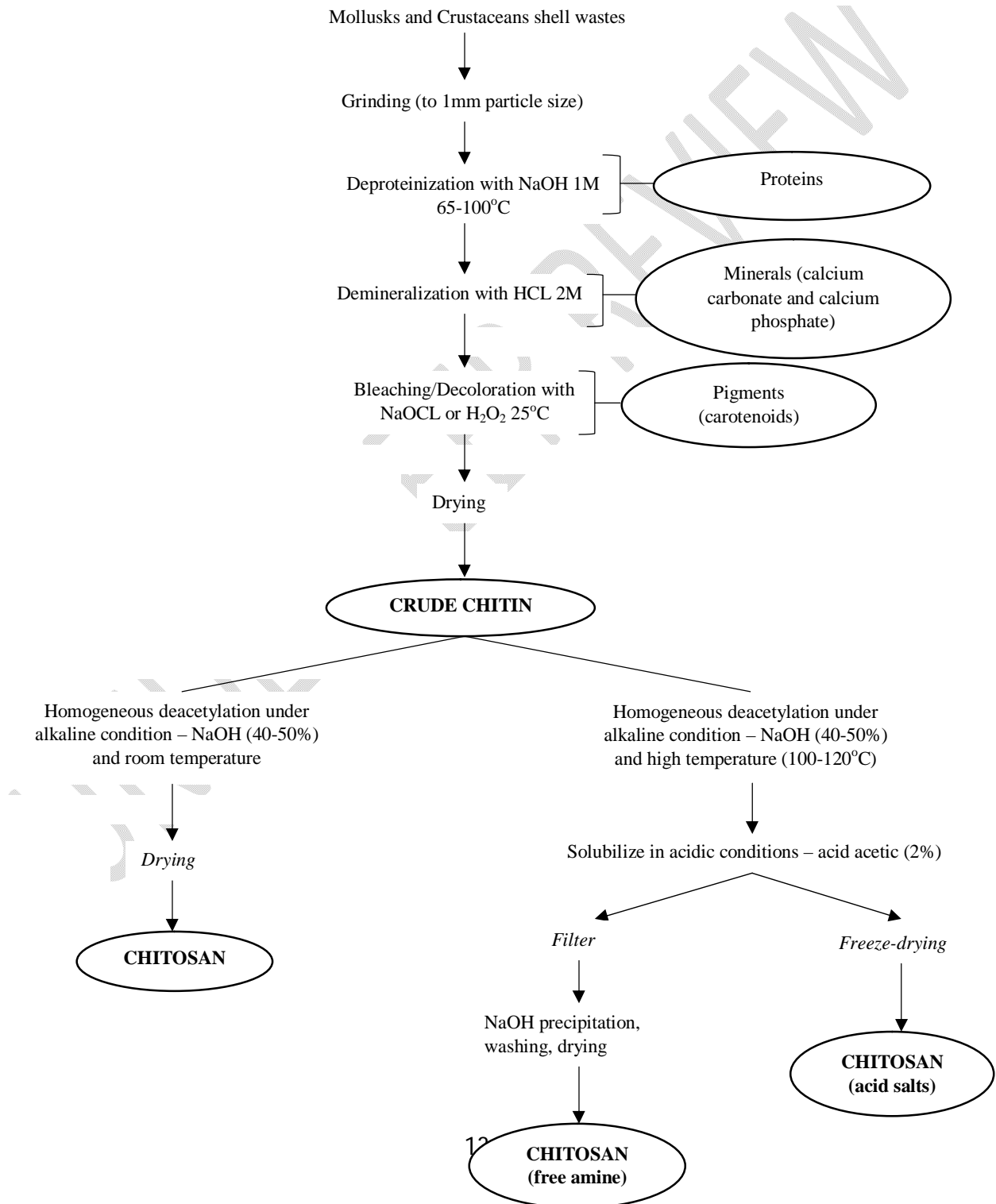


Figure 2a: Schematic Diagram of chemical preparation of Chitin and Chitosan[25]

However, the use of chemical method of chitin extraction could be hazardous, due to high acid and alkali concentrations, coupled with high temperatures. Moreover, chemical synthesis of these biopolymers present a lot of limitations such as non- environment friendly, requires much chemicals, non sustainability, much is spent on energy, and much wastes are produced whose products, including proteins and pigments, are difficult to recover [26, 27, 28]. Also, several issues involving best desirable control of reactions such as anomerization, altering the properties of chitin to reduce molecular weight, and increasing entropy to enforce depolymerization etc are difficult. The discovery of bioextraction of chitin as a newly green procedure, is a promising alternative to chemical process with better and more effective result and less hazardous to biological system.

