

UTILIZATION OF PRAWN WASTE — ISOLATION OF CHITIN AND ITS CONVERSION TO CHITOSAN

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A process is described for the preparation of chitosan from prawn waste. The process involves extraction of protein using 0.5% sodium hydroxide solution, bleaching the protein free mass with bleach liquor containing 0.3-0.5% available chlorine followed by demineralisation with 1.25 N hydrochloric acid in the cold and deacetylation using 1:1 (w/w) sodium hydroxide solution at 100°C for 2 hours.

INTRODUCTION

Chitosan is a high molecular weight linear polymer of amino D-glucose derived from chitin by a process of deacetylation. It is known to have wide and varied applications in industry such as sizing of rayon, cotton, synthetic fibres, wool, paper, cellophane, as adhesives, stabilising and thickening agents, and in pharmaceuticals and cosmetics etc. (Williams, 1959). In addition it is known to have applications as a chromatographic base (Nagasawa *et al.* 1970), ion exchange resin, and in clarification of water, wine etc. So far no such application of this product is known to have been resorted to in India perhaps because it is not indigenously available.

The phenomenal increase in the export of canned and frozen prawn products from India achieved during the past decade and a half presents in other way the problem of disposal of a huge quan-

tity of waste material comprising head and shell, which on a rough approximation comes to nearly 40,000 tons annually. It is only a very negligible portion that is being utilised directly as manure, the rest being discarded. This waste material on dry weight basis contains about 10% chitin providing a good source for the preparation of chitosan and thus offering good scope for the conversion of the waste to useful product of potential industrial application.

Takeda and Ab (1962) during their course of investigation on deacetylation of chitin have studied the use of mixed enzymes for the removal of incidental protein and decalcification using sodium salt of EDTA. The senior author in his later studies (1966) has used strongly alkaline hydroxylamine for the deacetylation of chitin. Lusena and Rose (1953) have described a method for converting chitin to chitosan using a 55% solution

of potassium hydroxide. Radhakrishnan and Prabhu (1971) have studied the preparation of chitosan from prawn waste by different methods for deacetylation of chitin using 50% aqueous potassium hydroxide and equal volumes of 50% aqueous sodium hydroxide and ethyl alcohol. However, their methods do not aim at recovering the 35-40% (on D.W.B.) protein present in the prawn waste. Substantial modifications have been effected to the process described by them in order that a major portion of this valuable protein is recovered and the process given an industrial bias, an account of which is presented in this paper.

MATERIAL AND METHODS

Initially prawn waste derived from a single species of prawns, *Matapenaeus dobsoni*, obtained from a single prawn processing factory in Cochin was utilised in these studies. Later the technique developed was tried with prawn waste from other species and mixed prawn waste from different species.

The fresh waste is washed in water and heated to boiling with 0.5% aqueous sodium hydroxide in the ratio 2:3 (by weight) for 30 minutes. The alkali is drained off and kept separately for the recovery of protein. The residual protein is removed by heating the residue to boiling with an equal weight of 3% sodium hydroxide solution, draining off the alkali and repeating the process once again. The residue is immersed in cold hypochlorite solution containing 0.3 to 0.5% available chlorine for about 30 minutes, when most of the pigments contained in the prawn waste are bleached. The liquor is drained off, the residue is washed and demineralised by immersing in 1.25 N hydrochloric acid at room temperature for

1 hour. The residue after draining off the acid and washing with water is subjected to the final process of deacetylation by dipping in 1:1 (w/w) sodium hydroxide solution for 2 hours at 100°C. The alkali can be used for deacetylation of subsequent batches. The deacetylated mass is washed several times till free of alkali, dried in sun, pulverized to the required size and stored.

RESULTS AND DISCUSSION

Recovery of protein from the prawn waste using a lower concentration of the alkali necessitates only a proportionately low amount of acid for neutralisation which further helps to bring down the final concentration of salt in the recovered protein. Use of bleach liquor for bleaching of pigments dispenses with the use of costly hydrogen peroxide described by Radhakrishnan and Prabhu (*loc. cit.* 1971.)

Demineralisation of protein free mass is an important step in the preparation of chitosan from prawn waste as the degree of demineralisation determines to a great extent the characteristics of the product, particularly the viscosity. With progressive increase in the concentration of hydrochloric acid the degree of demineralisation is increased, however, use of acid of concentration above 1.25 N adversely affects the viscosity of the final product. A comparative account of the concentration of acid used, time of treatment, content of acid soluble ash in chitin and viscosity of the final product are given in table I.

Demineralisation using hydrochloric acid at higher temperatures was not tried as it has been reported (Radhakrishnan and Prabhu, *loc. cit.* 1971) that this will result in reducing the viscosity of chitosan.

TABLE I
EFFECT OF DEGREE OF DEMINERALISATION ON
VISCOSITY OF CHITOSAN

Concentration of acid used. N	Time of treatment in minutes	Acid soluble ash in chitin %	Viscosity of 1% chitosan in 1% acetic acid (Centipoises)
0.75	30	48.44	14.63
	60	46.30	16.84
	120	41.52	18.86
	180	39.44	18.45
	∞	37.50	18.02
1.0	30	43.69	32.03
	60	38.28	36.56
	120	33.86	38.19
	180	23.95	39.42
	∞	20.32	40.03
1.25	30	24.34	106.85
	60	18.82	97.07
	120	6.33	58.05
	180	2.97	46.44
	∞	1.31	40.89
1.5	30	15.34	49.28
	60	7.90	43.95
	120	3.14	40.06
	180	1.46	38.84
	∞	1.31	34.58
2	30	2.71	37.66
	60	1.76	31.52
	120	1.03	26.94
	180	0.65	17.79
	∞	0.54	17.20

Deacetylation of the demineralised mass was carried out with 1:1 (w/w) solution of sodium hydroxide at a temperature of 100°C for 2 hours. It has been observed during the course of investigation that completely demineralised sample on deacetylation for 1½ hours gives a product which dissolves in 1% acetic acid at 1% level. However, the

time requirement is more with samples containing more of acid soluble ash. When the content of acid soluble ash is beyond a certain level, the prolongation of time of treatment does not seem to have any pronounced effect. Therefore it has been assumed that for a reasonably demineralised sample a treatment time of 2 hours can

TABLE II
EFFECT OF TIME OF DEACETYLATION ON VISCOSITY OF CHITOSAN

Concentration of acid N	Time of demi- nealisation in minutes	Time of deacety- lation in minutes	Viscosity of 1% chitosan in 1% acetic acid (Centipoise)
1.25	60	30	165.8
		60	226.9
		90	241.8
		120	186.4

be taken as adequate for deacetylation.

Viscosities of the products deacetylated for different periods are given in table II.

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