



Review

Extraction, chemical modification and characterization of chitin and chitosan



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ABSTRACT

Chitin is the second most common polymer after cellulose in earth, existing in the shells of crustaceans like crab and shrimp.

Chitosan is a natural amino-polysaccharide derived from chitin, known as one of the most abundant organic materials in nature, it has been widely used in several applications due to its natural origin and exceptional properties such as biocompatibility, biodegradability, non-toxicity, and chelating of metal ions. Chitin and chitosan are characterized by deacetylation degree, one of the most important chemical characteristics that can influence the performance of chitosan in many applications.

Chitosan is usually prepared by a thermochemical method, consuming time, energy and reagents.

In this review, various methods of chitosan extraction will be approached and compared; the importance of a new method of ecological extraction will be emphasized. Moreover, in order to improve the chitosan functionality, and better control these physicochemical properties, several chemical modifications have been reported. These chemical modifications lead to a broad range of derivatives with a wide range of applications in many fields. Recent examples of the distinct applications, with particular emphasis on environmental applications, have been presented.

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1. Introduction

Marine wastes resulting from the processing industries have increased significantly in recent years. The production of these marine

co-products, without parallel development of relevant recovery processes, leads to environmental degradation and causes serious pollution problems.

Several million tons of fishery wastes are produced every year. These wastes are very hazardous for environment because of their high biological and chemical oxygen demand, pathogens and organic matters, etc. However, these wastes are considered as a potential resource with

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high value added, they contain, mainly, proteins, minerals and chitin which transformed, by deacetylation, to chitosan. These molecules have a wide spectrum of applications in many fields, especially in wastewater treatment [1–4]. Besides activated carbon, bentonite, sawdust, zeolite and other biopolymers, chitosan is one of the most low cost adsorbent used for removal of heavy metals from wastewater [5–7].

Chitin is the second after cellulose as the most common and ample organic compound in nature. It is the second most common polysaccharide in the world after cellulose. Recently, the emphasis on environmentally friendly technology has stimulated interest in biopolymers and bio-based polymers, due to their functionality and more biodegradability than the synthetic polymer counterpart. The bio-based polymers have received increasing attention because of their outstanding physical and biological properties [8–10].

According to the current research, fishery wastes, especially the crustacean wastes, are a useful material which can be used for the preparation of chitin and chitosan. Furthermore, the most challenging part in recent year is to obtain chitosan-based materials with properties equivalent to those of fully synthetic products.

2. Chitin and chitosan: structure, origin and solubility

2.1. Structure and origin of chitin and chitosan

Chitin is the second most ubiquitous natural biopolymer after cellulose on earth; it's a linear amino-polysaccharide consisting mainly of β -(1 → 4)-linked 2-acetamido-2-deoxy- β -D-glucopyranose units and partially of β -(1 → 4)-linked 2-amino-2-deoxy- β -D-glucopyranose [4,11]. The structure of chitin and chitosan are depicted in Fig. 1.

Chitin is commonly found in invertebrates, as crustacean shells or insect cuticles, but also present in the vast majority of fungi, some mushrooms envelopes, green algae, cell walls and yeasts [8,12,13], chitin is estimated to be produced annually almost as much as cellulose [14]. In general, crustacean shells consist of 30–40% of proteins, 30–50% of calcium carbonate and phosphate and 20–30% of chitin as reported by J. Kumirska et al. [1,11], but these percentages vary depending on the source, or even the species, from which chitin is isolated, for example, *Crangon crangon* shrimp waste consist of 10–38% of proteins, 31–44% of minerals and 24–46% of chitin, according to M. Bajaj et al. [2]. The table 1 showed a proximate composition of some chitosan sources. This polymer has become of great interest as a new functional biomaterial of high potential in various fields [14].

Depending on its source, chitin exists as two main polymeric forms, namely β -chitin and α -chitin, which are arranged according to orthorhombic and monoclinic cells, respectively [21]. A third allomorph, γ -chitin, has also been described, which appears to be a combination of α and β forms rather than a different allomorph [11,17]. As shown in Fig. 2, the α -chitin, β -chitin and γ -chitin correspond to anti-parallel, parallel, and alternated arrangements of polymer chains, respectively. The β -chitin can be extracted from squid pens and easily converted to α -form by alkaline treatment [11,22].

