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Preparation of controllable porous starch with different starch concentrations by the single or dual freezing process

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ABSTRACT

Porous starch (PS) was created by replacing ice crystals in frozen starch gel with ethanol using a solvent exchange technique. In the single freezing process, the porous structures of PSs were controlled by changing the starch paste concentrations. With the increasing of concentrations from 5 to 20%, pore size, moisture adsorption, oil adsorption capacity and methylene blue (MB) adsorption of PSs decreased greatly, while the apparent density increased from 0.093 to 0.689 g/cm^3. In the dual freezing process, the porous structures of citric acid-modified PS (CAPS0) were full of starch pastes with different concentrations (1.5, 2.5 and 3.5%), and then frozen again. Compared to CAPS0, PSs from the dual freezing process exhibited larger apparent density and MB adsorption, but lower moisture adsorption and oil adsorption capacity. And the starch paste concentrations (1.5–3.5%) had few effects on the properties of PSs in the second freezing process.

1. Introduction

Porous starch (PS) is a kind of natural, economical and biodegradable adsorbent with abundant micro-sized pores, which has extensive application on food, pharmaceuticals, tissue engineering, agriculture, cosmetics, pulp and paper, and other industries (Chang, Yu, & Ma, 2011; Glenn et al., 2010; Torres, Boccaccini, & Troncoso, 2007). PS can be achieved by hydrolyzing the amorphous regions of granular starches with enzymes (α-amylase and glucoamylase) at sub-gelatinization temperature (Uthumporn, Zaidul, & Karim, 2010; Wang et al., 2009). The porous structures can also be obtained from the continuous starch phase. According to the traditional plastic processing method, corn starch and starch acetate were extruded in a twin-screw mixing extruder at the high temperature to produce the foams (Guan & Hanna, 2004). The microwave technology was a suitable method for the production of starch-based porous structures for tissue engineering (Torres et al., 2007) and packaging applications (Sjöqvist & Gatenholm, 2005). Water was used as a blowing agent as the superheated steam left the gelatinized mixtures, and rheological properties allowed it to expand and form the porous structure. In the method of Glenn et al. (2010), the microspheres were made by pumping an 8% aqueous high-amylose starch gelatinous melt through an atomizing nozzle. The atomized starch droplets were collected in ethanol, and dried under dry nitrogen to obtain the porous microspheres. Recently, supercritical CO$_2$ technology was introduced for the production of PS. Starch was dissolved in hot water to form solution, resulting in the formation of starch gel after cooled to room temperature. The water in the gel was then replaced by ethanol, followed by drying with supercritical CO$_2$ extraction. The obtained starch aerogel was composed of starch fibers and presented porous structure (Miao et al., 2008). Supercritical fluid extrusion (SCFX) was a novel extrusion technology for production of highly expanded starch foams. Instead of steam this process used supercritical CO$_2$ as a blowing agent. Cross-linking of starch blends by phosphorylation via reactive SCFX was used to produce starch foams (Manoi & Rizvi, 2010). It is very important to obtain controlled porous structures for the applications of PSs. PS was prepared by replacing ice crystals in frozen starch gel with the mixed solvent of ethanol and water using a solvent exchange technique. The sizes of the holes in PS were variable with the ratios of ethanol/water (Chang et al., 2011). During the processing of replacing ice crystals in frozen starch gel, many PS holes could collapse or close, when ethanol was progressively substituted by the ethanol/water solvent. Therefore, the more the water in the mixed solvent was, the smaller the hole size was in PS. In this work, two series of PSs were respectively prepared by varying different starch paste concentrations in the single or dual freezing process. The starch paste concentrations were expected to change the sizes of ice crystals; thereby control the porous structures, which were characterized by scanning electron microscopy (SEM). Moreover, the effects of starch paste concentrations on the pore structure,

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apparent densities, moisture adsorption, oil adsorption and dye adsorption were investigated and discussed.