4.3 Biological extraction of Chitin

The biological extraction method can be undertaken in two ways: the use of proteases (protein digesting enzymes), or microbial fermentation. [26, 29, 30].

4.3.1 Enzyme- mediated Deproteinization and Demineralization of chitin

One of the suggested biological method for the removal of protein from shells is the use of proteases isolated from plants, animals, fungi or other microbes. This approach does not involve the use of sodium hydroxide and the likes. The result does not lead to much wastes as in the

chemical approach and the yield also give rise to a nutritious protein derivatives (hydrolysates). Depending on the starting waste, the protease can lead to various deproteinization yields according to the conditions tested. It is important that removal of calcium carbonate (decalcification) be carried out first, this help to allow more penetration into the tissue and reduce enzymes inhibition which may hinder effective penetration of protein removing enzymes such as trypsin, pepsin, and pancreatin among others. Eventually, the resulting chitin has a better advantage in terms of physical and chemical properties than the one produced chemically. One of the best result was obtained by Mhamdi *et al.* [31] using heat stable serine alkaline protease from actinomycetes strain (*Micromonosporachaiyaphumensis* S103) to extract chitin from shrimp (*Penaeus kerathurus*) shell waste powder which prove better than other extraction methods. After 3 hours of enzymatic extraction (hydrolysis) at 45⁰C and pH 8, with enzymes to substrate ratio of 20U/mg, the percentage deproteinization was 93%. A similar high percentage deproteinization was obtained from the use of alkaline proteases obtained from *Portunussegnisviscera* and used to deproteinize blue crab (*P. segnis*- 85%) and shrimp (*P. kerathuru*- 91%) shells with enzymes to substrate ratio of 5U/mg of protein, after incubated for 3 hrs at 50⁰C[32, 33]

4.3.2. Chitin Bacteria Fermentation (Bacteria mediated chitin extraction)

The use of lactic or non-lactic acid bacteria is another cheaper method of extracting chitin from shell wastes. This Fermentation technique involves addition of selected microorganisms' strain which follows one-stage, and two- stage fermentation; auto fermentation and co-fermentation.

4.3.2.1. The use of Lactic Acid Bacteria

Fermentation involving Lactic Acid Bacteria (LAB) is a novel approach for chitin extraction, combining the use of acid and alkali at a very low quantity [30]. Another advantage of using LAB is that, it leads to the production of lactic and acetic acids. Production of pure proteins, minerals, and pigment from the liquid by-products of LAB- mediated chitin extract from waste shell is easier with bioextraction of chitin than chemical extraction method. The low pH produced during the extraction, especially when lactic acid is used to precipitate chitin helps to activate the release of proteases. This approach has also been employed to recover carotenoids from silage prawn waste. Different *Lactobacillus* spp strains have been used for fermentation. In recent times, purified chitin has been extracted from *Allopetrolisthes punctatus* (crab) with the use of *Lactobacillus plantarum* sp., a highly rich lactic acid producing gram positive bacteria, isolated from coho salmon [34]. The percentage decalcification was 85% while deproteination was 95.3%. This was undertaken within 60 h fermentation at 10% inoculum, 85% crab biomass and 15% sucrose) [34, 25]

4.3.2.2 Non-Lactic Acid Bacteria Fermentation

Ghorbel-Bellaajet *al.* [35] carried out an experiment to isolate a protease bacterium known as *Pseudomonas aeruginosa* A2 among other bacteria, which were regarded as inoculum source to prove that protease present in them can also be used for the recovery of chitin. The result obtained was similar to that of chemically extracted one which were used for commercial purpose. This result highlighted the ability of this enzymes to remove protein from shrimp shell

