

A Review on Chitin Derivatives and its Uses in Silver Nanoparticles Synthesis

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Abstract: Few decades ago, chitosan, a natural amino polysaccharide has estimated to produce in abundant annually. Chitosan is a derivative of chitin, produced through demineralization, deproteinization and deacetylation processes. Unique set characteristics presented by chitosan, which is aqueous acidic-soluble and harmless to environment has diverted the intention of scientific community to explore about its uses in nanoparticle synthesis. Availability of free amino groups in chitosan, which can reduce metal ions has offers some potential to replace current uses of synthetic reducing agent, thus give novelty towards green nanotechnology, especially in metal nanoparticles synthesis. The purpose of this work is to review the relevant information related to chitin and chitosan and their applications as natural reductant. Moreover, some new and futuristic approaches in this area also been discussed.

Key words: Bioactive Molecules • Chitosan • Green Technology • Metal Nanoparticle Synthesis

INTRODUCTION

Polysaccharide is a natural molecular structure that distributes broadly in nature. Chitin and chitosan, kind of nitrogenous polysaccharides are the second most abundant in nature after cellulose. They have widely present in marine life and easily extracted from fish scale [1], shrimp shell [2, 3], gastropod shell and operculum [4], cuttlebone [5], mangrove crab [6], prawn shell [7], mud crab [8] and clam shell [9]. Chitin represent in nature as white, hard, non-toxic, inelastic and nitrogenous polysaccharides, which is known as a homopolymer of β (1-4) linked to N-acetyl-D-glucosamine. Chitin has three different allomorphic forms, which are α , β and γ forms, where the α – chitin found majorly in nature [10]. Chitin has hydrophobic characteristics and it is insoluble in organic solvents due to high content of H-bond networks that control solubility, swelling and reactivity. Besides, low chemical reactivity in chitin may limits applications in many fields especially in biomedical field. Concerning the potential application of this bioactive compound, modification of chitin derivatives is explored. Chitin can be modified into chitosan through deacetylation process, a process of removing acetyl group in the polymer chains. It often been identified through the percentage of free

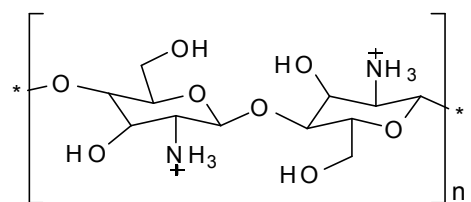
amine groups at the chitosan backbone, which is known as degree of deacetylation, DDA [11]. Although chitosan can be produced by *N*-deacetylated of chitin, but this process is almost never complete.

Chitosan is known as a polycationic biopolymers that composed of randomly distributed β (1-4) linked to D – glucoseamine. The present of positively charges of amine groups in chitosan has making the chitosan to dissolve in aqueous acidic condition at pH below than 6.0 [12]. At high pH solvent, which is pH more than 6.5, amine groups of chitosan will deprotonated, losing the positive charge ion and becomes insoluble [13]. The soluble-insoluble transition of chitosan occurs at pH range 6.0 to 6.5. Due to its ability that can dissolve in common solvents, chitosan is more preferable to be used in wide range of applications when it is compared to chitin. The advantages of pure chitosan are non-toxic, renewable, biodegradable, free from antigenic effect, polar in nature and can form stable complexes with heavy metals [14, 15]. Besides, high content of nitrogen in chitosan has allowed it to become a useful chelating agent. Figure 1 shows the solubility of chitosan in certain pH. Chitosan has versatile properties and can be used in different fields such as in biomedical [11], tissue engineering [16], textiles [17, 18] and food processing

industries [19]. It is also shows good antioxidant, a substance that delays cellular oxidation substrates. The antioxidant properties that shows by amino and hydroxyl groups that attracted to C-2, C-3 and C-6 positions of pyranose ring may attract simply the hydrogen atoms from free radical [5]. Considering the antioxidant properties of chitosan, it can acts as natural reducing agents in metal nanoparticles synthesis, thus promoting 'green' synthesis.