2. Materials and methods

2.1. Materials

Potato starch was supplied by Manitoba Starch Products (Manitoba, Canada). Soybean oil was produced by COFCO Northsea Oils & Grains (Tianjin) Co., Ltd., China. The dye methylene blue (MB) was provided by Tianjin Benchmark Chemical Reagent Co., Ltd., China. Ethanol and citric acid were analytical reagents purchased from Tianjin Chemical Reagent Factory, China.

2.2. Preparation of PS in the single freezing process

The preparation of PS was based on the method of Chang et al. (2011). Potato starch was added into 100 mL of distilled water. The mixture was heated at 90 °C for 0.5 h for complete gelatinization of the starch. It was then cooled at 5 °C to obtain the starch gel. The gel was cut into cubes (about 1 cm × 1 cm × 1 cm), and frozen at −10 °C. The frozen cubes were immersed in ethanol at room temperature. The cubes were immersed three times, for about 1 h each time, in ethanol. The cubes were dried at 50 °C for 6 h to remove the ethanol, and to obtain white solid PS cubes. PS5, PS8, PS10, PS15 and PS20 represented the PS cubes which were prepared from the starch gelatinization with different concentrations (5, 8, 10, 15 and 20 g starch in 100 mL distilled water), respectively.

2.3. Preparation of CA-modified PS (CAPS0)

CA modification was based on the method of Ma, Chang, Yu, and Stumborg (2009) with some modifications. CA was dissolved in ethanol (0.09 g CA/10 mL ethanol). The PS5 cubes were immersed in CA solution and conditioned for 12 h at room temperature. The weight ratio of CA and PS5 was 15/100. They were subsequently dried and reacted with CA at 130 °C for 2 h in a forced air oven. CA-modified PS (CAPS0) was immersed in ethanol and washed three times to remove unreacted CA, and then dried and used for testing.

2.4. Preparation of PSs in the second freezing process

Potato starch (1.5 g, 2.5 g or 3.5 g) was added into 100 mL of distilled water. The mixture was heated at 95 °C for 0.5 h for complete gelatinization of the starch. The obtained starch pastes were cooled to the room temperature, and then CAPS0 cubes were immersed into the starch pastes using ultrasonication until no bubbles appeared again. The cubes were taken out and frozen at −10 °C. The water in frozen cubes was exchanged with ethanol at room temperature. The cubes were immersed three times in ethanol. The cubes were dried at 50 °C for 4 h to remove the ethanol. CAPS1.5, CAPS2.5 and CAPS3.5 represented the PS cubes, which were immersed from the starch pastes with different concentrations (1.5 g, 2.5 g and 3.5 g starch in 100 mL distilled water), respectively.

2.5. Determination of the molar degree of substitution by CA

Molar degree of substitution (MS) is the number of CA per anhydroglucose unit (AGU) in starch. MS was determined using the method of Ma, Jian, Chang, and Yu (2008) with minor modifications. CAPS0 was ground to the powders in order to test the MS. Approximately 1.0 g of dry CAPS0 powders was accurately weighed and placed into a 250 mL conical flask. Then 50 mL of 75% ethanol solution was added and the conical flask was agitated and warmed at 50 °C for 0.5 h before cooling to room temperature. Standard 0.500 M aqueous sodium hydroxide solution (20 mL) was added; the conical flask was tightly stoppered and saponified at 30 °C with a magnetic stirrer for 24 h. The excess alkali was back-titrated with a standard 0.200 M aqueous hydrochloric acid solution and re-titrated 2 h later to account for any further alkali that may have leached from the starch. The sample was measured in triplicate. MS of CA substitution was 0.08 for CAPS0.

2.6. Scanning electron microscopy (SEM).

The fracture surfaces of PS were examined using a Philips XL-3 scanning electron microscope. PS was cooled in liquid nitrogen and then broken. The fracture surfaces of PSs were vacuum coated with gold for SEM.