wastes in order to recover chitin, and thus avoid the challenge of chemical method [35]. He also tried to optimize various variables such as concentration of shrimp shell wastes (50g/L), glucose concentration (50g/L), period of incubation, and size of inoculum to prove and confirm the efficacy of this bacteria. It was exciting to discover that percentage protein removal was 89% and that of decalcification was 96% [35]. Since *Bacillus* sp. is the common bacteria used to produce protease, research was conducted using six different strains of *Bacillus* spp to extract chitin from waste crab shell and supernatant of a fermented crab. The result shows that fermented crab supernatant has a very effective antioxidant and antimicrobial properties [36]. Concerning fungi as a source of proteolytic enzymes, *Aspergillus niger* strain 0576, 0307, and 0474, were selected by Teng *et al.* [37] and used to confirm the microbial hydrolysis of chitin. The study focus was to determine two different chitin origins as he added fermented shrimp shell to mushroom directly. Eventually, the proteolytic enzymes that were produced by fungi during the protein removal and decalcification of shell wastes, led to the production of amino acids, which is a source of nitrogen and was also useful in enhancing the fungal growth [37].

The schematic diagram in Figure 2b summarizes the biological method of chitin extraction and its deacetylation in order to produce chitosan.

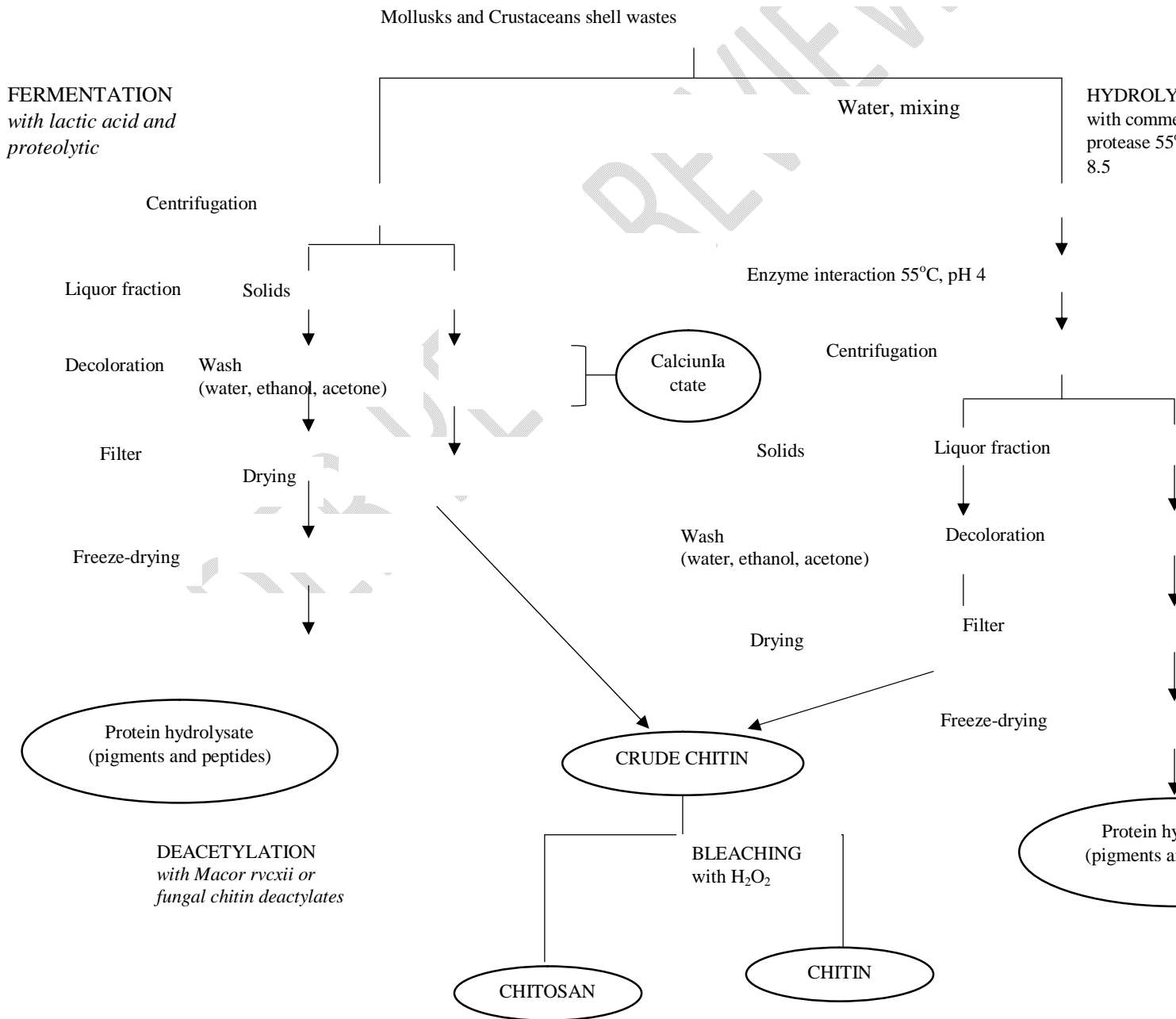


Figure 2b: Schematic diagram of enzymatic and microbial preparation of chitin and chitosan[25]

