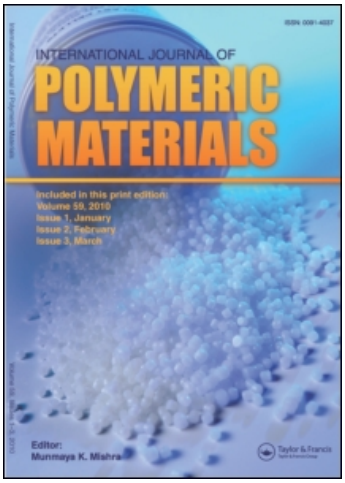

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Variation in Properties of Chitosan Prepared at Different Alkali Concentrations from Squid Pen and Shrimp Shell

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Chitin from squid pen (*Loligo* sp.) and kiddi shrimp shell (*Parapenaeopsis stylifera*) were treated at room temperature ($30 \pm 2^{\circ}$C) with four different concentrations of sodium hydroxide: 20, 30, 40, and 50% w/w. With 50% sodium hydroxide solution, within 108 h, the chitin from squid pen was deacetylated to give chitosan. But it required 126 h at 40% and 144 h at 30% concentration of sodium hydroxide. In the case of chitin from *Parapenaeopsis stylifera*, complete deacetylation took place after 120 h and 168 h at 50 and 40% concentrations of sodium hydroxide, respectively. But shrimp shell on treatment with 20 and 30% sodium hydroxide solutions and squid pen kept at 20% sodium hydroxide were not sufficiently deacetylated even after 480 h. Properties like degree of deacetylation, viscosity and molecular weight of the prepared chitosan samples were studied. Minimum alkali concentration required for the formation of chitosan at room temperature was found to be 30% for squid chitin and 40% for shrimp chitin. With the increase in the time of deacetylation, decreases in molecular weight and viscosity were observed in chitosan from both sources. Maximum viscosity was recorded by chitosan prepared from squid pen using 30% sodium hydroxide solution at room temperature.

Keywords chitin, chitosan, *Parapenaeopsis stylifera*, shrimp shell, squid pen

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INTRODUCTION

Today people show great interest in including seafoods in their daily menu because of their high nutritional value. Seafoods are rich sources of protein, yet seafood industries pollute the living environment by excreting a large quantity of waste materials. Since environmental regulations on discharged wastes are stricter nowadays, many attempts have been made to utilize these waste materials in a beneficial way [1]. Waste utilization is an important issue for the seafood industry from a regulatory standpoint and as a potential byproduct. So, a large volume of shell waste is currently processed into chitosan, a derivative of chitin [2]. Chitin is a biopolymer of N-acetyl glucosamine and is present in the exoskeleton of arthropods, setae in annelids, bivalve shells, cephalopods, and fungi. Chitin is the second most abundant mucopolysaccharide. Chitosan has a wide range of applications in cosmetics, textiles, photography, agriculture and the pharmaceutical industries [3]. Since chitosan has antibacterial, wound healing and antihepatotoxic properties, it will be a necessity also in today's medical needs.

Chitosan is prepared by the N-deacetylation of chitin. Major steps involved in the production of chitosan are the conversion of raw material into chitin by demineralization with dilute acid and deproteinization with dilute alkali; then chitin is deacetylated with concentrated alkali at high temperature [4]. Now chitosan has growing importance partly because it is a biodegradable and renewable source of materials, and partly because of the recent increased applications in a variety of areas [5]. The suitability of chitosan for various applications depends on its properties, like viscosity, molecular weight, degree of deacetylation, and turbidity, which, in turn, are influenced by its source and production conditions.

Thus the present study was conducted to examine the properties of chitosan prepared from two different sources of chitin, squid pen and shrimp shell, at different alkali concentrations at room temperature.

EXPERIMENTAL

Raw Material and Chemicals

Shrimp shell (*Parapenaeopsis stylifera*) and squid pen (*Loligo* sp.) were obtained from a processing plant near Cochin, India.

All chemicals used were of analytical grade and were supplied by M/s Sigma Chemical Company, St. Louis, MO, USA.

