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Adsorption of procyanidins onto chitosan-modified porous rice starch

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ABSTRACT

Polyphenolic bioflavonoids are easily oxidized when exposed to oxygen during the processing or storage. This research developed a porous chitosan-modified starch for the adsorption of procyanidins. The modified starch was fabricated by a facile surface modification of chitosan on porous rice starch. Besides the investigation of the morphologies and structures of starches, the adsorption kinetics of procyanidins onto starches was evaluated. The modified starch was mesoporous with a relative moderate specific surface area at 1.13 ± 0.05 m^2/g, and the interactions between starch and chitosan were intermolecular hydrogen bonds. The modification of chitosan resulted in the positive zeta potential of starch at pH 2-10. The enzymolysis reduced starch size slightly and induced a decrease in the apparent viscosity of starch suspension, while the modification of chitosan increased starch size and induced an increase in the apparent viscosity of the suspension. The adsorption capacity of the modified starch towards procyanidins was significantly improved and reached 96 ± 3% of the total amount of procyanidins, and the adsorption was chemisorption or strong surface complexation rather than mass transport. The results suggested that the porous chitosan-modified starch might be used as an efficient adsorbent for polyphenols.

1. Introduction

Owing to the relatively small particle size (2–8 μm), highly digestible and hypoallergenic nature (Chen & Tappel, 1996), rice starch is commonly used in the paper making, medicine, infant foods and food products for gastric patients. Porous or modified starches have broadened the spectrum of starch uses (Belingheri, Ferrillo, & Vittadini, 2015). Enzymolysis is an effective method to fabricate porous starches (Dura, Błaszczak, & Rosell, 2014). Due to its relatively large surface area and porous characteristic, porous starches have been widely used as adsorbents for some polyphenolic materials (H. Wang et al., 2016; Y. Wang et al., 2012) to protect their antioxidant activities.

Chitosan has shown a great promise in food industry owing to its non-toxicity, biodegradability and biocompatibility. Due to the three types of functional groups (amino/acetamido group, primary and secondary hydroxyl groups at C-2, C-3 and C-6 positions, respectively) on the backbone, chitosan can be widely used as modifying agents in polymer composites (Don, King, & Chiu, 2002; Xu, Kim, Hanna, & Nag, 2005), or as absorbents for the removal heavy metal ions (Popuri, Vijaya, Boddu, & Abburi, 2009) or dye (Vakili et al., 2014) from solutions. Some natural polyphenol antioxidants such as vitamin E (Park & Zhao, 2004) and tea polyphenols (L. Wang, Dong, Men, Tong, & Zhou, 2013) can be protected by being incorporated into chitosan based films. Recently, chitosan has been used to fabricate chitosan-coated tea polyphenols nanoparticles (Liang et al., 2011) and vitamin E incorporated chitosan microspheres (Yenilmez, Başaran, & Yazan, 2011). These achievements indicate the strong affinity of chitosan towards polyphenol. Procyanidins (PA), a group of polyphenolic bioflavonoids with strong anti-oxidative activity, is easily oxidized when exposed to oxygen during the processing or storage. Several representative achievements have been obtained on the adsorption of PA on starch (Le Bourvellec, Bouchet, & Renard, 2005; Le Bourvellec, Guyot, & Renard, 2004; Liu et al., 2016).

In present work, we fabricated porous chitosan-modified starch from rice starch and evaluated its adsorption towards PA. The porous rice starch was prepared by the enzymolysis of α-amylase

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and amyloglucosidase. The morphologies and structures of starches, zeta potentials and rheological properties of starch suspensions were investigated, and the adsorptions of PA onto starches were evaluated by sorption kinetics as well.

2. Materials and methods

2.1. Materials

Rice starch was provided by Jiang Nan University which was pretreated by being freeze-dried (−50 °C, 24 h). Amyloglucosidase (1.67 kat/L, from Aspergillus niger), α-amylase (0.067 kat/L, from Bacillus subtilis) and chitosan (degree of deacetylation ≥ 95%, viscosity 100–200 mPa s) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Procyanidins (PA, from grape seeds, specification: 95% OPC, appearance: brown red powder) was provided by Shanghai Jiaoyuan Biochemical Co., Ltd. (Shanghai, China). Sodium carbonate, acetic acid, citric acid-sodium citrate buffer, and Folin-Ciocalteu phenol reagent were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared in Milli-Q water obtained from a purification system (Millipore, Bedford, MA, USA).

