

Short communication

Hydration energy of the 1,4-bonds of chitosan
and their breakdown by ultrasonic treatmentHui Liu ^{a,*}, Yu-Min Du ^b, John F. Kennedy ^{c,d}^a School of Environmental Studies and MOE Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China^b Department of Environmental Science, Wuhan University, Wuhan 430072, China^c Birmingham Carbohydrate and Protein Technology Group, School of Chemical Sciences, University of Birmingham, Birmingham B15 2TT, UK^d Chembiotech Laboratories, University of Birmingham Research Park, Vincent Drive, Birmingham B15 2SQ, UK

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Abstract

A chitosan molecule with polymerization of 25 was simulated using Hyperchem Release 7.1 for Windows Molecular Modeling System, and the hydration energies of the 1,4- β -D-glucosidic bonds were computed. As a result, the hydration energies of the glucosidic bonds are: GlcNAc–GlcNAc (0.85 kcal/mol) > GlcN–GlcNAc (0.75–0.76 kcal/mol) \approx GlcNAc–GlcN (0.74–0.75 kcal/mol) > GlcN–GlcN (0.65–0.67 kcal/mol). Former experimental results showed that chitosans with higher deacetylation degree (DD) are more easily degraded, and ultrasonic degradation decreased the DD of initial chitosans with a lower DD (<90%), but the DD of initial chitosans with a higher DD (>90%) changed no more than 2%. It is concluded from the analysis that the hydration energy between 1,4- β -D-glucosidic bonds of chitosan may be closely related to the breakdown by ultrasonic treatment. The higher the hydration energy is, the more difficult the breakdown will be. So the degradation of chitosan by ultrasound is not random; it follows the sequence: GlcN–GlcN > GlcNAc–GlcN \approx GlcN–GlcNAc > GlcNAc–GlcNAc. This conclusion appropriately supports the above experimental results.

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1. Introduction

Sonication (Chen, Chang, & Shyur, 1997; Cravotto, Tagliapietra, Robaldo, & Trotta, 2005; Czechowska-Biskup, Rokita, Lotfy, Ulanski, & Janusz, 2005; Muzzarelli & Rocchetti, 1985; Wang & Lin, 1989) is an energy saving, environmentally friendly and effective method of degrading polymers.

The effect of ultrasonic conditions on the degradation of chitosan has been reported by several workers. Chen et al. (1997) studied the effect of ultrasonic conditions, including parameters of chitosan concentration, reaction temperature, type of solvent and ultrasonic time and storage in acidic solution, on changes in the molecular weight (MW)

and polydispersity (MW distribution) of treated chitosan. Results showed that chitosan was degraded faster in dilute solutions and faster in lower temperature solutions. Degradation increased with prolonged ultrasonic time. The polydispersity decreased with ultrasonic treatment for all ultrasonic conditions. DD affected the ultrasonic degradation rate and rate constant increased with increasing DD of the chitosan. However, study of Trzciński and Staszewska (2004) showed that the general rate parameter (k) increased with the degree of *N*-acetylation. The effects of ultrasonic conditions on changes of deacetylation degree (DD) of treated chitosan have also been studied, but the results are sometimes controversial. Some researchers considered that ultrasonic treatment does not change the DD of the treated chitosan (Chen & Hwa, 1996; Chen & Tsaih, 1998; Tsaih & Chen, 1997; Wang, Bo, Li, & Qin, 1991; Wang & Lin, 1989), whereas Muzzarelli and Rocchetti (1985) reported the

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sonification leads to immediate chain degradation and to detectable deacetylation after more prolonged periods of treatment, especially at a pH of 1.0.

Our previous study (Liu, Bao, Du, Zhou, & Kennedy, 2006) showed: (1) chitosans with higher DD were more easily degraded; (2) ultrasonic degradation decreased the DD of initial chitosans with a lower DD (<90%), but the DD of initial chitosans with a higher DD (>90%) did not change any more than 2% especially in a short degradation time.

