

Review Article

PHYSICOCHEMICAL PROPERTIES OF CHITIN AND CHITOSAN FROM DIED HONEY BEES APIS MELLIFERA OF UZBEKISTAN

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Abstract

This article presents the results of obtaining biopolymers of chitin and chitosan from Uzbekistan a new promising source- honeybee bodies *Apis Mellifera*. To obtain chitin, at the first stage, the protein (deproteinization) and mineral (demineralization) constituents of substrate, i.e. put them in soluble state and removed. Demineralization was carried out with 2 M hydrochloric acid for 5 hours at room temperature. The process of deproteinization is carried out by processing the crushed raw materials with 1 N sodium hydroxide solution for 1 hour at a temperature of 80°C. Each process was accompanied by washing the raw materials to a natural wash water reaction (pH=7). At the next stage, chitin deacetylation under the influence of a 35% aqueous NaOH solution at a temperature of 85°C for 4 hours produced chitosan, which is a high molecular weight glucosamine polymer, and dried at 50-55°C. The resulting mass was decolorized with a 3% H₂O₂ solution and washed ethanol.

Keywords: chitin, chitosan, deproteinization, demineralization, deacetylation.

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INTRODUCTION

In the conditions of acute shortage of natural resources and exacerbation of environmental problems the special value is acquired by research, allow mastering and introducing new technologies for obtaining biopolymers from renewable

natural sources of raw materials [1-4]. A special place among biopolymers is occupied by chitin and its very common modification, chitosan [5-6].

Chitin generates a linear aminopolysaccharide consisting of N-acetyl-2-amino-2-deoxy-O-glycopyranose units (fig.1).

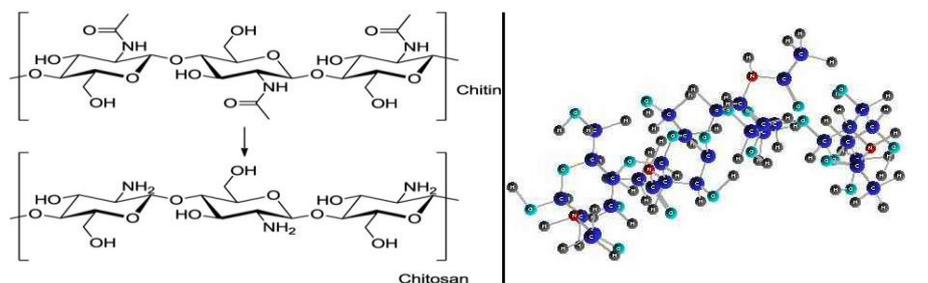


Figure 1. Structure molecule chitosan

Chitin is natural polysaccharide of major importance. The name "chitin" is derived from the Greek word "chiton", meaning a coat of mail. The use of chitin was first described by the French chemist, Henri Braconnot in 1811 [7]. The structure of chitin (C₈H₁₃O₅N)_n is similar to that of cellulose, but with 2-acetamido-2-deoxy--D-glucose (NAG) monomer

units, which are attached to each other via β(1-4) linkages [8]. Chitosan is the deacetylated form of chitin (that can have varying degrees of deacetylation), and it is soluble in acidic solutions (sometimes with difficulty) (fig.1.) [9]. Usually chitosan in Russia is obtained from the shrimp crabs and other shellfish (fig.2).



Figure.2. The Fotograf shrimp, crabs and o shellfish

Honey bees live and die, their age is short. The working bee lives in the summer for just over a month. But even dead bees can give us quite a bit in terms of treatment. Dead bees, their bodies are called the dead bees. Beekeepers often just throw it away. Little bodies, like all living thing contain :

-proteins;

-fats;

-carbohydrates;

-mineral substance;

Three important components contain bee subs:
chitosan, heparin and bee venom.



Fig:3

Due to the wide beekeeping in Uzbekistan, there is also the possibility of obtaining raw materials for the production of chitin and chitosan from bee submoris on a significant scale.

