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Research Note

Physicochemical and functional properties of chitosans affected by sun drying time during decoloration

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ABSTRACT

The typical production of chitosan from crustacean shell consists of demineralization, deproteinization, decoloration, and deacetylation. Selected physicochemical and functional properties of chitosans as affected by various decoloration times (4, 5, 6, 7 or 8 h) using sun drying were evaluated. Moisture content (6.67–6.89 g/100 g), degree of deacetylation (81.91–82.73%), and color L^* value (78.32–79.43) of chitosans were not affected by sun drying time. However, color a^* and b^* values decreased when sun drying time was over 4 h. The viscosity of chitosan solution (0.5 g/100 mL acetic acid) decreased gradually with increasing sun drying time, with a more pronounced effect observed at 8 h of sun drying. There was no change in water-binding capacity (WBC) of chitosans decolorized by sun drying between 4 and 6 h; however, further increase in sun drying time from 6 to 7 or 8 h increased WBC of chitosans. DPPH radical scavenging activity of chitosans increased with increasing sun drying time. This study demonstrated that white-colored chitosans could be produced by an alternative decoloration step using sun drying for 4 h following the deacetylation step. However, increasing sun drying time to 7 h produced chitosan with increased WBC and DPPH radical scavenging activity.

1. Introduction

The typical production of chitosan from crustacean shell generally consists of four basic steps: demineralization (DM), deproteinization (DP), decoloration (DC), and deacetylation (DA) (No & Meyers, 1995). In chitin production, the DM and DP steps produce a colored chitin product. When a bleached chitinous product is desired, pigments can be removed with organic solvents (ethanol, ether, absolute acetone, or chloroform) or bleaching agents (sodium hypochlorite solution or hydrogen peroxide) (No & Meyers, 1995). In general, the organic solvents are not as effective as the bleaching agents in removing pigments from crab or crawfish shell (No & Lee, 1995; No, Meyers, & Lee, 1989). Decoloration by a bleaching agent in the chitin preparation initially produces white chitin that was subsequently converted into light-brown chitosan after the deacetylation step (Youn, No, & Prinyawiwatkul, 2007). Therefore, an alternative, yet effective and economical decoloration method that will yield white-colored chitosan should be developed.

Our previous research (Youn et al., 2007) demonstrated that decoloration of chitosan could be achieved by sun drying after deacetylation without using a bleaching agent. Compared to decoloration by bleaching, decoloration by sun drying for 4 h produced a whiter chitosan with higher viscosity without affecting water- and fat-binding capacities. To date, the effect of prolonged sun drying time during decoloration on physicochemical and functional properties of chitosan is not known.

The objective of the present research was to compare selected physicochemical and functional properties of chitosans decolorized by sun drying at various times.

2. Materials and methods

2.1. Materials

Dried crab (*Chionoecetes opilio*) leg shell was obtained from Keumho Chemical (Seoul, Korea). The shell was ground through a Wiley mill (model 4, Thomas Scientific, Swedesboro, NJ, USA) with a 2-mm mesh screen and subsequently sifted with 20 (0.841 mm) and 40 mesh (0.425 mm) sieves using a portable sieve shaker (JISICO, Seoul, Korea). The ground shell with 0.841–0.425 mm particle size was used throughout this research to obtain

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reproducible and consistent results. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was purchased from Sigma–Aldrich Co. (St. Louis, MO, USA).

2.2. Production of chitosan

The production of chitosan involved the demineralization (DM), deproteinization (DP), deacetylation (DA), and decoloration (DC) steps (Youn et al., 2007). The ground crab leg shell was demineralized with 1 mol/L HCl for 30 min at ambient temperature with a solid/solvent ratio of 1:15 (w/v). Following the DM step, the demineralized shell was collected on a 100-mesh sieve, washed to neutrality in running tap water, rinsed with deionized water, and filtered to remove excess moisture. The DP step was accomplished by treating the demineralized shell with 3 g/100 mL NaOH for 15 min at 15 psi/121 °C and a solid/solvent ratio of 1:10 (w/v). The residue was then washed, filtered as mentioned above, and dried at 60 °C for 4 h in a forced-air oven. The DA step was achieved by treating chitin under conditions of 15 psi/121 °C with 45 g/100 mL NaOH for 30 min and a solid/solvent ratio of 1:10 (w/v). For the DC step, the resulting chitosan was collected, washed as mentioned above, and dried by sun drying (approximately at 23 °C) for 4 (Youn et al., 2007), 5, 6, 7, and 8 h.

2.3. Determination of moisture and degree of deacetylation (DD)

The moisture content was determined in triplicate using a halogen moisture analyzer (HG53, Mettler Toledo, Greifensee, Switzerland) under the following test parameters: drying temperature, 105 °C; switch-off, auto60. The DD was determined in triplicate according to a colloid titration method (Tôei & Kohara, 1976) using 0.0025 mol/L potassium polyvinyl sulfate ($f = 1.00$, Wako Pure Chemical Ind., Osaka, Japan).