2.7. Apparent density

The apparent density of PSs, also called bulk density, was defined as the mass of material divided by the total volume it occupies (Wong, Chu, Leung, Park, & Zong, 2011). The data was averaged over 5 cubes.

2.8. Moisture adsorption

Dried PS cubes were stored in a closed chamber with a relative humidity (RH) of 75% at 20 °C for a period of time. The moistures in PS cubes were calculated based on the final weight (w) and original weight (w_0) as follows:

$$\text{Moisture content} \quad (\text{wt\%}) = \frac{w - w_0}{w_0} \times 100\% \tag{1}$$

2.9. Oil adsorption capacity

The dried PS cubes (weight = w_0) were immersed in soybean oil for 0.5 h at room temperature with constant stirring. The mixture was filtered in the funnel under gravity. When there is no more oil dripping from the filter paper, PS was weighed (w). The oil adsorption capacity was calculated as follow:

$$\text{Adsorption capacity} = \frac{w - w_0}{w_0} \tag{2}$$

2.10. Adsorption experiments

Adsorption experiments were conducted using the glass bottles containing $10\,\text{g}\,\text{L}^{-1}$ of PS and the dye MB $0.064\,\text{mmol}\,\text{L}^{-1}$ ($23.93\,\text{mg}\,\text{L}^{-1}$). The glass bottles were placed on a slow-moving platform shaker and aliquots of approximately 10 mL were taken at different time intervals during the reaction. The dye MB concentrations in the solution were analyzed by UV–vis spectrometry and relative dye adsorption versus reaction time determined.

3. Results and discussion

3.1. Morphology

Potato starch granules were destroyed in the starch gelatinization at 90 °C. After cooling the paste to room temperature and freezing it, water was immobilized in the gel. Porous structures were created after replacement of ice crystals in the frozen gel with ethanol. As shown in Fig. 1, PSs with different porous structures were resulted, when ice crystals in gel from different concentrations of starch pastes were replaced with ethanol in the single freezing process. With the increasing of starch paste concentrations, the size of the holes in the resulting PS gradually decreased.