But, due to the fact that this is a fairly expensive process, the question was raised about obtaining chitin and chitosan from other sources. The most accessible for industrial development of chitosan in the Republic of Uzbekistan is the honeybees. This product is new Uzbekistan to ensure import substitution.

Biodegradable polymer chitosan is an environmentally friendly product. Chitosan derived from bees pins.

- Effectively cleanses the body of toxins.
- Enhances immunity, improves blood circulation.
- Promotes tissue regeneration in the skin.
- Binds fats and glucose in the body.
- It has an antispasmodic effect, relieves fatigue.]
- Chitosan helped reduce the bad cholesterol and triglycerides in the blood while increasing the good HDL cholesterol.
- It has the unique ability to attach itself to fats in the stomach before they have metabolized, trapping the fat thereby preventing absorption into the digestive tract.

- Rather than being absorbed, the fast is eliminated from body.

According to the chemical structure, it is close to cellulose and only inferior to its prevalence in nature [11]. The structure of chitin is a crystal lattice, and therefore the degrees of solubility and swelling of chitin in various media are rather low. Chitosan is a product of chitin deacetylation and is the most studied of its water-soluble derivative. In prevalence, it is second only to cellulose and is reproduced in nature from completely renewable natural raw materials [2-4].

Experimental

Increasing interest in chitosan is due to the expansion of its practical application as a specific sorbent, biologically active compound, etc. Chitosan is able to enter into reactions of both intermolecular interaction with polyelectrolytes, forming interpolymer complexes as well the complexation with metal ions.

A special kind of chitosan is "Apis Mellifera bee", more potent biologically active substance than crustaceans chitosan (fig 4.) A significant reserve of raw materials for the production of chitosan is the sub-population of bees Apis Mellifera.

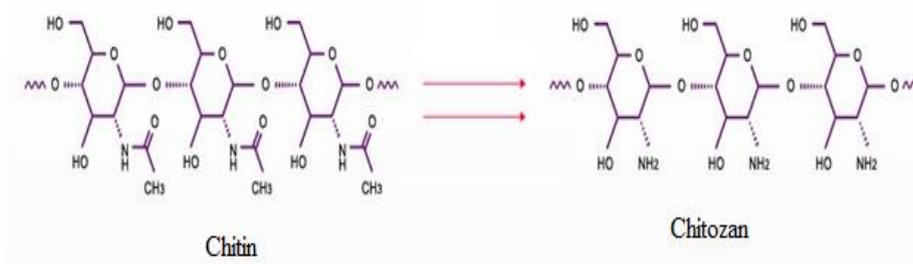


Figure 4. Apis Mellifera Honey bees (bringing honey)

In this connection, it is quite reasonable to obtain reproducible biopolymers of chitin and chitosan from bees wax *Apis Mellifera*. (*Apis Mellifera*) Honey bees, mainly failed during the wintering period and falling to the bottom of the shelter. In summer, the death of bees is much more significant than in winter, but less noticeable, as they usually die outside the shelter [2]. Apisan is obtained from beeswax, or as it is called scientifically low-molecular chitosan-melanin complex [4].

In the summer during the active harvest and in the spring after wintering, the bee family is renewed by almost 60-80%. The strength of the bee family (the mass of worker bees in the bee family, measured in kg) is, on average, 7.5-8 kg. This makes it possible to treat bee shavers as a new promising source of chitin and chitosan along with traditional types of raw materials [5].

The FTIR spectra of Chitin and chitosan obtained from Honey Bee extraction were studied in the FT-IR Nicolet S50 branded spectrometer (Thermo Fisher Scientific, USA).



