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Short communication

Degradation of chitosan by an electrochemical process

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ABSTRACT

Degradation of chitosan by electrochemical process was investigated and the effect on the degradation of chitosan was demonstrated by means of determination of viscometry and gel permeation chromatography (GPC). The structures of the original and degraded chitosan were characterized by Fourier transform infrared spectra (FT-IR) and ultraviolet spectra (UV) analysis. The experimental results showed that chitosan can be effectively degraded by an electrochemical process.

1. Introduction

Chitosan is a natural polymer generally obtained by full or partial deacetylation of chitin isolated from crustacean shells. Due to many unique properties such as biocompatibility, biodegradability, nontoxicity and nonantigenicity, chitosan and its derivatives have a broad range of applications in various areas such as biotechnology, water-treatment, agriculture, medication and food science (Majeti & Kumar, 2000). However, chitosan has a high molecular weight and low solubility in most solvents, which causes practical problems in its applications. When chitosan is degraded, its solubility and some biological, chemical and physical functions can be improved (Liu et al., 2006; Qin et al., 2006).

Degradation of chitosan can be achieved using both chemical and biochemical reagents such as acid (Rege & Block, 1999), hydrogen peroxide (Qin, Du, & Xiao, 2002) and enzyme (Li, Du, & Liang, 2007). The use of intense energy (electrical, mechanical and electromagnetic radiation energy) can be an alternative and does not require chemical and biochemical reagents. Degradation of chitosan have been investigated by ultrasonic radiation (Czechowska-Biskup, Rokita, Lotfy, Ulanski, & Rosiak, 2005), microfluidization (Kasaai, Charlet, Paquin, & Arul, 2003), gamma radiation (Choi, Ahn, Lee, Byun, & Park, 2002) and ultraviolet radiation (Andrady, Torikai, & Kobatake, 1996).

In this paper, a novel degradation method was established by using an electrochemical process. Chitosan was treated by electrolysis with $Ti/TiO_2–RuO_2$ electrode. The degraded chitosans were characterized and analyzed by viscometry, gel permeation chromatography (GPC), Fourier transform infrared spectra (FT-IR) and ultraviolet spectra (UV).

2. Experimental

2.1. Materials

Chitosan, with degree of deacetylation (DD) of 89.8% and viscosity average molecular weight (M_v) of 479 kDa, was purchased from Jinke Biochemical Co. (Zhejiang, China). All other chemicals were of analytical grade. The water used was distilled. $Ti/TiO_2–RuO_2$ electrode ($5 \times 7\ cm^2$) was prepared by thermal deposition of TiO_2 and RuO_2 (Ti/Ru molar ratio = 7:3) on Ti plate.

2.2. Electrolysis of chitosan

0.3% (w/v) chitosan in 0.2 mol/L acetic acid (CH_3COOH)–0.3 mol/L sodium acetate (CH_3COONa) solution was first prepared. The electrolysis of 250 mL chitosan solution was performed in a reactor (Dia. 7 cm × H. 12 cm) with $Ti/TiO_2–RuO_2$ as anode, stainless steel as cathode ($5 \times 7\ cm^2$) and the spacing of 20 mm between two electrodes. A DC potentiostat was used as the power supply for the electrolysis. During the electrochemical treatment the solution was stirred constantly and the temperature was controlled at 60 °C. After degradation, the resulting solution was neutralized with 2 mol/L NaOH solution to pH 8–9, added ethanol (twice volume of the solution), filtered off, washed thoroughly

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with ethanol, and the products were collected after drying overnight in a vacuum at 60 °C.

2.3. Characterization

The M_v of chitosan was determined by a viscometric method reported in literature (Wang, Bo, Li, & Qin, 1991). The relative viscosity, η_r, of chitosan in 0.1 mol/L CH_3COONa–0.2 mol/L CH_3COOH solutions was measured using an Ubbelohde capillary viscometer at 30 °C. The intrinsic viscosity, $[\eta]$, was calculated according to the following equation: $[\eta] = (\eta_{sp} + 3ln\eta_r)/4c$. Here, η_{sp} referred to the incremental viscosity, and c was the concentration of chitosan (g/mL). Then, the M_v of chitosan was calculated based on the Mark–Houwink equation (Wang et al., 1991): $[\eta] = k{\cdot}M_v{}^a$ with $k = 1.64 \times 10^{-30} \times DD^{14}$, $a = -1.02 \times 10^{-2} \times DD + 1.82$.

GPC was used for qualitative evaluation of the reduction in molecular weight of chitosan on GPC instrument (Waters Co.) equipped with a refractive index detector. GPC measurement was carried out at 30 °C using connected columns (TSK G4000-PWxl and G3000-PWxl) with 0.1 mol/L CH_3COONa–0.2 mol/L CH_3COOH solution as an eluent at a flow rate of 0.7 mL/min.

The potentiometry method was used to determine the DD of original chitosan and its degraded products (Lin, Jiang, & Zhang, 1992).