Preparation of Chitosan

Shrimp waste was deproteinized with 3% w/v NaOH in the ratio 2:3 for three days at room temperature and the residue was washed and demineralized

with 1.25 N hydrochloric acid at room temperature for 1 h to obtain chitin. The residue was thoroughly washed and dried. Chitin from squid pen was produced by deproteinization with 3% w/v NaOH at room temperature for three days and demineralization with 0.2 N hydrochloric acid for 1 h at room temperature. The thoroughly washed residue was dried and used for chitosan production. Shrimp chitin and squid pen chitin were deacetylated using 20, 30, 40, and 50% w/w NaOH solutions at room temperature. The samples were tested for their solubility in 1% acetic acid at intervals till complete solubilization was achieved, i.e., it became chitosan. From that time onwards samples were taken for analysis and the treatment with alkali was continued.

Analytical Determinations

Protein and ash content of the raw material and chitin were determined by the method of AOAC [6]. Molecular weight was measured as described by Rong and Homg [7] using Schott Gerate AVS 410 equipment. Viscosity of 1% chitosan solution in 1% acetic acid was determined by a Brookfield DV-E rotational viscometer using a DAA 86 spindle; shear rate (1/sec.) is 1.29 · rpm. According to the spectroscopic method given by Muzzarelli [8], degree of deacetylation was estimated with the use of a Schimadzu UV-160 spectrophotometer.

RESULTS AND DISCUSSION

Protein and ash content of the chitin were determined. Table 1 shows the protein and ash of the raw material and chitin from both sources. Squid pen has low ash content because it contains a small quantity of minerals [9].

At 50% sodium hydroxide concentration, squid chitin was deacetylated to such an extent that it was readily soluble in 1% acetic acid to give a clear solution, i.e, it became chitosan, within 108 h as compared to shrimp chitin, which took 120 h for deacetylation. Similarly, squid chitin required 126 h at 40% and 144 h at 30% NaOH to attain sufficient deacetylation. But shrimp chitin at 40% NaOH took 168 h for its conversion into chitosan. Shrimp shell kept at 20 and 30% NaOH and squid pen kept at 20% NaOH did not undergo sufficient deacetylation to become soluble in 1% acetic acid solution even after

Table 1: Protein and ash content of two raw materials and chitin prepared from them.

Parameters	Shrimp shell	Shrimp chitin	Squid pen	Squid chitin
Protein % (dry wt basis)	45.34	1.83	52.27	0.08
Ash % (dry wt basis)	32.23	1.21	0.43	0.04

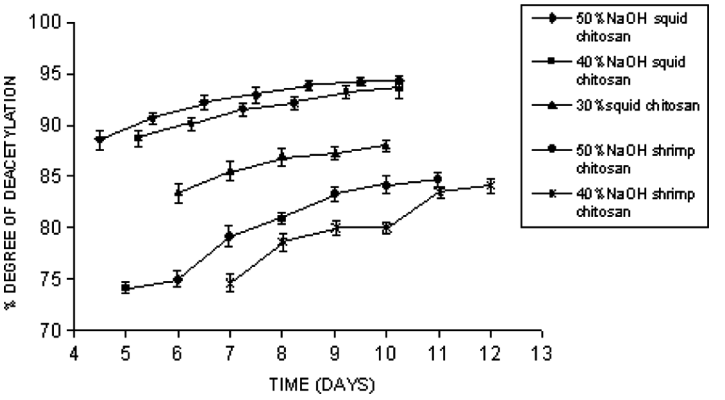

Figure 1: Changes in the degree of deacetylation of chitosan prepared from squid pen and shrimp shell at different alkali concentrations.

480 h. Chitin from shrimp shell has an α-structure, in which the chitin main chains are arranged in an antiparallel fashion with strong intra- and intermolecular hydrogen bonding, unlike the β-chitin obtained from squid pen. In β-chitin, the chitin chains are arranged in a parallel mode with relatively weak hydrogen bonding. So, the deacetylation of squid chitin takes place more rapidly than shrimp chitin [9]. Also the deacetylation time of β-chitin is less than that required for α-chitin [10]. This may be the reason for the shorter deacetylation time for chitin from squid pen.