The principle behind the means of physical degradation, such as sonication, is to provide the added energy needed to break the chemical bonds. Since chitosan is a linear copolymer of 1,4-linked 2-amino-2-deoxy- β -D-glucopyranosyl (GlcN) and 2-acetamido-2-deoxy- β -D-glucopyranosyl (GlcNAc) units, the 1,4-D-glucosidic bonds between different D-glucopyranose units may have different energies, which mainly affect the ease, or otherwise, of degradation difficulty. Therefore in this paper, a chitosan molecule with a degree of polymerization of 25 was simulated using Hyperchem Release 7.1 for Windows Molecular Modeling System, and the hydration energies of the 1,4-D-glucosidic bonds were computed. The experimental results of the previous works (Liu et al., 2006) are explained using the computed data.

2. Experimental Method

The chitosan molecule was simulated using Hyperchem Release 7.1 for Windows Molecular Modeling System, Hypercube Inc. The MM⁺ method was selected for the molecular mechanics potential and options. The energy of the molecule was minimized when the Algorithm is Steepest Descent and the Termination Condition is RMS gradient of 0.1 kcal/mol or 8745 maximum cycles. When the converged = YES, the optimal conformation of the molecule is formed. The hydration energy (in QSAR properties) of the selected bond was computed.

3. Results and discussion

3.1. Mimic of chitosan molecule and calculation of hydration energy of the 1,4- β -D-glucosidic bonds of chitosan

The simulated chitosan molecule with degree of polymerization of 25 is shown in Fig. 1. The stable formation of chitosan molecule is a linear chain. The sequences of the D-glucopyranosyl units and hydration energy of the glucosidic bond of chitosan are shown in Fig. 2. Purposely, there are different 1,4- β -D-glucosidic bonds, i.e. containing those between GlcN–GlcN, GlcN–GlcNAc, GlcNAc–GlcN, GlcAc–GlcAc in the simulated chitosan molecule, in order that all the hydration energies of the different kinds of 1,4- β -D-glucosidic bonds could be computed.

Fig. 2 shows that the hydration energy of the GlcNAc–GlcNAc glycosidic bond (0.85 kcal/mol) is highest. That of GlcNAc–GlcN (0.74–0.75 kcal/mol) is similar to that of GlcN–GlcNAc (0.75–0.76 kcal/mol). The GlcN–GlcN glucosidic bond showed lowest hydration energy (0.65–0.67 kcal/mol). The further any GlcN–GlcN glucosidic bond was from a GlcNAc unit and the end of the molecular chain, the lower its hydration energy proved to be.

3.2. Explanation of the experimental results

The hydration energy of chitosan glucosidic bonds may be related to the ease of breakdown of them. Those with higher hydration energy seem to be degraded with more difficulty. In this way, the degradation difficulty should be GlcNAc–GlcNAc > GlcNAc–GlcN \approx GlcN–GlcNAc > GlcN–GlcN. So, more GlcN units lead to easier degradation. This suggestion can easily explain the previous experimental conclusion (Liu et al., 2006), that is, chitosans with higher DD are more easily degraded.

Another experimental conclusion (Liu et al., 2006) is that ultrasonic degradation decreased the DD of initial chitosans with a lower DD (<90%), but the DD of initial

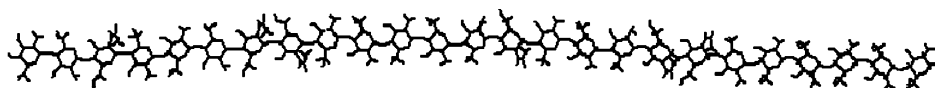


Fig. 1. Computerised chitosan molecule with polymerization of 25.