FT-IR spectra of original and degraded chitosan were recorded in powder form in KBr discs at the range of 4000–400 cm^{-1} on a Bruker Vector 22 FT-IR spectrophotometer.

UV spectra of original and degraded chitosan were obtained using Shimadzu UV-1201 spectrophotometer at the range of 200–500 nm.

3. Results and discussions

3.1. Effect of electrolysis on molecular weight and DD of chitosan

In order to examine whether an effect of electrochemical method is operative in the degradation of chitosan, a series of experiments were designed. The M_v of chitosan was plotted as a function of the reaction time. The results are illustrated in Fig. 1.

When the initial chitosan was exposed to electrolysis [case (d) 160 mA/cm^2 in Fig. 1], the M_v of chitosan dramatically decreased from 491 to 33 kDa for 60 min. It was obvious that electrolysis was a quite effective method for degradation of chitosan. Fig. 1 also shows that when the current densities were varied from 40 to 160 mA/cm^2 and the corresponding current potentials were varied from 4.2 to 10.5 V, the M_v of chitosan was decreased to 159, 91, 59 and 33 kDa at 60 min [case (a)–(d) in Fig. 1], the rate of decrease in the M_v of chitosan was 67.6%, 81.4%, 88.0% and 93.3%, respectively. It indicated that the increase of current density would result in the decrease of the M_v of chitosan, and therefore led to a better degradation of chitosan. Moreover, it can be seen that a linear relationship existed between the $1/M_v$ and reaction time (inset in Fig. 1). This indicated that a random scission of chitosan chains occurred.

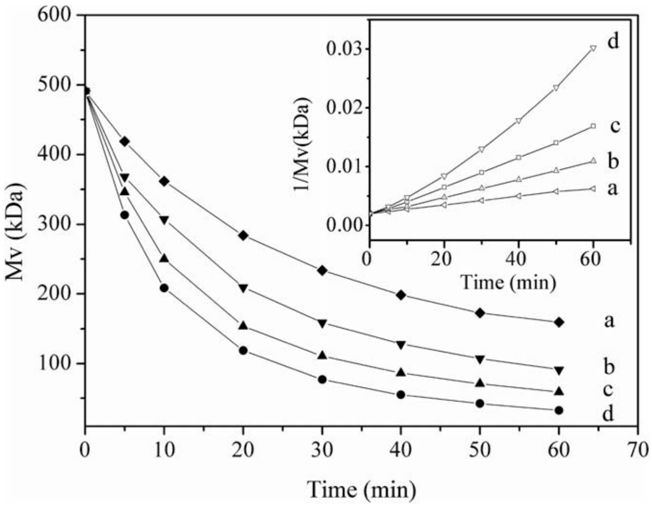

Fig. 1. Variation of M_v of chitosan with treatment time at different current densities of 40 mA/cm^2 (a), 80 mA/cm^2 (b), 120 mA/cm^2 (c), and 160 mA/cm^2 (d). Inset: $1/M_v$ versus treatment time.

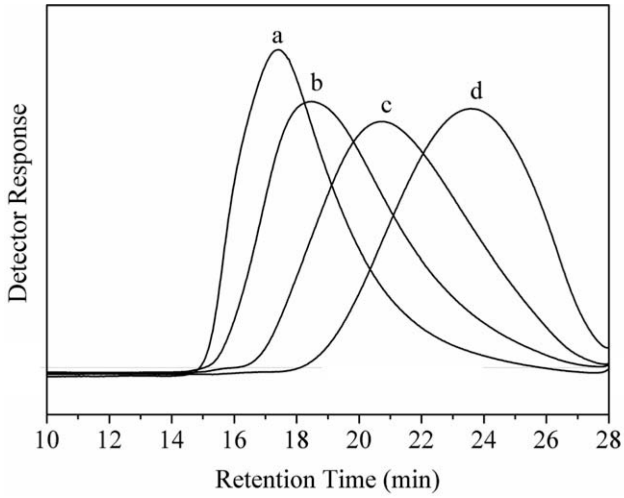

Fig. 2. GPC chromatograms of chitosan at the different electrolysis times: original chitosan (a), 10 min (b), 30 min (c), 60 min (d).

For further demonstrating the effect of electrochemical degradation of chitosan, GPC was used for qualitative evaluation of the reduction in molecular weight of chitosan and its distribution. Fig. 2 shows GPC chromatograms of original chitosan and its degraded products resulting from electrolysis at the current density of 160 mA/cm^2 for 10, 30 and 60 min. The shift of the chromatograms toward more retention times could be observed in Fig. 2. In GPC chromatogram, samples with lower molecular weights would have more retention times (Hsu, Don, & Chiu, 2002). Therefore, the results in Fig. 2 confirmed that the molecular weight of chitosan decreased with an increase in the time of electrolysis.

In addition, from Table 1 which shows the DD of original chitosan and its degraded products, we can see that the DD of degraded chitosan samples did not apparently change with the increase of electrolysis time, suggesting that the protonated amino groups were stable during the electrochemical treatment.