4.3.3 Enzymatic Deacetylation of Chitin

Although chemical deacetylation could help in mass or industrial production, but its toxicity, non-ecofriendliness, high energy consumption and less-biocompatibility is a major drawback. However, the advent of enzymatic deacetylation of chitin is an innovative approach that make use of enzymes know as chitin deacetylase, which present an excellent alternative that does not exhibit this limitation. A research was conducted using viral, fungi and bacteria chitin deacetylase enzymes, isolated from each of these microbial sources. After the experiment, 14 partially acetylated chitosan tetramers with a well-defined degree of deacetylation, and some traces of acetylation, which only requires further purification to achieve an excellent deacetylation was produced [38]

Figure 3a depicts the chemical structures of pure chitin before deacetylation, while Figure 3b shows the chemical structure of chitosan; a deacetylated form of chitin with one of the acetyl group already removed, and replaced with amine.

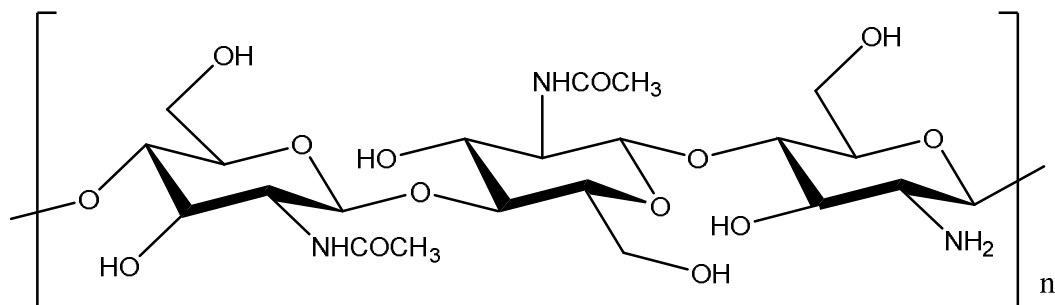


Figure 3a: Chemical structure of chitin [25]

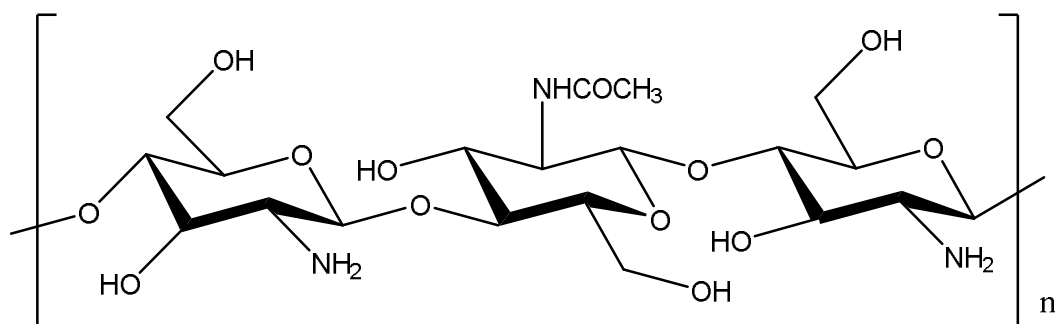


Figure 3b: Chemical structure of chitosan [25]

4.4 Molecular weight (Mw)

The Mw of commercial chitosan is between 100 and 1200 kDa [39, 40]. The molecular weight of chitin and chitosan differs based on the source and the extraction methods used. When the molecular weight is high, the solubility of chitosan in a solvent will be very low which also affect its viscosity (high viscosity) and thus limits its availability for aquaculture and agricultural use. When the molecular weight is lower, such as in chitosan extracted from shrimp and conus shell, their antibacterial activity will be very high [41]. Chitosan with a moderate molecular weight has anti-cholesterol capacity. High-performance liquid chromatography (HPLC) and

Viscometry approach are usually employed to determine the molecular weight of chitosan and chitin[42, 25]. Chitin has different molecular weights based on their sources, which can be tapped into, for various uses. Antiseptic and anticancer agents requires low molecular weight which can also be found in most crustaceans and some mollusks, and thus makes them excellent candidates in drug production.

