PERGAMON
www.elsevier.com/locate/watres

PII: S0043-1354(99)00211-0

Wat. Res. Vol. 34, No. 3, pp. 1057–1062, 2000

Printed in Great Britain
0043-1354/00/$ - see front matter

TECHNICAL NOTE

OPTIMAL CONDITION FOR MODIFICATION OF CHITOSAN: A BIOPOLYMER FOR COAGULATION OF COLLOIDAL PARTICLES

CHIHPIN HUANG*M, SHUCHUAN CHEN and JILL RUHSING PAN

Institute of Environmental Engineering, National Chiao Tung University, 75 Po-ai Street, Hsinchu
3009, Taiwan, Republic of China

(First received 14 September 1998; accepted in revised form 1 May 1999)

Abstract—Chitosan, an acetylated derivative of chitin, is a biodegradable cationic polymer. Chitosan can be a promising substitute for alum in the coagulation process, because of its potential feasibility in coagulation without posing any health threat as the residual aluminium and other synthetic polymers do. In this study, various pretreatment conditions were tested in search of the optimum chitosan modification. Batch tests with synthetic source water suggest that the optimal pretreatment condition to prepare modified chitosan coagulant is deacetylation by 45% alkali solution for 60 min, followed by dissolution in 0.1% hydrochloric acid. © 2000 Elsevier Science Ltd. All rights reserved

Key words—chitosan, biopolymer, water treatment, coagulant

INTRODUCTION

In conventional water treatment systems, alum has been the most widely used coagulant because of its proven performance, cost-effectiveness, relative ease of handling and availability. Recently, much attention has been drawn on the extensive use of this coagulant. Besides the large amount of sludge produced, high level of aluminium remained in the treated water has raised concern on public health (Driscoll and Letterman, 1995). McLachlan (1995) discovered that intake of large quantity of alum salt may cause Alzheimer disease. To minimise the detrimental effect accompanied with the use of alum, polymers are added either with alum or alone and have gradually gained popularity in water treatment process. Synthetic polyelectrolytes generally produce sludge of better dewatering characteristics and facilitate better filtration. However, their long-term effects on human health are not well understood.

Chitin, a cellulose-like biopolymer, is widely distributed in nature, especially in marine invertebrates, insects, fungi and yeasts. Its deacetylated derivative, chitosan, is a linear cationic polymer of high molecular weight, readily soluble in acidic solutions. It is also biodegradable, non-toxic, and has been used in the coagulation of suspended solids from various food processing wastes (Knorr, 1983). Since chitosan is effective in coagulation without any known disadvantage, it can be a promising substitute for synthetic products (Kawamura, 1991). Chitosan has been applied in the coagulations of bentonite and koalinite particles in our laboratory (Huang and Chen, 1996). The preliminary studies suggested that chitosan can be a potent coagulant for the surface water treatment. When investigating the adsorption of chitosan on kaolin, Domard *et al.* (1989) showed that the adsorption can be described by the Langmuir equation and that the greatest adsorption was achieved when the chitosan was fully deacetylated. The objective of this study is to search for the optimum condition for chitosan pretreatment by evaluating the coagulation efficiencies of chitosan prepared from different conditions.

MATERIALS AND METHODS

Chitosan preparation

Chitin isolated from a crab shell was crushed to a powder form and then deacetylated by NaOH (45%, w/w) at 100°C. The product was rinsed several times with deionized water until the pH of the chitosan suspension reached 7, followed by drying at 80°C for 48 h. Chitosan was dissolved in acetic acid and hydrochloric acid of various concentration by stirring at room temperature or mildly heated until completely dissolved to make 1% stock solution.

Synthetic source water

Given amount of bentonite powder, product of Hayashi

---

*Author to whom all correspondence should be addressed Fax: +886-35-725-958; e-mail: cphuang@green.ev.nctu.edu.tw