3.2. FT-IR spectral analysis

The FT-IR spectrum (Fig. 3) of the degraded chitosan was similar to that of the original chitosan. The band at 3430 cm^{-1} was attrib-

Table 1
Degree of deacetylation (DD) of original chitosan and its degraded products.

Chitosan sample	Electrolysis time (min)	DD (%)
1	0	89.8 ± 1.2[a]
2	5	89.3 ± 1.1
3	10	89.0 ± 0.9
4	20	88.5 ± 1.2
5	30	88.0 ± 1.1
6	40	87.8 ± 0.9
7	50	87.4 ± 1.1
8	60	87.2 ± 1.2

[a] Mean ± standard derivation of three independent experiments under conditions of 0.3% (w/v) chitosan, 0.2 mol/L acetic acid, 0.3 mol/L sodium acetate, 160 mA/cm^2 current density and 60 °C operating temperature.

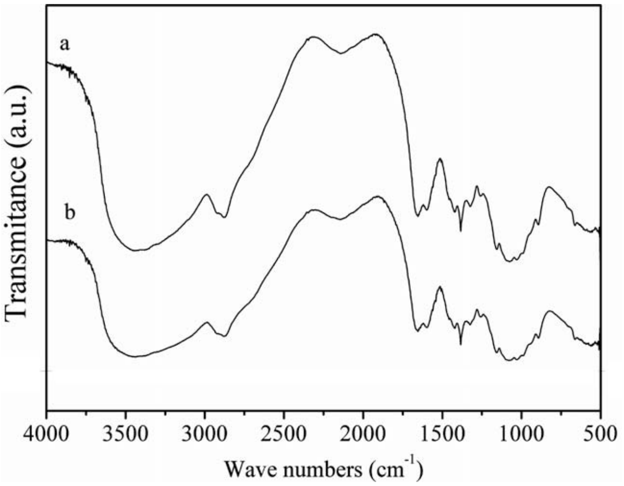

Fig. 3. FT-IR spectra of original chitosan M_V 491 kDa (a) and degraded chitosan M_V 33 kDa (b).

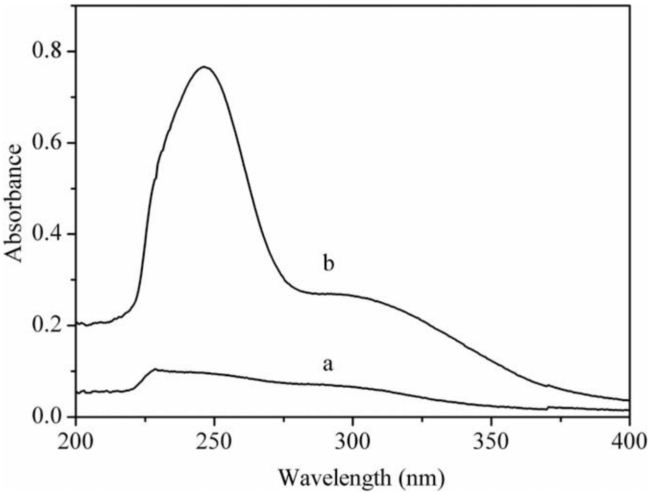

Fig. 4. UV spectra of original chitosan M_V 491 kDa (a) and degraded chitosan M_V 33 kDa (b).

uted to the stretching vibration of O–H and N–H. The band at 1595 cm^{-1} corresponded to the binding vibration of –NH_2. The bands at 1160 and 895 cm^{-1} were assigned to the absorption peaks of β-D-(1 → 4) glycosidic bond in chitosan. The assignments of the peaks were based on the data reported in the published literature (Feng, Du, Li, Hu, & Kennedy, 2008; Huang, Zhuo, & Guo, 2008; Wang, Huang, & Wang, 2005; Yue, He, Yao, & Wei, 2009). The result of FT-IR spectra suggested that there was no obvious modification of chemical structure of degraded chitosan.

3.3. UV spectral analysis

The UV spectra of original and degraded chitosan are shown in Fig. 4. As can be seen in Fig. 4, two new absorption bands at 248 and 299 nm were observed. Based on the data reported in the published literature, these absorption bands could be ascribed to carbonyl or carboxyl groups (Czechowska-Biskup et al., 2005). Therefore, the result in Fig. 4 indicated that the carboxylic or carboxyl groups might be formed during degradation. It was most likely that these carboxylic or carboxyl groups were the new side groups of the degraded chitosan.

4. Conclusions

The chitosan was effectively degraded by electrochemical process which was verified by viscometry and GPC. The molecular weight of chitosan decreased with the increase of electrolysis time and current density. The DD of degraded chitosan did not apparently change compared with the DD of original chitosan. The result of FT-IR analysis suggested that there was no obvious modification of chemical structure of degraded chitosan. The result of UV spectra analysis indicated that the carboxylic or carboxyl groups might be formed during the degradation. Therefore the degradation method of chitosan by electrochemical process is feasible, convenient and potentially applicable.

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