4.5 Degree of deacetylation (DD)

Deacetylation degree (DD) is a parameter that is used to know the percentage or ratio of glucosamine ($C_6H_{13}NO_5$) monomers units in undeacetylated or partially deacetylated chitin structure compare to a fully deacetylated one(100% chitosan). Solubility of chitin depend largely on its degree of deacetylation. At least, with 50% deacetylation degree, solubility in aqueous acetic acid solution can be achieved [43]. Various spectrometric and chromatographic approach can be used to determine the degrees of deacetylation of chitin or chitosan. This includes Proton and Carbon Nuclear Magnetic Resonance Spectroscopy (PCNMR), High-Performance Liquid Chromatography(HPLC),Ultraviolet (UV) Spectroscopy and Infra-red(IR) Spectroscopy, [44, 45].

Depending on extraction technique, degree of deacetylation plays a major role in the biological, physico-chemical and mechanical properties of chitin and chitosan. Studies shows that at higher deacetylation degree,chitin can be used in scaffolds and implantations in the biomedical engineering, which can find good applications in human and veterinary medicine; this is a significant development as regards the application of the degree of deacetylation [40, 46].

Moreover, according to El-Naggar *et al* [47], an optimum deacetylation degree was realized in 6hrs when treated chitin with sodium hydroxide. It was also noted that there was increase in the

DD of chitosan when increased the concentration of sodium hydroxide and the temperature. Thus, conclusion was draw on the fact that the highest DD took place at 107°C when treated with 60% NaOH [47, 48].

5.0 Application of Chitosan and Chitosan nanoparticles in Aquaculture

The advent of Nanotechnology in the 21st century is a landmark discovery. Although still emerging, it has significantly influence material science at a nano scale (1-100 nm), with a tremendous impact on physical and chemical properties of materials and thus optimized its potentials through increase surface area compare to volume. This discovery has made it possible to use nanoparticles in divers applications which ordinarily would not have been possible outside the nanoscale [49]. Chitosan nanoparticles are easy to prepare with low cost, non toxic, highly biocompatible, highly stability, and ecofriendly materials, and are applicable in veterinary medicine and plant pathology. It has been adjudged as effective feed inclusion for therapeutic and prophylactic treatment in fish [50]. Moreover, chitosan nanoparticles has found various applications due to their minute size, shape and crystallinity which characterizes its effectiveness as nanoparticle against the target cells [51]. The low side effect of Chitosan and Chitosan nanoparticles made them applicable in a variety of useses, couple with their ability to enhance fish growth [52, 53, 54]. Additionally, chitosan and chitosan nanoparticles can be encapsulated to carry drugs [55]. Likewise, they can be usefor the treatmet of pond water owingto their chelating ability [56, 57]. In view of these, chitosan and chitosan nanoparticles are good products, and are applicable in water quality enhancement[58].

5.1As calcium Supplement

Waste shell have been considered as raw materials in form of natural shells, calcined shells and several biopolymers and their derivatives which includes chitin and chitosan. Animal shells has always been a source of calcium and has been used to produce food suppliments, likewise chitin and chitosan has find good application in food and pharmaceutical industries. They have also been used as biopackaging materials [43, 8]. Calcium extracted from shell has been used for strong teeth and bone, and livestock blood circulation, high quality milk and egg-shells [6]. It is a cheaper source of CaCO_3 and performing equally to limestone in Ca supplementation in fish diet [4]. The CaCO_3 extracted from oyster shells is also used as a food supplement for Ca replacement in fish diet and human. The extracted CaCO_3 can easily be absorbed in the intestine, and thus enhance the density of bone minerals, for instance in the lumber region, to fill in calcium deficiency especially among aged population [59].