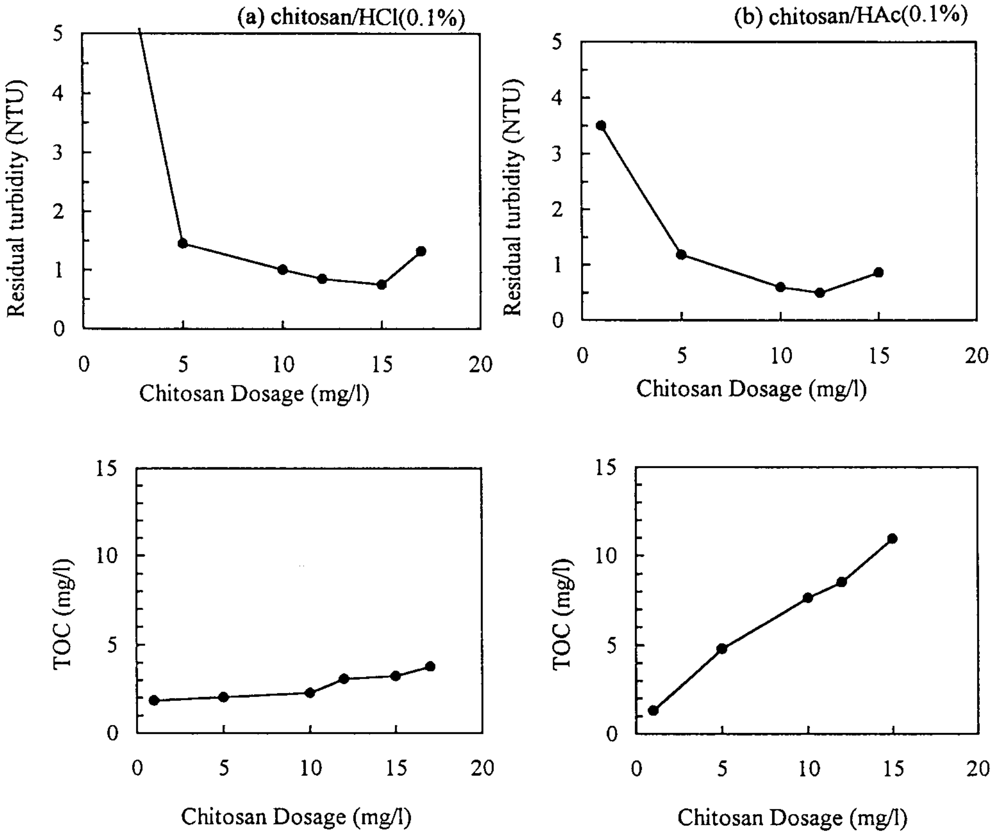

Fig. 1. residual turbidity and TOC of supernatants after coagulation by chotosan: (a) chitosan/HCl, (b) chitosan/HAc.

Pure Chemical Industries Ltd., Japan, was added into $NaClO_4$ solution (ionic strength $= 10^{-2}N$) to prepare a synthetic suspension with 90 NTU turbidity. A $NaClO_4$ solution was used in the preparation in order to in order to provide background ionic strength in the distilled water.

Flocculation tests

A conventional jar test apparatus (Phips and Bird, USA) was used for flocculation experiments. Throughout the experiment, the pH of the suspension was maintained by adding strong base (0.1 M NaOH) or strong acid (0.1 M $HClO_4$). After the coagulant was added to the suspension, the beaker was rapidly mixed at 100 rpm for three minutes, followed by 20 min of slow mixing (30 rpm). The suspension was then settled for 10 min and the sample was withdrawn from the top one inch of the suspension for turbidity measurement, following the standard nephelometry procedure (HACH Ratio, USA). The settling velocity and the diameter of flocs were measured with the photographic method using Panasonic NV-LC1 camera.

Analysis of the degree of deacetylation

The degree of deacetylation (DD) of chitosan was determined by the colloid titration method (Mima *et al.*, 1983). Chitosan was first dissolved in 0.1 M acetic acid to make a 0.01% solution and then titrated with 0.0025 N polyvinyl sulphate potassium (PVSK) with 1% toluidine blue (TBO) as indicator. The acetyl content of chitosan was calculated from the amount of the titrant used.