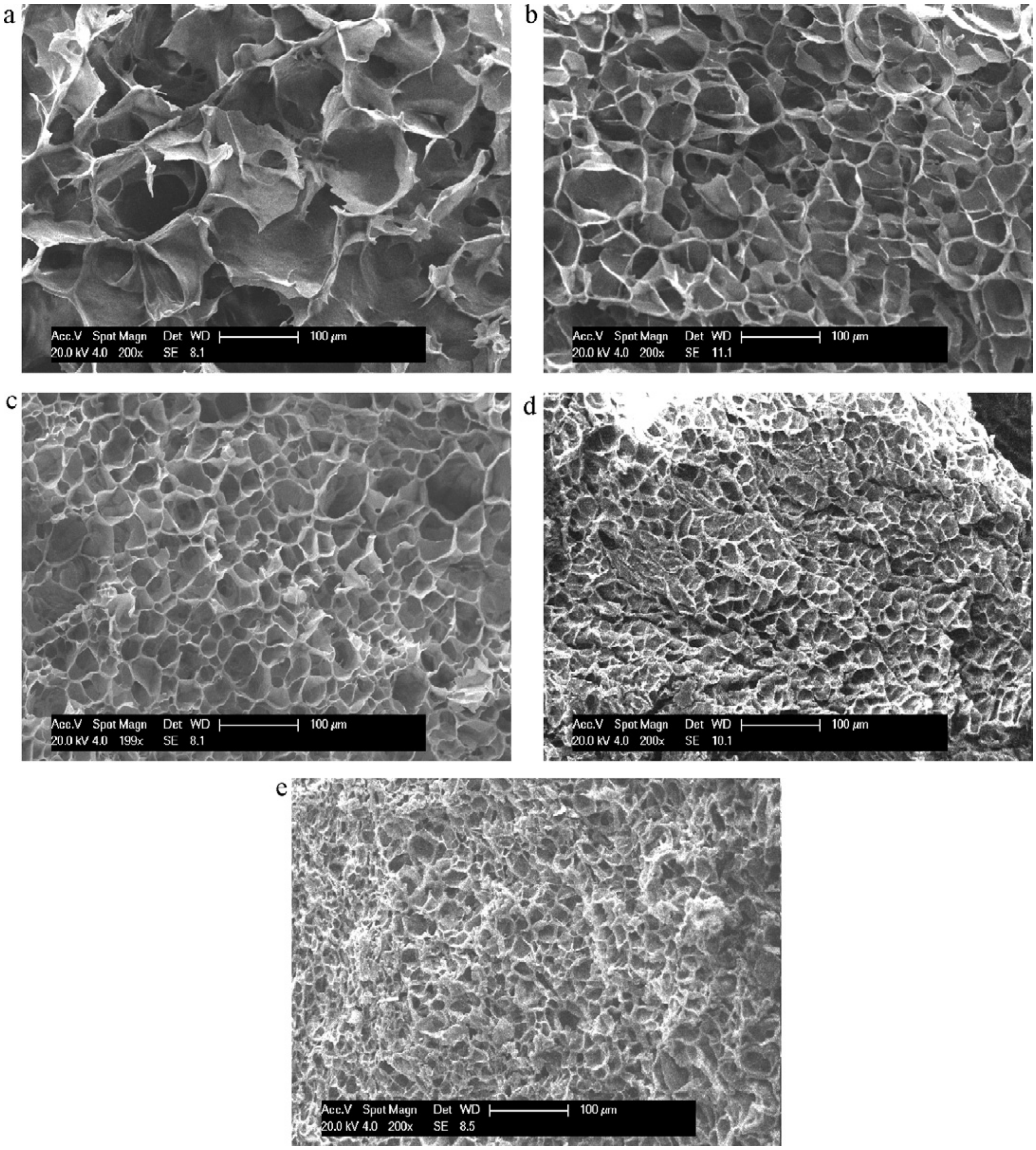

Fig. 1. SEM micrograph of the fractured surface of PS, prepared from different starch paste concentrations in the single freezing processing (a, PS5; b, PS8; c, PS10; d, PS15 and e, PS20).

PS5 exhibited the pore size of about 100 μm, while the pore sizes of PS15 and PS20 were only about 10–20 and 5–10 μm, respectively. When the concentrations of starch pastes were increased, the formation of ice crystals was controlled by the more intensive starch molecules in the gel, and PSs with the smaller pore sizes were obtained by exchanging ice crystals with the smaller sizes in gel with ethanol.

PSs could be obtained in the dual freezing process. The smaller holes were expectedly prepared in the resulted porous structure of PSs, if starch pastes were filled in the pores from the single freezing process, and then frozen again. Because PSs were frozen from starch pastes by the first freezing process, the porous structures could gradually dissolve into starch pastes, ready for the second freezing process. As citrate starches did not swell and gelatinize in hot water as a result of cross-linking reaction (Ma et al., 2008, 2009), CAPS0 was prepared before immersing in starch pastes with different concentrations (1.5, 2.5 and 3.5%). As shown in Fig. 2, compared to CAPS0, CAPS1.5, CAPS2.5 and CAPS3.5 exhibited more walls in the original holes. And there was no obvious difference among the morphology of PSs from the dual freezing process.

3.2. Apparent density

The apparent densities were calculated by dividing the mass of the samples by the apparent volumes. Fig. 3 reveals the dependence of apparent densities on the starch paste concentrations in the single or dual freezing process. In the single freezing process, with the increasing of starch paste concentrations from 5 to 20%, the apparent densities of PSs significantly increased from 0.093 to 0.689 g/cm^3. Compared to CAPS0, the apparent densities of CAPS1.5, 2.5 and 3.5 were only enhanced a little in the second freezing process. The starch pastes, filled in the holes of CAPS0, did not obviously improve the apparent density because of the low starch paste concentrations (1.5–3.5%). However, the higher starch paste concentrations would result in the higher viscosities, which could hinder the filling of starch pastes in the holes of CAPS0.