5.2As protein Supplement

Useful feed ingredients could be obtained from shell wastes of crustaceans. This includes shell, heads and jointed legs of shrimps, which consist of essential amino acids such as lysine [60]. The product of shell fermentation can be used as feed ingredients in fish production [61]. Protein obtained during chitin extraction from shell wastes can be used to supplement fish or animal feed, while the wastes is being transformed into to chitin, and then chitosan through deacetylation process. This is two-way advantage. While protein is being obtain, though a by-product, chitin is also being extracted as a primary product, apart from calcium which is also obtained (Decalcification) and is useful as a mineral source. However, the best approach to easily recover protein by-product is through enzymatic and microbial extraction so that the obtained by product (protein) will be safe (non toxic) for other beneficial use [62].

5.3For fish growth improvement

Positive effect of Chitosan and its nanoparticles form as inclusions in fish diet at optimal dose depends largely on fish species. According to Abdel-Ghany and Salem [63], it was discovered that Japanese eel, *Paramigurus dabryanus*, did not reflect any change in their growth performance, even after 3 months of experiment at varying inclusions. Moreover, it is also noteworthy to mention that rather than improving growth performance in *O. niloticus*, it decreases their growth rate, nonetheless, when used to feed *Paralichthys olivaceus*, *Cyprinus carpio* and *Dicentrarchus labrax*, there was a tremendous growth increase after supplemented with Chitosan [63, 64]. According to Zaki *et al.*, [64], chitosan has potential to bring about a healthy intestinal epithelium and induce growth through increase in microvilli absorbance surface. Conversely, high concentration of Chitosan in fish diet can lead to over growth of microvilli which can hamper fish growth performance resulting in intestinal blockage occasioned by overgrowing microvilli [63]. In another study, *O. niloticus* demonstrated a unique response, with increase growth, even when 0.5 g/kg was used [63]. Moreover, it was recorded that, after fortified fish diet with chitosan at various concentrations (1800 mg/kg, 4000 mg/kg, 7500 mg/kg, 10000 mg/kg and 20000 mg/kg) of fish diets, and was used to feed *Carasius auratus* juvenile for 75 days; 4000 mg Chitosan per kg diet gives the optimum level of Chitosan supplementation [65]. So far, it was deduced that using chitosan nanoparticles at different dietary inclusion for *O. niloticus*, growth performance can be enhanced owing to increase feed intake and feed utilization. Likewise Chitosan nanoparticles can also increase fish growth through its positive impact on microvilli and goblet cells of intestinal epithelia [53, 66]. Thus the use of Chitosan and its nanoparticle form can induce fish resistance to pathogens and ultimately ensure fish health [67].

5.4 Asimmunostimulants

Mortality rate reduction and immunity can be achieved with chitosan when properly administered [68, 63]. In a situation where stress condition is inevitable and has been causing increase mortality rate; for instance chitosan supplementation in *Oncorhynchus mykiss* diet, at 2.5 g/kg depicted a marked survival rate despite the stress condition [63]. In an experiment carried out by Ranja *et al* [69] in which dietary concentration of chitosan (0, 5, 10 and 20 g/kg diet) was fed to *Lates calcarifer* for 60 days, it was noted that all the treatment depicted a greater immune response than control group. Moreover, 10 g/kg group diet exhibit an exceptional innate immune response and hematological parameter on the 45th day of the experiment. This result is in tandem with the finding by Salem [63] and Zaki *et al* [64]. Also, another graded diet fortified with various concentrations of chitosan (0, 5, 10 and 15 g per kg diet) was fed to *Mugil cephalus*, the results shows that highest immune response was noticed on 10 and 15g chitosan concentration per kg [68]. Likewise, addition of chitosan to *Cyprinus carpio* diet improve its immune response [70]. Finally, Cha *et al.* [71] stated that, the ability of Chitosan to act as immunostimulant was credited to its ability to prompt non-specific or general immunity in a living cell. Again, Chitosan's potency against bacteria pathogens in *labeorohita* enhances immunity and resistance against environmental change [72, 73]. The same report was found about *Misgurnus anguillicaudate* according to Yen *et al* [74]. Inherent immunity in *O. niloticus* was also boosted when applied Chitosan nanoparticles by increasing the total WBCs [53]. It was also discovered that when combine selenium with chitosan (CS-Se), the lysosome activity increases due to their synergistic effect and thus enhanced the immunity of *Paramisgurnus dabryanus* [75]. Abdel-Tawwab *et al.* [66] recorded the same result when fed *O. niloticus* with diet fortified with chitosan nanoparticles at varying concentrations (0.25, 0.5, 1.0 and 2.0 g/kg diet). In summary,

the immunostimulatory action of chitosan nanoparticles on fish plays a notable beneficial role towards the growth of aquaculture [76].