Molecular weight determination

The molecular weight (M) of polymers was measured by the viscometer based on the well-known Mark–Houwink equation $\eta = \kappa M^{alpha}$. The intrinsic viscosity (η) of chitosan samples was measured with an Ubbelonde viscometer in 0.2 M CH_3COOH/0.1 M CH_3COONa aqueous solution at $30 \pm 0.1°C$. The κ and α in the equation have been determined in the literature and were adjusted by the DD of chitosan according to the following equation (Wang *et al.*, 1991):

$$\kappa = 164 \times 10^{-30} \times DD^{14.0}$$

$$\alpha = -1.02 \times 10^{-2} \times DD + 1.82.$$

Table 1. Viscosity of chitosan coagulants prepared from various concentrations of hydrochloric and acetic acids

Acid solution	Hydrochloric acid			Acetic acid		
pH value	1.2	1.0	0.5	2.5	2.0	1.5
Concentration (%)	0.06	0.1	0.64	1.2	7.2	30
Viscosity (cps)	15	11	2.4	26	21.5	15

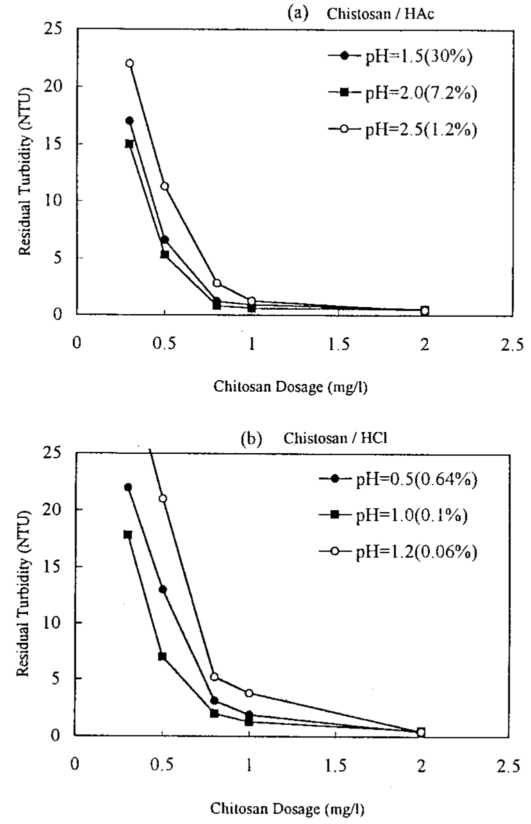

Fig. 2. Residual turbidity of supernatants after coagulation by chitosan dissolved in different concentration of acid solution: (a) acetic acid, (b) hydrochloric acid.

Charge density determination

The charge density (CD) of cationic polymers was determined by titration with standard polyvinyl sulphate potassium (PVSK) (Dentel *et al.*, 1993). To avoid pH effect on charge determination, 50 ml of pH 4 buffer solution was added to 1.0 g polymer along with two drops of 0.1% TBO.

RESULTS AND DISCUSSION

Selection of acid solvent for chitosan

Chitosan is virtually insoluble in water under normal conditions. It can dissolve in carboxylic acid solutions, in which acetic acid (HAc) has been a most common solvent for chitosan. However, this organic solvent might increase the organic content of suspensions, which were coagulated by chitosan. In this study, therefore, we selected one of inorganic acids, hydrochloric acid (HCl), as an alternative solvent to evaluate the coagulation capacity of HCl-prepared chitosan.

First of all, Chitosan was prepared in 1% solution of HAc and HCl separately to make 1% stock solutions, which was then diluted to 0.1% before each experiment. The residual turbidity and total organic carbon (TOC) of the supernatants after chitosan coagulation are presented in Figs. 1(a) and (b). The pH's of experiments 1(a) and (b) are 1.0 and 3.0. Significant decrease in residual turbidity and increase in TOC were found in both sol-

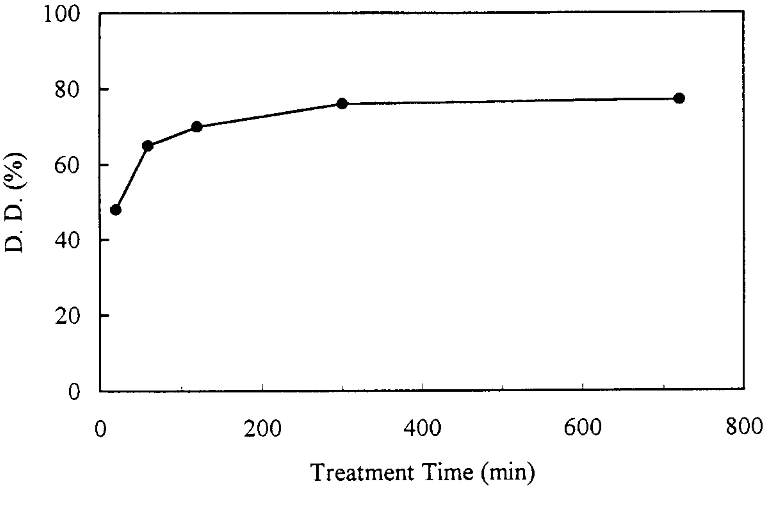

Fig. 3. The relationship between the degree of deacetylation (DD) and treatment time.