Table 1
Proximate composition of different chitosan sources.

Sources	% Protein	% Ash	% Chitin	% Moisture	% Lipid	Ref.
Shrimp shells	32.77	32.46	36.43	45.65	–	[15]
Shrimp shells (<i>P. longirostris</i>)	29.23	25.06	26.98	3.25	15.48	[16]
Shrimp shells (<i>Penaeus durarum</i>)	34.02	42.26	23.72	–	–	[17]
Insect cuticles (cicada sloughs)	39.8	11.7	36.6	8.7	2.7	[18]
Crabs shells	16.68	66.58	16.73	–	–	[17]
Mussel shells	9.99	23.25	23.25	–	–	[19]
Squid gladius (<i>L. vulgaris</i>)	36.52	2.57	31.2	–	0.32	[20]

The α -chitin is the most stable and abundant polymorph; it is usually isolated from the exoskeleton of crustaceans, yeast cell walls and arthropod cuticle in general [23,24].

In industrial processing, this polymer is mainly extracted from crustaceans, crab and shrimp shells, by acid treatment followed by alkaline treatment to eliminate the calcium carbonates and proteins respectively. In addition, a decolorization and purification step are often added to remove pigments and obtain a pure product without impurities [10,25].

2.2. Chitin and chitosan solubility

Chitin has a strong intra and intermolecular hydrogen bonding network, which provides the insoluble property of this polymer in common organic and inorganic solvents [21].

The most important derivative of chitin is chitosan obtained by partial deacetylation of chitin under alkaline conditions [26], and thus composed of N-acetyl-D-glucosamine and D-glucosamine units [27]. The presence of multiple functional groups in this polymer, such as hydroxyl and amino groups, on its polysaccharide chain provides the flexibility for preparing molecularly imprinted polymers and for structural modifications [28].

Each D-glucosamine unit contains a free amino group, and these groups can take on a positive charge which gives important properties of chitosan such as solubility and antimicrobial property. These groups make a good chelating ligand capable to binding to a variety of metal ions and can adsorb the dye anions by electrostatic attraction. Additionally, these amino groups might be protonated providing solubility of chitosan in diluted acidic solutions [29–31].

Chitosan is mainly characterized by the deacetylation degree and the molecular weight, these parameters affect strongly many physicochemical and biological properties of chitosan such as solubility, hydrophilicity, crystallinity and cell response.

The degree of N-acetylation is basically employed to differentiate chitin from chitosan, and the presence of amino groups, in the chitosan structure, gives to this polymer many peculiar properties. When the acetylation degree is higher than 50%, the polymer is named chitin, and when the acetylation degree is less than 50%, the polymer is

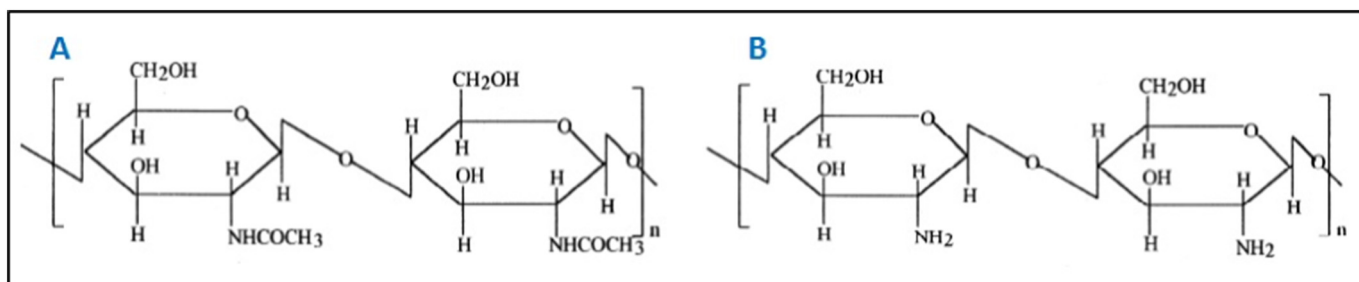


Fig. 1. Chemical structure of chitin (A) and chitosan (B).

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