3.3. Moisture adsorption

Water sensitivity is an important criterion for many practical applications of PSs. Fig. 4 shows the relation of moisture con-

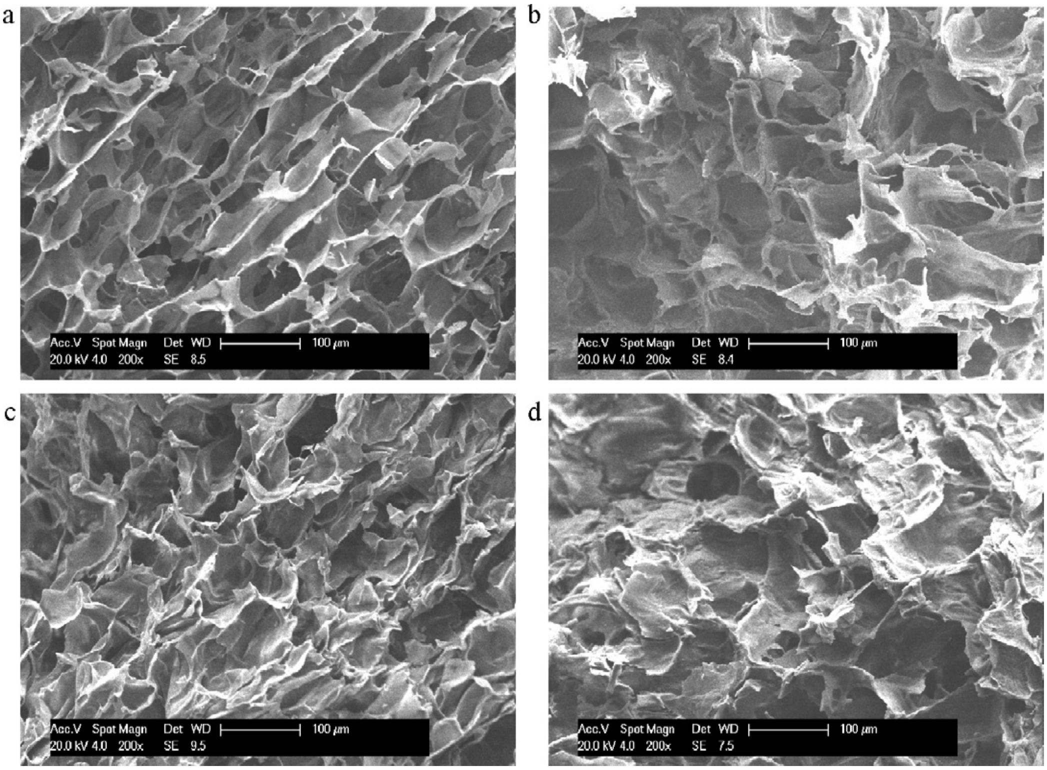

Fig. 2. SEM micrograph of the fractured surface of CAPS0 (a), CAPS1.5 (b), CAPS2.5 (c) and CAPS3.5 (d) in the dual freezing processing.

tents in PSs with different storage time at RH 75%. It took about 6 days for PSs to reach adsorption equilibrium; similarly several days were required for thermoplastic starch materials (Ma, Yu, & Kennedy, 2005). The porous structure did not obviously improve the rate of moisture adsorption. When the starch paste concentrations increased from 5% to 20% in the single freezing process, the moisture contents at equilibrium decreased from 45.2% to 32.5%. It could be related to the decrease of specific surface areas of PSs. More and smaller pores were observed with the increasing of starch paste concentrations in Fig. 1, but the apparent densities were distinctly increased, so the specific surface areas of PSs actually decreased. The moisture content of CAPS0 at equilibrium was about 58.8%, while the ones for CAPS1.5, 2.5 and 3.5 varied a little from 46.6 to 42.1%. The second freezing process could shrink the specific surface areas, but starch paste concentrations (1.5–3.5%) had little effect on the specific surface areas.