2.4. Measurement of viscosity and color

Viscosity was determined in triplicate with a Brookfield viscometer, model LVDV-II+ (Brookfield Engineering Labs., Stoughton, MA, USA). Chitosan solution was prepared in 1 mL/100 mL acetic acid at a 0.5 g/100 mL concentration on a moisture-free basis. Viscosity measurements were made using a small sample adapter at a shear rate of 5.28 s^{-1} in the solution (8 mL) at 25 ± 0.3 °C, and reported as mPa s. Color of chitosan powders was measured with a portable Minolta Chroma Meter CR-200 (Minolta Camera Co. Ltd, Osaka, Japan) using illuminant C and 2° observer, and reported as L^* (lightness), a^* (+ for redness and − for greenness) and b^* (yellowness). Each chitosan sample was placed in a polystyrene petri-dish (5.4 cm diameter × 1.4 cm height) and packed by gently tapping the petri-dish on the bench top. The orifice of the Minolta Chroma Meter was covered with clear plastic wrap (Glad Products Co., Oakland, CA, USA) and placed flat against the surface of chitosan powders. Three measurements were made at different locations on each of the triplicate samples. In addition, the whiteness index of chitosan powders was calculated as $100 - [(100 - L^*)^2 + a^{*2} + b^{*2}]^{1/2}$.

2.5. Water-binding capacity (WBC)

WBC of chitosan was measured in triplicate using a modified method of Wang and Kinsella (1976). Water absorption was initially carried out by weighing a centrifuge tube (50 mL) containing 0.5 g of sample, adding 10 mL of water, and mixing on a vortex mixer for 1 min to disperse the sample. The contents were left at ambient temperature for 30 min with intermittent shaking for 5 s every 10 min and centrifuged at 3200 rpm for 25 min. After the supernatant was decanted, the tube was weighed again. WBC was calculated as follows: WBC (%) = [water bound (g)/sample weight (g)] × 100.

2.6. DPPH radical scavenging activity

DPPH radical scavenging activity of chitosan was determined in triplicate by the method of Blois (1958) with some modifications. 0.4 mL of chitosan solution (1 g/100 mL in 1 mL/100 mL acetic acid) was added to 3 mL of 0.1 mmol/L DPPH radical methanolic solution. The reaction mixture was shaken vigorously, stored in the dark at room temperature for 30 min, and the absorbance measured at 517 nm using a spectrophotometer (Ultraspec® 1000, Pharmacia Biotech Co., Cambridge, England). The free radical scavenging activity was calculated by the following equation:

$$\text{Scavenging activity (\%)} = \left[1 - \left(\text{absorbance}_{\text{sample}} / \text{absorbance}_{\text{control}}\right)\right] \times 100.$$

2.7. Statistical analysis

All experiments were carried out in triplicate, and means ± standard deviations were reported. All data were analyzed using ANOVA. Means of the main effects were separated by Duncan's multiple-range test using the SPSS (Statistical Package for Social Sciences, SPSS Inc., Chicago, IL, USA) software package. The Pearson correlation coefficients between viscosity and WBC, and between viscosity and DPPH were calculated as well. Statistical significance was concluded at $P < 0.05$.

3. Results and discussion

3.1. Moisture content and degree of deacetylation

The moisture content of chitosans decolorized by sun drying time for 4, 5, 6, 7 and 8 h was 6.89 ± 0.04 g/100 g, 6.72 ± 0.06 g/100 g, 6.81 ± 0.10 g/100 g, 6.76 ± 0.22 g/100 g and 6.67 ± 0.20 g/100 g, respectively. The moisture content of chitosan dried by sun drying varies depending on season, relative humidity, and intensity of sun light (Youn et al., 2007). In our present study conducted during September, sun drying at approximately 23 °C for more than 4 h but up to 8 h did not significantly ($P > 0.05$) further decrease the moisture content of chitosan. Korea Food and Drug Administration (KFDA) (1995) defines that the moisture content of chitosan powder should be below 10 g/100 g. The moisture content of five chitosans decolorized by sun drying in the present study was all less than 7 g/100 g. The degree of deacetylation of all five chitosans was also not affected ($P > 0.05$) by sun drying time, having a range of 81.91 ± 0.73 to 82.73 ± 0.40%.

3.2. Color

Color L^*, a^* and b^* values of chitosans decolorized by sun drying from 4 to 8 h are shown in Fig. 1. In chitosan production, decoloration by sun drying for 4 h produced a white-colored chitosan (Youn et al., 2007). In this study, sun drying for more than 4 h did not affect the color lightness (L^*) values (78.32–79.43) of chitosans. The whiteness index of chitosan powders was 75.73, 75.89, 76.81, 76.53, and 75.78, respectively, after 4, 5, 6, 7, and 8 h of sun drying. Therefore, sun drying for more than 4 h had no significant effect on whiteness of chitosans. However, there was an observable trend that a^* and b^* values decreased with increasing sun drying time over 4 h. Although some significant differences in color a^* and b^* values were observed among five chitosans by the instrumental