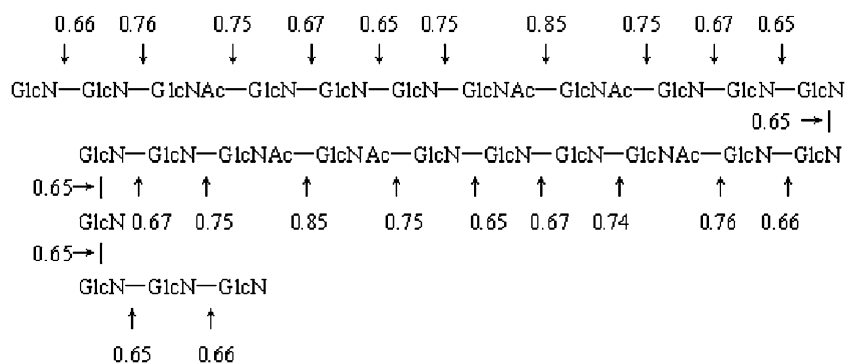


Fig. 2. Hydration energy of the D-glycosidic bonds of chitosan with a degree of polymerization of 25.

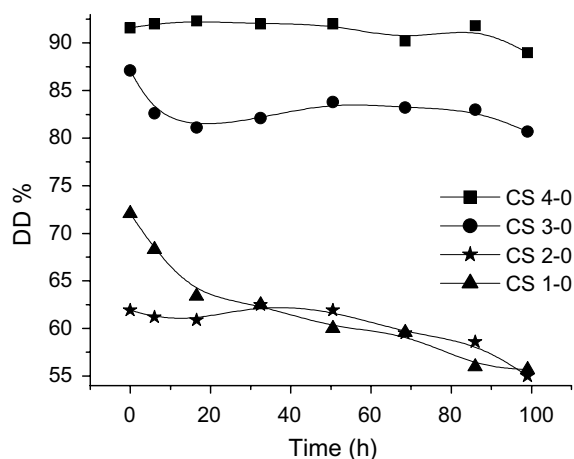


Fig. 3. Deacetylation degree (DD) of chitosan products at different depolymerization times (Liu et al., 2006).

chitosans with a higher DD (>90%) changed no more than 2% especially in a short degradation time (Fig. 3). This conclusion can also be explained by the hydration energy suggestion. In the previous experiment (Liu et al., 2006), initial chitosan was ultrasonicated for different times, and the degraded solutions were neutralized with 0.1 M NaOH to precipitate the degraded chitosans. They were collected and washed with distilled water until neutral then dried at 50 °C. In this way, only water insoluble chitosans could be collected. The soluble oligosaccharides were washed away.

The initial chitosan with lower DD (<90%) containing 4 different 1,4- β -D-glucosidic bonds is not degraded randomly. The GlcN–GlcN glucoside bond, especially that far from the GlcNAc unit and the end of the molecular chain, should be broken firstly. And then GlcNAc–GlcN and GlcN–GlcNAc bonds follow. The GlcNAc–GlcNAc glycosidic bond probably remains, because it is the most difficultly degraded. So the resultant soluble oligosaccharide dominantly contains GlcN units, and the GlcNAc units mainly remain insoluble (with high MW). As a result, the ultrasonic treatment decreased the DD of initial chitosans with a lower DD. However, the initial chitosan with high DD (>90%) contains predominantly GlcN–GlcN, rarely GlcNAc–GlcNAc, so the DD of the resultant insoluble chitosan is not affected remarkably. Even though, as the ultrasonic treatment time prolonged, the DD of the resultant insoluble chitosan decreased slightly, because the percentage of GlcNAc unit in the resultant insoluble fraction increased.

4. Conclusion

The hydration energy between the various 1,4- β -D-glucosidic bonds of chitosan is closely related to their pattern of breakdown by ultrasonic treatment. The higher the hydration energy is, the more difficult the breakdown will be. So the degradation of chitosan by ultrasound is not random, but follows the sequence: GlcN–GlcN > GlcNAc–GlcN \approx GlcN–GlcNAc > GlcNAc–GlcNAc.

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