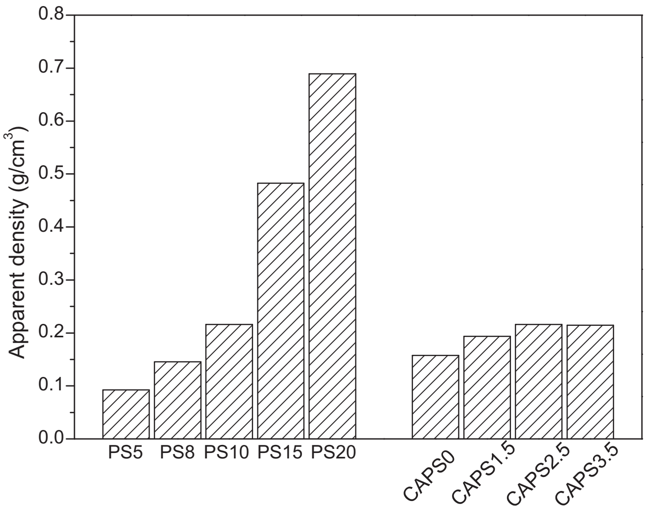

Fig. 3. Apparent densities of PSs, prepared from different starch paste concentrations.

3.4. Oil adsorption

As shown in Fig. 5, the oil adsorption capacity of PS5 reached 5.84 g g^{-1} (oil/PS) while PS20 had merely 0.33 g g^{-1}. With the increasing of starch paste concentrations, the oil adsorption capacity of PS decreased rapidly. Despite the hydrophilic nature of starch, PS5 showed good capacity for oil adsorption; this could be attributed to the porous structures which trapped and retained oil. When starch paste concentrations increased, the pore volumes of PSs decreased and possessed less oil adsorption capacity.

The oil adsorption capacity of CAPS0 reached 7.27 g g^{-1} because of larger pore volume and hydrophobic surface of CAPS0. Compared to PS 5 and CAPS0, CAPS1.5, 2.5 and 3.5 exhibited lower oil adsorption (about 3.3–3.8 g g^{-1}). It indicated that the effect of pore volume on oil adsorption could be more apparent than the hydrophobic modification of CA.

3.5. Adsorption of methylene blue (MB)

Fig. 6(a) illustrates the amounts of MB as a function of time, adsorbed by PSs from different starch paste concentrations in the single freezing process. The amounts of MB dye adsorbed at equilibrium from the experimental curves were 0.73, 0.57, 0.49, 0.42 and 0.35 mg g^{-1} for PS5, PS8, PS10, PS15 and PS20. This order could be related to the specific surface areas of PSs. The adsorption behavior of PS5 for MB could be described well by the pseudo second-order model, while other PSs in the single freezing process could not. The pseudo second-order mode is expressed as Eq. (3) (Xie, Qian, Wu, & Ma, 2011):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \qquad (3)$$