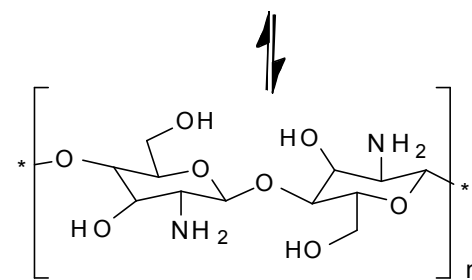
In past decades, study on green synthesis of nanoparticles has obligate new exploration in nanotechnologies study. Nanoparticles (Greek word 'nanos'- means 'dwarf') is delineate as miniature solids or particles that imperceptible to human vision in size range 1 to 100 nm [20]. Unique chemical and physical properties for instance; small sizes which is around 10^{-9} nm and varies shapes and morphologies have give advantages in surface materials study. The properties of nanoparticles are size dependent at this scale range (~100 nm or smallest), which is special and differ significantly from those presented in bulk materials [21]. Modification on materials into nano scale has increased their reactivity because of larger surface areas can expose in contact with surrounding materials [22]. Small size of nanoparticles that fit to most of natural processes has draw benefits as most of inner cells works at nano scale. Due to this condition, researchers tend to discover and designs new tools, which lead to development of new technologies in biological applications. Distribution of nano scale materials throughout the living organisms is well investigated. Green nanoparticles synthesis is eco-friendly synthesis that endorses the uses of renewable bioactive compounds as reducing agents.

This synthesis used biological principles to generate nano scale materials with size below 100 nm. It is a cost effective synthesis that is environmentally safe and profuse in nature. Vital aspect in green synthesis implies the uses of biological entities as reducing agents, chose non-toxic solvent medium and stabilizing agents for nanoparticles preparation [23]. Substitution of hazardous chemicals and solvent in previous synthesis for example; sodium borohydride [24], anionic mercapto ligands [25], surfactants [26, 27], dendrimers [28] and polymers [29] with chitosan have given significant impacts on environment. In this review, the potential challenges on extracting chitin and chitosan from natural sources and the uses of the extracted chitosan in preparing silver nanoparticles will be further discussed.



Low pH (pH < 6.0)

Aqueous- acidic soluble



High pH (pH > 6.5)

Aqueous acidic insoluble

Fig. 1: Solubility of chitosan.

Production of Chitin and Chitosan from Natural Sources:

Chitin and chitosan existed mainly in exoskeleton of crustacean and exhaustive research works on chitin and chitosan from shrimp bio-waste using different techniques are reported frequently [3, 30-32]. Low biodegradation rates of these bio-wastes contributed the accumulation in large quantities and becomes as source of pollution but, since the extraction techniques of chitin and its derivatives were found few decades ago, this finding gave new alternative to fully utilized this bio-waste, which is not only suit for shrimp but included others crustacean bio-waste too. Basic constructions for exoskeleton of crustacean are made up from the combination of inorganic minerals and organic compounds; which is known as calcium carbonate, CaCO_3 , proteins molecule that embedded to CaCO_3 , which known as Conchin and a potential bio-active compound, the chitin, respectively [33]. Isolation of chitin required removal processes of CaCO_3 and proteins molecules, namely as demineralization and deproteinization process. Then, chitosan will be produced during the deacetylation process in concentrated alkaline solution at elevated temperature.

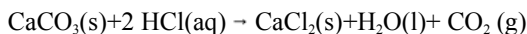


Fig. 2: Chemical equations for demineralization process.