Table 2. Characteristics of chitosan samples after deacetylation

Sample No.	Concentration of NaOH (%)	Reaction time (min)	DD (%)	Molecular weight
1	45	20	48	–
2	45	60	68	1.69×10^6
3	45	120	73	1.62×10^6
4	45	300	77	1.63×10^6
5	45	720	78	1.68×10^6
6	60	300	86	4.70×10^6

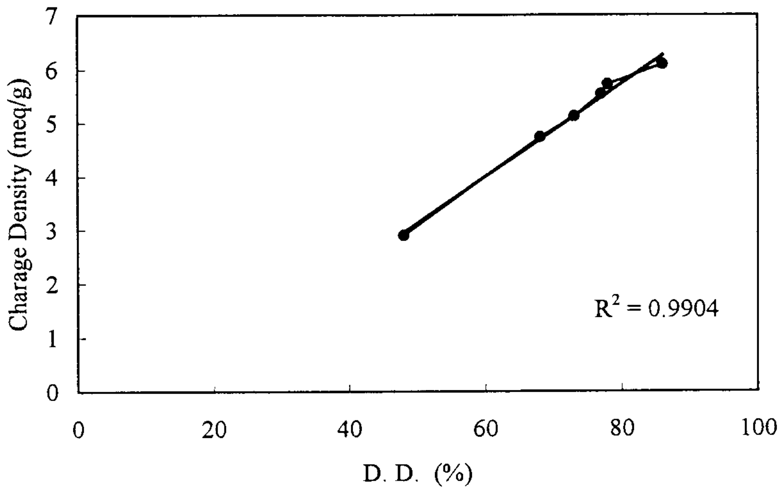

Fig. 4. The relationship between the charge density and degree of deacetylation.

utions. Although the chitosan/HAc coagulant is as efficient as the chitosan/HCl coagulant, the TOC after coagulated with chitosan/HAc increased substantially. Therefore, we considered HCl to be a better choice for chitosan preparation from the viewpoints of either avoiding organic input or treatment efficiency.

Acid solvents of various concentrations were used to prepare chitosan solution. The viscosity of these coagulant solutions were measured and listed in Table 1. It is obvious that the viscosity of dissolved chitosan coagulants decreased with the increasing concentration of acid. When the positive charge of chitosan is neutralised by the negative ion in acid solution, the conformation of the chitosan polymer changes. The chitosan becomes more compact in more acidic solution and therefore lower the viscosity of the solution. To search for the optimal acid concentrations, chitosan was prepared in various concentrations of HAc and HCl solutions. The residual turbidity values from the jar trials are presented in Figs. 2(a) and (b). Best efficiency was found at pH 2.0 (i.e. 7.2% HAc solution) in chitosan/HAc and at pH 1.0 (i.e. 0.1% HCl solution) in chitosan/HCl. This is the result of the combined effects of protonation of amino group NH_2^+ and the conformational change due to the neutralisation by additional anions as mentioned before. Since less TOC was produced in HCl solution and less amount was required to achieve the same coagulation performance, the 0.1% HCl solution was selected for the preparation of chitosan coagulant.