Changes in the degree of deacetylation of squid pen chitosan and shrimp chitosan with time, at different alkali concentrations are shown in Figure 1. It is clear from the graph that in all the samples, the degree of deacetylation increases with time and squid pen chitosan was deacetylated more than shrimp chitosan. Also, alkali concentration has a significant effect on the time of deacetylation and degree of deacetylation [11].

Changes in the viscosity of different chitosan samples are shown in Tables 2 and 3. Maximum viscosity was obtained in squid pen chitosan and

TABLE 2: Changes in viscosity of squid pen chitosan at different alkali concentrations.

	Viscosity in mPa · s of 1% solution in 1% acetic acid		
Days	**30% NaOH**	**40% NaOH**	**50% NaOH**
4.5	–	–	3300 ± 12
5.5	–	3305 ± 13	1560 ± 9
6.5	2200 ± 11	1910 ± 10	498 ± 5
7.5	1048 ± 9	760 ± 7	182 ± 4
8.5	617 ± 5	304 ± 7	108 ± 2
9.5	226 ± 4	176 ± 5	94 ± 2
10.5	211 ± 4	158 ± 3	80 ± 2

Table 3: Changes in viscosity of shrimp chitosan at different alkali concentrations.

	Viscosity in mPa · s of 1% solution in 1% acetic acid	
Days	**40% NaOH**	**50% NaOH**
5	–	468 ± 5
6	–	468 ± 5
7	470 ± 4	457 ± 4
8	464 ± 3	432 ± 3
9	457 ± 3	421 ± 4
10	459 ± 1	417 ± 2
11	446 ± 2	408 ± 3
12	412 ± 4	395 ± 2

Table 4: Changes in molecular weight of squid chitosan at different alkali concentrations.

	Molecular weight (X10^6 Daltons)		
Days	**30% NaOH**	**40% NaOH**	**50% NaOH**
4.5	–	–	2.17 ± 0.12
5.5	–	2.17 ± 0.11	2.17 ± 0.12
6.5	2.17 ± 0.10	2.17 ± 0.11	2.17 ± 0.12
7.5	2.17 ± 0.10	2.17 ± 0.11	0.92 ± 0.01
8.5	1.39 ± 0.05	2.00 ± 0.10	0.92 ± 0.01
9.5	1.12 ± 0.03	1.38 ± 0.10	0.89 ± 0.01
10.5	1.12 ± 0.03	1.24 ± 0.10	0.87 ± 0.01

the viscosity decreased with an increase in deacetylation time and strength of alkali. As the deacetylation time and strength of alkali increases, degradation of the polymer chain occurs and, as a result, the viscosity decreases [12]. Molecular weight changes in squid and shrimp chitosan samples with respect

Table 5: Changes in molecular weight of shrimp chitosan at different alkali concentrations.

	Molecular weight (X10^6 Daltons)	
Days	**40% NaOH**	**50% NaOH**
5	–	1.24 ± 0.02
6	–	1.24 ± 0.02
7	1.34 ± 0.01	1.10 ± 0.01
8	1.34 ± 0.01	1.10 ± 0.01
9	1.29 ± 0.01	0.84 ± 0.01
10	1.29 ± 0.01	0.84 ± 0.01
11	1.10 ± 0.02	0.82 ± 0.01
12	1.02 ± 0.02	0.80 ± 0.01

to the time and alkali concentration are given in Tables 4 and 5. Reduction in molecular weight was observed with an increasing degree of deacetylation. When the degree of deacetylation increases more and more acetyl groups will be lost from the polymer chain, resulting in the decrease of molecular weight, which, in turn, decreases viscosity too [13].

CONCLUSION

In the present study, we have found that the minimum alkali concentration required for the deacetylation of chitin to chitosan from squid pen, at room temperature, was 30% and from shrimp shell it was 40%. Time and alkali concentration for deacetylation were less for squid chitin than chitin from shrimp. Chitosan prepared from squid pen had better properties than chitosan from shrimp shell.

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