5.5. As antibacterials

Synthesized chitosan has a good antibacterial properties. It has capacity to prevent bacterial growth on fish or meat, and has bacterial suppressing rate of 99.9%. Therefore, it has potential to raise their keeping quality up to 10 days especially during summer, without negative effect on those who consume them [43, 77]. Chitosan has ability to prevent *Bacillus cereus* spore germination and growth. Experiment was conducted on bacterial spore with concentrations corresponding to 10^2 – 10^3 CFU mL⁻¹, which is relevant to spore concentrations in food, the result shows that less chitosan was required to prevent bacterial growth, compared to higher spore numbers (equivalent to 10^8 CFU mL⁻¹) [78].

5.6. For cholesterol reduction

Chitosan can be used to reduce low density lipoprotein (LDL)-cholesterol level and its fat-binding properties [79]. Two weeks ingestion of chitosan oligosaccharide can lead to reduction in LDL-cholesterol by 6% and jack up high-density lipoprotein (HDL)-cholesterol by 10% [80]. Chitosan has ability to scavenge fats in the alimentary tract, and pick up cholesterol debris through ionic bonding by its attraction to bile salts and acids, which helps to reduce weight; chitosan is non-absorbable and effective only in the alimentary tract, hence increase fecal release of common fats is as a result of weight loss due to chitosan. This is applicable in man and animals including aquatic lives [80].

5.7 As antioxidants

Chitosan with its several derivatives have antioxidant activity [39]. The ability of chitosan to reduce oxidation damages in cells as well as activating the inherent ability of fish such as *cyprinocarpio* to scavenge dangerous free radicals when applied at a proper dose such as 0.5g/kg, 1g/kg, 2g/kg or 5g/kg diet, make it an excellent antioxidant of animal source.[63, 74, 81]. However, the study shows that it is necessary to include Vitamin C in order to improve Chitosan's antioxidant activity in *C. carpio*[81]. Chitosan nanoparticle on the other hand has greater potency, not because of its antioxidant activity alone but at the nano scale, its physical and chemical properties has been enhanced and thus could inflict a deadly blow on toxic free radicals especially in *O.niloticus* and also enhance its inherent antioxidant activity [74]. Also, when fortified *Salmo salar* with chitosan nanoparticles, it reduces lipid oxidation and with greater scavenging activity against free radicals [66]. It was also reported that, as the dietary supplementation of chitosan nanoparticle increases, so also its antioxidant potency increases [66, 82]

5.8As drug carriers

The use of N-N-N trimethyl CS chloride (TMC) to enhance drug delivery capacity of chitosan which work well at higher wide pH range than when only chitosan is used, has been adjudged as an excellent chitosan derivatives for effective drug delivery [83]. For instance, microscopic examination of vaccinated *Paralichthys olivaceus* fish using CS-DNA oral vaccination showed an excellent result, depicting that chitosan has the potential for effective drug delivery. Conversely, the literature revealed that certain part of the fish body could not be affected by the CS-DNA vaccine such as hind gut. It does not also induce immune – gene expression or serum circulation. Also, CS-DNA enhances solubility of Chitosan in nucleic acid and optimizes cell reception of the embedded drug carried by Chitosan[55]. It was also gathered

that CS-DNA vaccine has the capacity to prevent disease pathogen such as bacteria and virus from infecting fishes with a high survival rate. This result was attributed to the ability of chitosan nanoparticles to induce immune related gene. Chitosan nanoparticles is a potential drug carrier and antioxidant which help to enhance immune system, it has an excellent capacity to infiltrate tissues and reach the targeted region. In addition, research has shown that chitosan nanoparticles is a useful oral DNA vaccine for fish [76, 84, 85]. It was also discovered that it is possible to ingest chitosan and its nanoparticle form through urinary system which make them well applicable and useful in medical and pharmaceutical industry [86]. Both substances (Cs and its nanoparticle form) can deliver drug directly through fish alimentary canal, such as vitamin, mineral, and vaccine and also increase mucoadhesive ability of the intestine, thus enhancing drug absorption potential of the intestine [87]. Study also revealed a successful immunization of *Labeorohita* against *Edwardsiella tarda* (bacteria) using CSNPs-DNA vaccine which allows good expression of *E. tarda*'s immune genes [88].