Characteristics of chitosan with different treatment condition

Chitosan was prepared from the hot, concen-

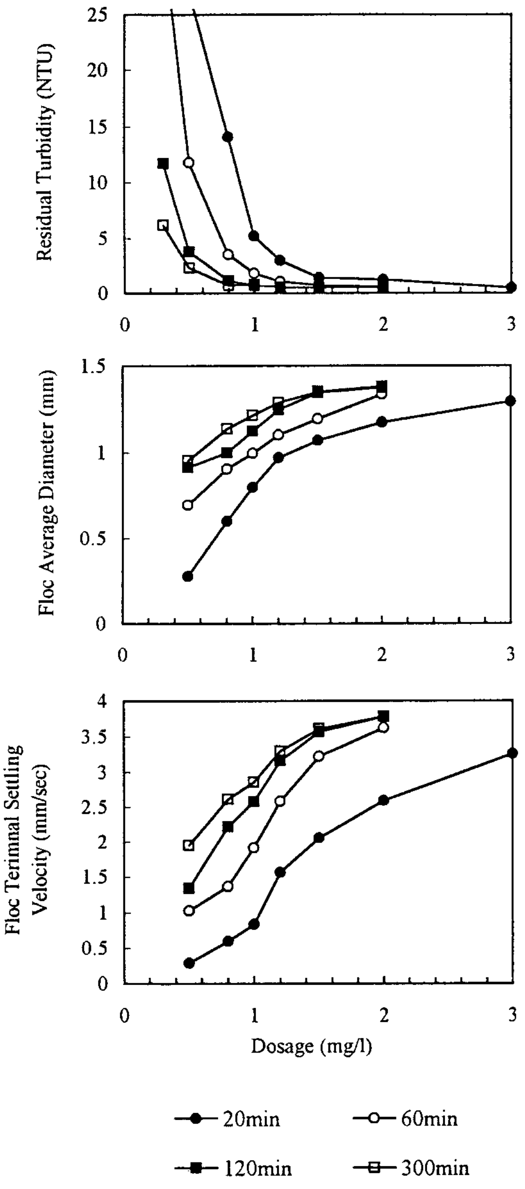

Fig. 5. The coagulation efficiency of chitosan coagulants with different deacetylation treatment time.

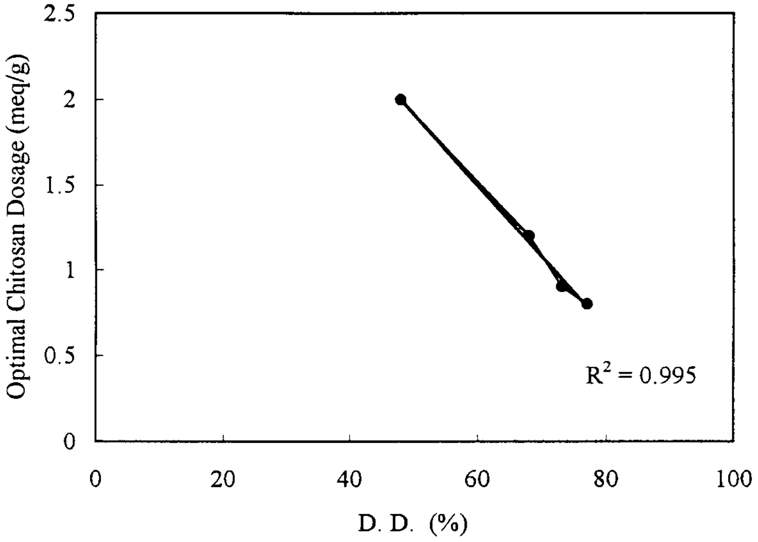

Fig. 6. The relationship between the degree of deactelylation and optimal chitosan dosage.

trated alkali treatment of chitin. The degree of deacetylation (DD) is defined as the ratio of the number of amino groups in chitosan to the sum of the amino and acetyl groups. At a reaction temperature of 100°C, a series of chitosan of different DD and molecular weight were prepared from different combinations of alkali concentration and treatment time. The values of D.D. and molecular weight of six deacetylated products are given in Table 2.

The relationship between the DD and the reaction time under the same alkali concentration (45%) is given in Fig. 3, which shows that longer treatment time produce products of higher degree of deacetylation. The charge density of chitosan is directly proportional to the degree of deacetylation, as shown in Fig. 4.

Coagulation efficiency of chitosan from different treatment

Coagulation efficiency is evaluated by the residual turbidity, average diameter and terminal settling velocity of the floc. Fig. 5 shows the coagulation efficiency of chitosan coagulants from different treatment time (i.e. 20, 60, 120 and 300 min). It is obvious that longer treatment time produced chitosan with better coagulation efficiency. However, this increase in efficiency is not proportional to the increase in treatment time. A linear relationship between the DD of chitosan and the optimal chitosan dosage was found in Fig. 6, which indicates that amino group of chitosan is the active site for coagulation. The effect of alkali concentrations on coagulation efficiency during deacetylation is shown in Fig. 7. The sample No. 4, having lower degree of deacetylation but higher molecular weight, has