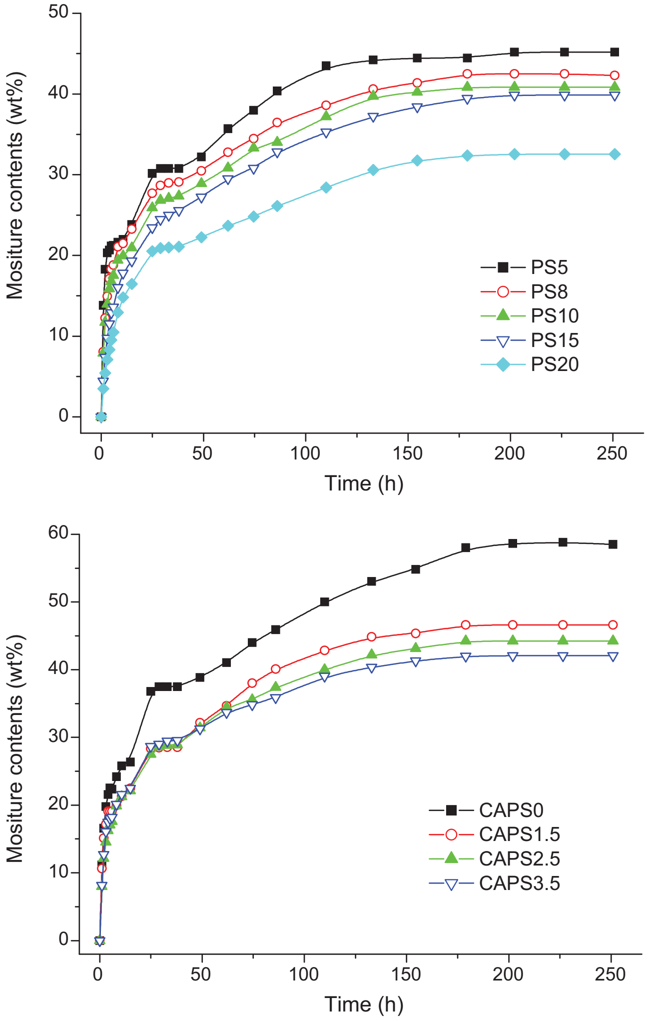

Fig. 4. Effect of different starch paste concentrations on oil adsorption capacity of PS. (a) The single freezing processing and (b) the dual freezing processing.

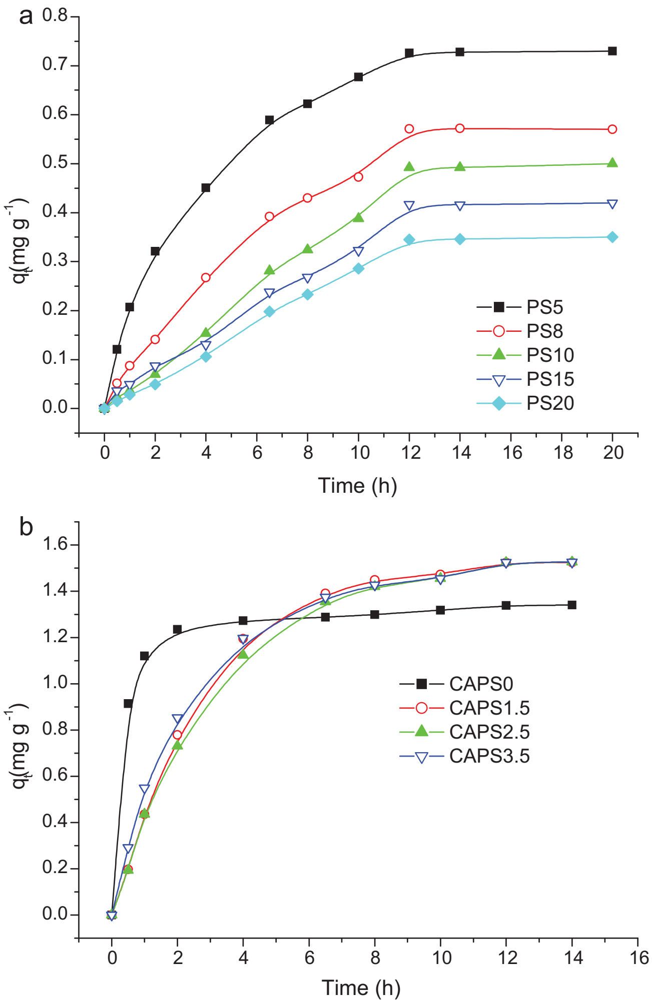

Fig. 6. Effect of time on adsorption for MB by PSs, prepared from different starch paste concentrations. (a) The single freezing processing and (b) the dual freezing processing. Initial concentration: MB 0.064 mmol L^{-1} (23.93 mg L^{-1}) and PS 10 g L^{-1}.