2.2. Porous chitosan-modified starch preparation

According to our experimental results (Figs. S1–5), the preparation of porous starch was performed as follows: starch sample (2 g) was dispersed in 40 mL citric acid-sodium citrate buffer (0.2 mol/L, pH 5.4) containing 0.06 mL of an mixture of α-amylase and amyloglucosidase (1:3, mL/mL), and then placed on a shaker platform (120 rpm, 45 °C) for enzymolysis, which was terminated after 3 h by the addition of 1 mL NaOH solution (2 mol/L). After being centrifuged (8000 × g, 5 min), the sediment was resuspended in 40 mL Milli-Q water and centrifuged again. The washing procedure was repeated three times to remove residual enzymes. Finally, the collected sediment was freeze-dried (−50 °C, 24 h) in the freeze-dryer (Type FD-1A-50, Boyikang Corp., Beijing, China) and dried in a baking oven (130 °C, 4 h). After being screened through a 75 μm sieve, porous starch was obtained.

A weight of 3 g as-prepared porous starch was dispersed in the chitosan solution by dissolving chitosan powder (1 g) in 400 mL acetic acid solution (2 g/L) and then stirred at 20 °C for 30 min. After naturally sedimenting for 24 h, the supernatant was removed and the precipitate was freeze-dried (−50 °C, 24 h) in the freeze-dryer to avoid the gelatinization according to the reference (B. Zhang et al., 2014). Finally, the porous chitosan-modified starch was dried in a baking oven (130 °C, 4 h) and screened through a 75 μm sieve.

2.3. Morphology and structure

Scanning electron microscopy (SEM, SU8020, Hitachi, Tokyo, Japan) was used to observe the morphology of starch, and each specimen was sputter-coated with a layer of gold. Nitrogen adsorption–desorption experiments were performed on a Beckman Coulter SA 3100 instrument (Beckman Coulter, Brea, California, USA). The specific surface areas of starch were determined by Brunauer-Emmett-Teller (BET) method, and pore size distributions were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halen (BJH) method. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet 6700 spectrometer (Thermo Nicolet, USA) using KBr pellets. X-ray diffraction (XRD) patterns were obtained by an X-ray diffractometer (X' Pert Pro MPD, Philips, Eindhoven, Netherlands) with Cu Kα radiation (λ = 0.15406 nm). The degree of crystallinity of sample was calculated according to the two-phase method (Nara & Komiya, 1983). Briefly, a curve connecting the baseline of the peaks was plotted on the diffractogram, where the area above the curve was assumed to correspond to the crystalline domains and the area below to the amorphous part. The ratio of the area above the curve to total area was taken as the degree of crystallinity.

2.4. Determination of color and particle size

A CR-300 color difference meter (Minolta Corp., Osaka, Japan) was used to determine the starch color and the total color difference (△E) was calculated as follow (Barreiro, Milano, & Sandoval, 1997):

$$\Delta E = \sqrt{(L - L_0)^2 + (a - a_0) + (b - b_0)} \quad (1)$$

where lightness (L), redness (a) and yellowness (b) of samples are represented (L_0, a_0 and b_0 for native starch), respectively; Ranges applied in ΔE are according to the reference (Cserhalmi, Sass-Kiss, Tóth-Markus, & Lechner, 2006): 0–0.5 (not noticeable), 0.5–1.5 (slightly noticeable), 1.5–3.0 (noticeable), 3.0–6.0 (well visible) and 6.0–12.0 (great difference), respectively.

A Malvern Mastersizer 2000 light scattering (Malvern Instruments Ltd., UK) was used to evaluate the particle size distribution (PSD) of starch suspensions (8.8 g/kg), which was prepared by adding starch sample to Milli-Q water and stirred at 20 °C for 30 min. The volume-based average diameter D[4,3] and area-based average diameter D[3,2] were measured as follow:

$$D[4,3] = \sum_i n_i d_i^4 \Big/ \sum_i n_i d_i^3 \quad (2)$$

$$D[3,2] = \sum_i n_i d_i^3 \Big/ \sum_i n_i d_i^2 \quad (3)$$

where n_i was the number of particles of diameter d_i.

2.5. Zeta potential

Zeta potential was determined using a Zetasizer Nano-ZS90 apparatus (Malvern Instruments, Worcestershire, UK) to evaluate starch surface charge. The testing suspensions (10 g/L) were prepared by dispersing starches in PBS buffer under magnetic stirring at 20 °C for 1 h. A volume of 1 mL suspension was injected into a plug-type electrode, and then the electrode was placed in the test cell. Triplicate measurements were taken at 20 °C for each specimen.

2.6. Rheological properties

The steady-state shear behavior of the samples were performed in the range of shear rates from 0 to 500 s^{-1} using the rheometer (DHR-3, TA Instrument, USA) with a 40 mm parallel plate geometry. The dimension of the gap was set at 1000 μm and all the measurements were carried out.

2.7. Adsorption test

Each starch sample (1.0 g) was added to 30 mL PA solution (2 g/L). After being shaken for 2 h (120 rpm, 25 °C), the suspension was withdrawn, centrifuged (8000 × g, 5 min), and diluted by 50-fold before detection. The Folin-Ciocalteu method was applied to determine the amount of PA in supernatant (Škerget et al., 2005). The adsorption capacity (%) and quantity (q_t) of PA were calculated