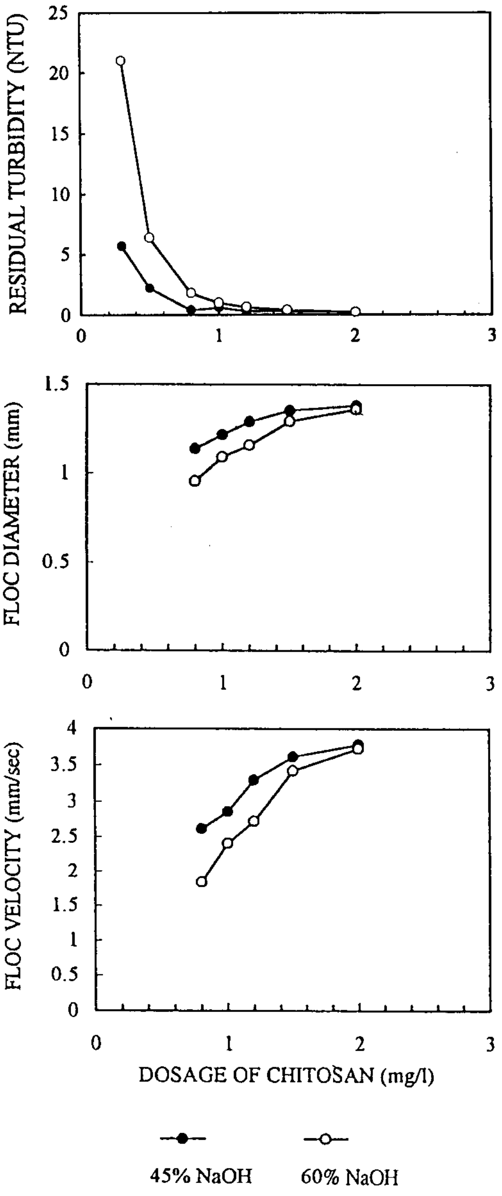

Fig. 7. The coagulation efficiency of chitosan coagulants deacetylted with different alkali concentrations.

lower optimal coagulation dosage than the sample No. 6. Although higher DD was obtained in sample No. 6 (e.g. 86%), poor coagulation, higher residual turbidity, smaller floc diameter and slower settling velocity, was observed (as shown in Fig. 7). The smaller floc was due to the decreased bridging action from chitosan of lower molecular weight.

CONCLUSION

Batch tests with synthetic turbidity water were performed to evaluate the coagulation efficiency of chitosan prepared with different concentrations of acetic acid and hydrochloric acid and various degree of alkali treatment. The results recommend that the optimal pretreatment condition to prepare modified chitosan coagulant is deacetylation by 45% alkali pretreatment for 60 min and dissolution by 0.1% hydrochloride solvent.

Acknowledgements—This work was partially funded by the National Science Council, ROC. The authors wish thank Dr. Li Chin-Fung, National Taiwan University, for the supply of crab chitin and Dr. Chung Ying-Chien, National Science Council, for the information of chitosan preparation.

REFERENCES

Dentel S. K., Abu-Orf M. M. and Griskowitz, N. J. (1993) Guidance Manual for Polymer Selection in Wastewater Treatment Plant. Chap. 3. Water Environment Research Foundation, Project 91-ISP-5, pp. 101–111.

Domard A., Rinaudo M. and Terrassin C. (1989) Adsorption of chitosan and a quaternized derivative on kaolin. *J. Appl. Polymer Sci.* **38**, 1799–1806.

Driscoll C. T. and Letterman R. D. (1995) Factors regulating residual aluminium concentrations in treated waters. *Environmetrics* **6**, 287–309.

Huang Chihpin and Chen Yin (1996) Coagulation of colloidal particles in water by chitosan. *J. Chem. Tech. Biotechnol.* **66**, 227–232.

Kawamura S. (1991) Effectiveness of natural polyelectrolytes in water treatment. *J. AWWA* **10**, 88–91.

Knorr D. (1983) Dye binding properties of chitin and chitosan. *J. Food Sci.* **48**, 36–41.

McLachlan D. R. C. (1995) Aluminum and the risk for Alzheimer's disease. *Environmetrics* **6**, 233–275.

Mima S., Miya M., Iwamoto R. and Yoshikawa S. (1983) Highly deacetylated chitosan and its properties. *J. Appl. Polymer Sci.* **28**, 1909–1917.

Wang W., Bo S., Li S. and Qin W. (1991) Determination of the Mark–Houwink equation for chitosan with different degrees of deacetylation. *Int. J. Biol. Macromol.* **13**, 281–285.