Demineralization process begins with the treatment of crustacean bio-wastes using dilute hydrochloric acid, HCl in different concentration between 0.25 to 2.0 N with different solid to solution ratio (*w:v*) [3, 30, 32]. Dilute acid was used to prevent chitin from hydrolyzed [31]. During the treatment, emission of carbon dioxide, CO₂ gas occurred when the acid penetrated the surface of the shells. This process was observed by releasing of bubbles during the treatment. Emission of CO₂ gas was depended on the level of mineral contents in the species. Besides, duration of the demineralization process and the way of the process performed, either continuous or by stages also affected the structure of chitin [4]. Figure 2 shows general chemical equations for the demineralization process.

Deproteinization is a process to convert the albumen into water soluble amino acids. Three different techniques were suggested for protein removal, which are chemical, physical and biological extractions, where the chemical extraction was majorly performed in industry. The reaction is done in low bases concentration at low temperature to prevent loses of acetyl group, thus maintain the polymerization of chitin chain. Several studies have clearly reported that this process was conducted in varies concentrations of diluted sodium hydroxide, NaOH solution under reflux at temperature range 60 to 110 °C [7], [34]–[36]. Meanwhile, Kumari *et al.* [37] reported the deproteinization of fishery waste at ambient temperature. Reaction periods play a crucial role to eradicate protein contents; which is in between 18 to 24 hours [35, 38, 39]. The treatment was repeated until clear solution is obtained, proved that the protein content was fully extracted. Some studies reported protein removal from enzyme and bacteria [30, 40, 41]. Kjartansson *et al.* [32] used sonication-assisted for protein removal in North Atlantic shrimps. The sample was sonicated for 1 and 4 hours at 41 W/cm³. The properties of chitin are depends on the crystallinity degree, molecular weight or its average of polydispersity and the degree of acetylation, DA [42, 43].

Deacetylation is a process involved removal of acetamido into amide group from chitin backbone chain using hydrolysis process [45]. From this process chitosan, which is consists cationic polyelectrolyte of primary amine groups that acidic aqueous soluble is produced [46]. This process can be carried out using

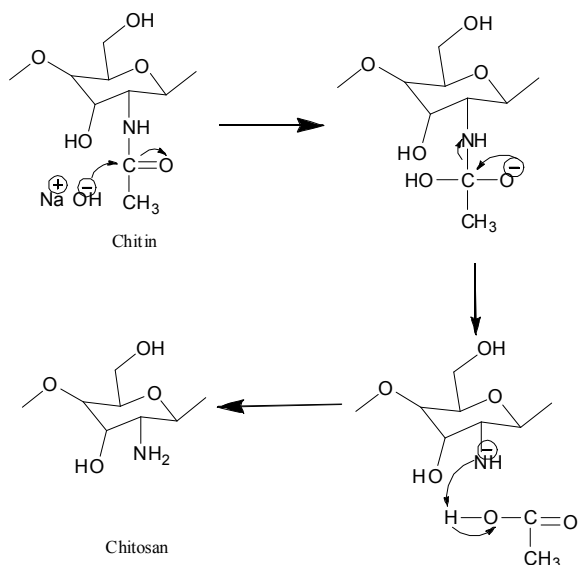


Fig. 3: Mechanism for conversion of chitin to chitosan.

traditional protocol or physical assisted techniques. Traditional protocol of chitin deacetylation is frequently reported by refluxing the chitin in aqueous sodium hydroxide (concentration, 25 – 50%) at elevated temperature for several hours [47, 48]. However, this treatment is time consuming and used harsh chemical that might reduce the DDA of chitosan. Besides, steeping the chitin in sodium hydroxide at room temperature for several hours before refluxing at elevated temperature may increase the DDA [49]. Another alternative approach is suggested for chitosan synthesis, which is more ‘green’ and consuming short time of reaction is used. This method used microwave – assisted of alkaline hydrolysis for chitosan production [35, 50]. Figure 3 shows the mechanism of chitin converted to chitosan and Figure 4 shows the overall processes of chitin and chitosan production.