RESULTS AND DISCUSSION

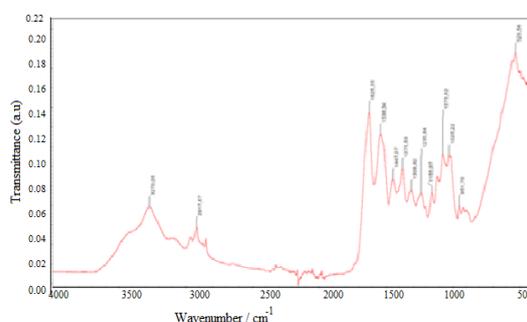
We used dry bee-picking, collected during the spring renovation of the bee family and containing a significant amount of chitin. Raw material is a black-brown mass with a specific smell. On a detailed examination, whole undeveloped bees and various parts of bees (head, chest, legs, abdomen, wings, etc.) are seen. Bees pine contains the minimum amount of mineral substances, since the cuticle of insects is practically not mineralized. The mass of the undercoat was dried at a temperature of about 35°C, with a thin layer. The dried raw material mass of 30 g was crushed and demineralized (DM), followed by deproteinization (DP) according to the following scheme (Figure 5).



Figure 5. The scheme laboratory technology obtained of Chitin and chitosan from Honey Bee

Demineralization (DM) was carried out according to the Hackman method by treating bees with 2M hydrochloric acid for 5 hours at room temperature. Deproteinization was carried out by treating the ground raw material with 1N sodium hydroxide solution for 1 hour at 80°C. The mass was filtered and dried at room temperature. Each process was followed by washing the raw material to neutral reaction of the wash water (pH = 7).

The Figure 6 FT-IR spectra of Chitin and chitosan obtained from Honey Bee.



a)

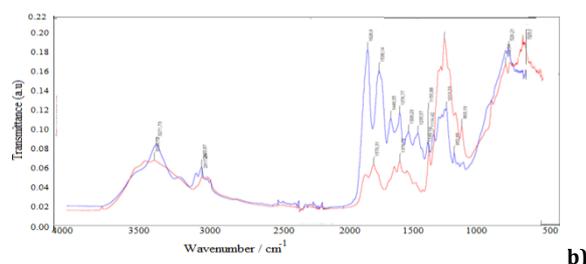


Fig. 6. FTIR spectra of (a) Chitin obtained from Honey Bee extraction and (b) Chitosan

As can be seen from the figure 6, The band in the region of 1660 cm^{-1} corresponding to stretching vibrations of the C = O bond of carbonyl groups in acid amides (amide I) and lane in the region of 1560 cm^{-1} , corresponding to the sum of the vibrations of the N - H and C - N bonds in amides (amide II band). The main infrared absorption bands for the studied samples are in the region of $3600\text{-}600\text{ cm}^{-1}$. In the region of $1700\text{-}1500\text{ cm}^{-1}$, the main absorption bands characteristic of chitin are observed [6], due to stretching vibrations of the N - H group, associated with an acetyl group C = O (band amide I) and bending vibrations of N-H and C-N bonds in amides (amide II band). The presence in the IR spectrum of a band at 1656 cm^{-1} indicates that the chitin in the studied CGC is in the a-form. In the region of spectrum $3600\text{-}3000\text{ cm}^{-1}$ there is a wide band, due to the characteristic stretching vibrations of OH and NH groups of secondary amines, included in intermolecular and intramolecular hydrogen bonds. It should be noted that in.

In this region of the spectrum, deformation vibrations of OH groups of sorbed molecules are also observed water. In the range of $1400\text{-}1300\text{ cm}^{-1}$ IR spectra of these bands 1320 and 1380 cm^{-1} , corresponding to vibrations of the CH and C-N bonds of the amide bands, appear; in the region of $1200\text{-}1000\text{ cm}^{-1}$, a wide intense band with maxima of 1080 and 1160 is observed cm^{-1} , related to stretching vibrations of CO groups of primary and secondary alcohols. In the spectra of CGC and chitin in the region of $970\text{-}850\text{ cm}^{-1}$ (Fig. 6, curves a) and b)) two arms are observed: at 897 cm^{-1} (vibrations of the glucopyranose ring near C (6) and deformation vibrations of the CH) and at 953 cm^{-1} (stretching vibrations of C - O and C - C and deformation pendulum CH_2). IR data indicates that the group at C (6), which has a free rotation, may be associated intramolecular hydrogen bonding with bridge oxygen and a nitrogen atom in an adjacent glucosamine unit (Fig. 2), which is consistent with the results of [7]. In addition, the chitosan spectrum was compared with the device's software data base, and the spectra were found to be compatible with each other at a high percentage. Also, the X-ray diffractogram of chitosan, obtained as a result of deacetylation of chitin, was analyzed (Figure 7). As can be seen from the X-ray diffractogram study, the crystal state of the chitosan and chitin molecules is different when deacetylation (at) is carried out at different percentages (at-8%, 36%, 57%, 81%) it became known that the crystallization rate of chitin fell, which is a decrease in the level of three-dimensional distribution of chitin, especially when deacetylation reached 36%.