5.9. For the treatment of fish farms wastewaters

Heavy metals have been one of the major water quality threat in fish farming. They have high atomic mass and denser than water at about ratio 5:1, and are very harmful to fish [89]. Aluminium, although has been used over times but due to its negative side effect of being responsible for Alzheimer disease in man, when consumed fish raised in water that has been treated with aluminium; but chitosan, due to its chelating property is able to remove heavy metals including aluminium (which is also an heavy metal) from fish pond water. Therefore, when synthesize Chitosan with iron III oxide, it forms a powerful composite with superior ability to absorb lead, cadmium and aluminium. This synergistic combination was made possible due to the hydroxyl and amino group present in chitosan [56, 90].

Chitosan nanoparticle is also useful in the removal of Copper from water. However, the concentration of copper in the solution also determines the concentration of chitosan nanoparticles to use [91]. However, while both chitosan and chitosan nanoparticles can be used for the removal of heavy metal in water, the research shows that chitosan nanoparticle is far more efficient due to its high chelating power. This was confirmed by Seyedmohammadi *et al.* [92] in his research which depicted the optimum condition at which chitosan and chitosan nanoparticle can effectively absorb Zn (90.80% and 99.19% respectively) at pH 7 and 25°C. The nanoscale size, crystalline nature of the nanoparticles, numbers and types of the functional groups present also contribute to this [57]. This is where Nanotechnology plays a significant role in the valorization of crustacean, gastropods and other animal shells waste yields, to ensure effective and efficient utilization, towards improved aquaculture.

5.10. As biopackaging agent

Polymeric materials of animal shells origin are suitable to produce safe and environment-friendly plastic, which can be used in human or veterinary medicine, household and industry, especially as biopackaging materials [93]. Packaging films made from fossil products should be substituted for biodegradable materials to improve environmental wellness. In view of this, biopolymers can be used as a natural alternative to outdated ones which are plagued with several limitations [98]. Chitosan-based food packaging includes systems that have the ability to prevent microbial growth. This is necessary especially in fish processing, packaging and transportation in order to maintain high quality fish and fisheries products. The antimicrobial biopackaging materials obtained from chitosan have been one of the best packaging materials so far [94].

6.0 Conclusions

Shell produced from mollusks and crustaceans these days are mostly seen as wastes, despite the fact that they were once items of historical value, and some have been used as legal tender in exchange for goods and services. Nevertheless, shell waste repurposing and valorization are highly important to determine strategies in order to make them a standard valuable resource as highlighted in this paper, most especially in fisheries and aquaculture. Ecofriendly and non-toxic chitin extraction and deacetylation methods have been discussed in detail and were recommended. Collection method is never a problem, since these wastes can be found in large quantities at the fishing jetties and processing companies; as well as restaurants, artisanal fishermen, and domestic sources. Effort should therefore be made to collect them in a well-organized manner, exploring every collection avenue earlier stated to ensure a stable supply of shell, to give room for a large scale chitin and chitosan production. As earlier discussed, chitosan can be synthesized into nanoparticles, and nanocomposites when synergized with other nanoparticles. These can be found good applications in aquaculture as earlier discussed. Finally, chitin and chitosan are potential sources of several opportunities which has great possibility to take aquaculture to a higher pedestal. To gain full advantage and control, sustainable shell waste bioeconomy and redirection of use will require an integrated support from both state and federal government through necessary legislation just as it applies in fishery legislation.

Ethical approval

Not applicable

Highlights

- Massive wastes of Crustacean and Mollusk shells in Nigeria coastal and inland water environment were reviewed and discussed.
- Dearth of adequate knowledge on effective valorization of chitinous wastes shells, apart from historical use was reviewed and provided a way forward.
- Re-utilization possibilities of chitinous waste shells of Crustaceans and Molluscs through eco-friendly and sustainable technology to improve fish production were established.
- A comprehensive review of Extraction methods of chitin and chitosan from chitinous shell wastes were explored.
- Application of chitosan and chitosan nanoparticles for a robust aquaculture practice, economic development and job creations were outlined and discussed.

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