Potential Uses of Chitosan in

Nanoparticles Preparation: Currently, there is a growing need to develop an eco-friendly metal nanoparticles synthesis and these challenges have lead to the prologue on ‘green chemistry’ principal, which is endorse the uses of environmentally and renewable bioactive compounds in the synthesis. The idea of synthesized silver, Ag nanoparticles using green technique was initiated as it promising a clean method, which gives a significant impact on environment and society. In addition, Ag nanoparticles has high therapeutic properties that may suitable used as antimicrobial agents. With the awareness

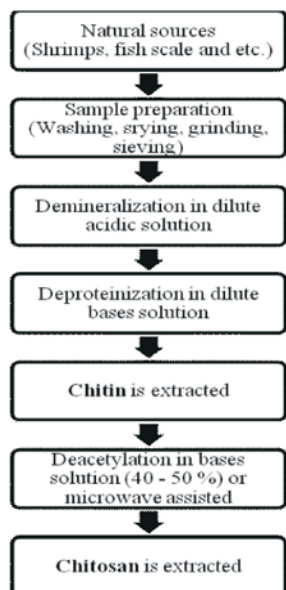


Fig. 4: Preparation processes of chitin and chitosan from natural sources.

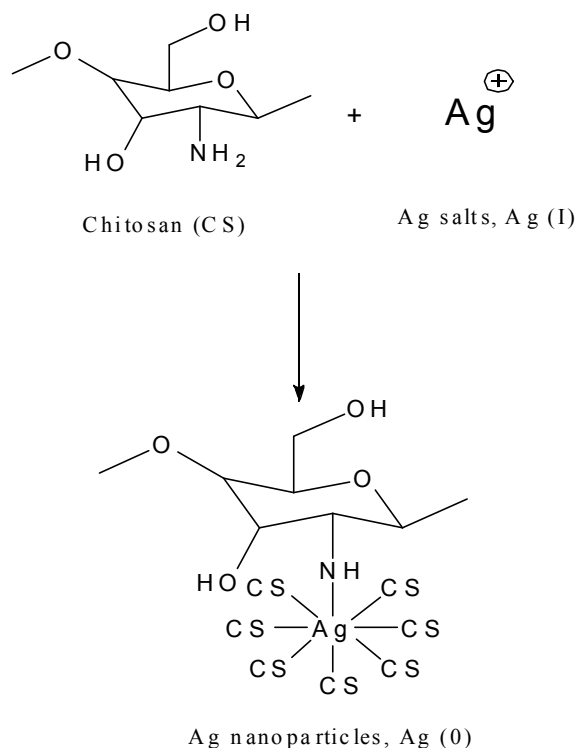


Fig. 5: Mechanisms of Ag nanoparticles – chitosan synthesis

and concern on environmental protection, biological entities such as chitosan is used as reducing and stabilizing agents and some studies on Ag nanoparticles – chitosan production (Figure 5) have been reported

[51-53]. The synthesis occurred in ‘one – pot’ by spreading the chitosan solution in silver nitrate, $AgNO_3$ solution aided by NaOH solution in one medium at room temperature. Some parameters such as reaction time, concentration of precursor and reducing agent and pH of solution are used are important to get the optimize Ag nanoparticles. The chitosan was dissolved in dilute aqueous acidic solution (observed as milky-white solution for pure chitosan) for several hours before it mixed with $AgNO_3$ and NaOH.

CONCLUSION

Chitin is found majorly in nature and their chemical structure is almost same to cellulose, but does not have the cellulose properties. The rigid structure of chitin causes chitin to insoluble in most organic solvents. Modification of chitin structure by removing the acetyl groups presented in chitin backbone chain have overcome the solubility problem, thus increase the application of its derivatives, chitosan. The accessibility of amine groups that attached to the chitosan chain has enhanced its uses in synthesizing metal nanoparticles, particularly focused on Ag nanoparticles. Besides, the non-toxic properties of chitosan have endorsed the cost-effective of green Ag nanoparticles synthesis. Besides, the antigenic effect of Ag nanoparticles is already known and the application of Ag nanoparticles – chitosan can be broaden.

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