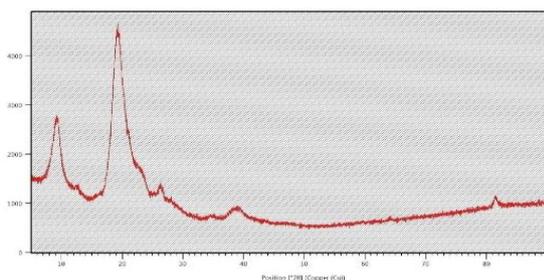


Fig. 7. X-ray study of chitosan from honey Bee excrement

At 57% of the sample detected extremely noticeable structural depreciation. At $2\theta = 19.5^\circ$ and 10.2° corners, intensive deflection maximums were observed. And the structure of the crystal lattice of the chitosan molecule is preserved in this area, but in another plane the crystalline structure is defected or broken.

An elemental analysis of chitosan obtained from the death of bees was also performed, and microscopic images of the structure of chitin and chitosan were taken using a scanning microscope (Fig. 8).

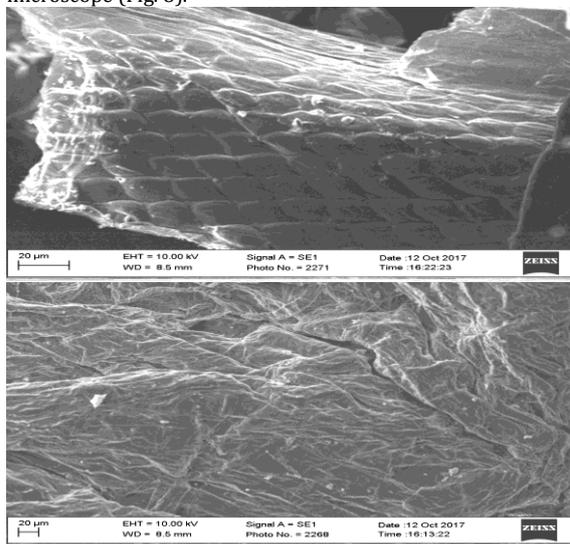


Fig. 8. Microelectronic structure of chitin (a) and chitosan (b) from bee substentle

The data in Fig. 8 indicate that during the treatment of chitin with an alkali solution, its molecules quickly come to an amorphous and then to a crystalline state, that is, amorphization occurs, the crystal lattices are gradually destroyed. From structural molecular and IR spectrometric data, we can conclude that when deacetylation of chitin turns into chitosan, that is, the molecular structures and crystals of chitosan are different from the molecular structures and crystals of chitin.

CONCLUSION

The melting of the synthesized application (chitosan) in various solvents was studied. Petition (chitosan) is poorly soluble in water. This is due to the fact that the interaction of its chitosan molecules is stronger with water molecules. Again, chitosan is well soluble in vinegar, lemon, gravel and yantar acids. The solvent in the solution retains its structure relative to the dissolved substance. Chitosan has a greater sorbitizing effect than insoluble in the molten state. Therefore, it can be used as a polyelectrolyte.

Thus, biopolymers of chitin and chitosan were obtained and characterized on the basis of a new advancing source - dry Apis Mellifera honey bee. Taking into account the natural origin of Apis Mellifera Honeybees and its degree of renewability, it can be concluded that this raw material is of great importance as a raw material for the production of polyelectrolytes with a set of unique properties.

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