where k (mg g^{-1} h^{-1}) is the second-order rate constant and q_t (mg g^{-1} PS) and q_e (mg g^{-1} PS) represent the amounts of dye adsorbed at any time t (h) and at equilibrium, respectively. The second-order rate constant k and q_e can be obtained from the intercept and slope of the line in a t/q_t versus t plot. Some kinetic parameters, estimated from the experimental data in Fig. 6 and Eq. (3), were listed in Table 1.

For the MB adsorption of CAPS0, CAPS1.5, CAPS2.5 and CAPS3.5, a linear relationship with high correlation coefficients ($R > 0.99$) between t/q_t and t indicated the adsorption process could be described by the pseudo second-order model. In terms of $q_{e,exp}$, PSs (about 1.5 mg g^{-1}) from the second freezing process exhibited much better adsorption for MB than CAPS0 and PSs from the single freezing process, while the difference among the MB adsorption of PSs from the second freezing process was very little. CAPS0 also showed more rapid adsorption for MB than other PSs.

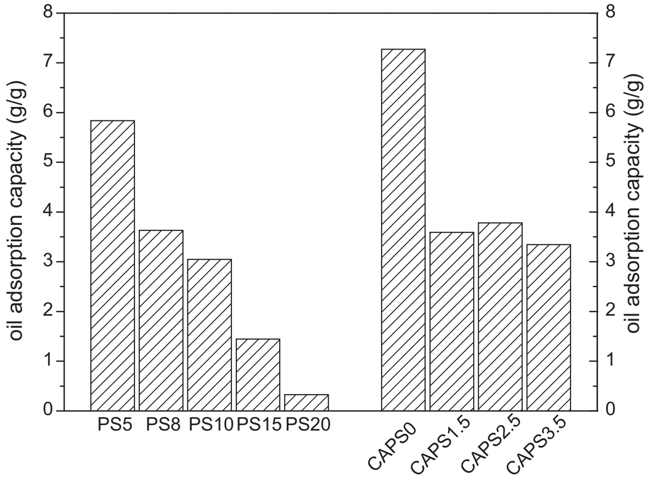

Fig. 5. Effect of different starch paste concentrations on moisture absorption of PS. (a) The single freezing processing and (b) the dual freezing processing.

Table 1
Adsorption kinetic constant of PSs modeled by a pseudo second-order equation.

Samples	T_{eq} (h)	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	k (mg g^{-1} h^{-1})	R
PS5	14	0.73	0.87	0.357	0.998
CAPS0	8	1.34	1.36	2.84	1
CAPS1.5	12	1.52	1.96	0.154	0.992
CAPS2.5	12	1.53	1.98	0.141	0.994
CAPS3.5	12	1.53	1.80	0.248	0.999

4. Conclusion

The freezing-solvent exchange technique was developed to prepare controllable PSs with different starch paste concentrations in the single or dual freezing process. For PSs from the single freezing process, the porous structure and the adsorption for moisture, oil and MB greatly decreased with the increasing of starch paste concentrations from 5 to 20%. The pore size, apparent density, moisture adsorption, oil adsorption and MB adsorption for PS5 were 100 μm, 0.093 g/cm^3, 45.2%, 5.84 g g^{-1} and 0.73 mg g^{-1} for PS5, while they were 5–10 μm, 0.689 g/cm^3, 32.5%, 0.33 g g^{-1} and 0.35 mg g^{-1} for PS20, respectively. PSs from the dual freezing process exhibited the lower moisture and oil adsorption capacity than CAPS0, but better MB adsorption at equilibrium with longer equilibrium time.

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