

Facile Production of Purple Sweet Potato Porous Starch as Low Cost Food-based Adsorbent for Microencapsulation

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This study aimed to develop a facile synthesis process of porous starch wall materials from purple sweet potato (PSP) for microencapsulation *via* enzymatic treatment. The optimum extraction conditions of purple sweet potato starch (PSP-S) were first attained by an orthogonal experiment. Response surface methodology was performed through the enzymatic hydrolysis of PSP-S using an α -amylase and glucoamylase complex to optimize the process parameters for the production of porous starch. Optimal reaction conditions were: the mass ratio (w/w) of glucoamylase to α -amylase of 6.39, amount of substrate of 19.5 g, and amount of enzymes of 0.53%. The surface morphology, microstructure, and thermal stability of the obtained samples were characterized with scanning electron microscopy, Fourier-transform infrared, and thermogravimetric analyses, respectively. The purple sweet potato porous starch (PSP-PS) had a stable oil adsorption capacity, and the molecular structure and thermal stability of porous starch were not substantially different from those of native starch. This study offers a simple yet efficient approach to produce fully biodegradable food-based porous materials for potential applications in oil microencapsulation.

Keywords: Porous purple sweet potato starch; Complex enzymatic hydrolysis; Adsorption

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INTRODUCTION

Starch is a highly investigated biopolymer because of its wide range of sources, renewability, and relatively low cost (Xie *et al.* 2013; Pokhrel 2015; Hemamalini and Dev 2018; Koh *et al.* 2018; Zhu *et al.* 2018a,c). Native starch is unsuitable as an organic adsorbent due to its low surface area and pore volume, which restrict its development for industrial applications. Porous starch is a novel modified starch that serves as an excellent natural adsorbent because of its abundant pores from the surface to the center of its granules (Guo *et al.* 2013; Dura *et al.* 2014; Benavent-Gil and Rosell 2017a; Benavent-Gil *et al.* 2018). The pore diameter of porous starch is approximately 1 μm , and half of its volume turns into a porous structure (Zhang *et al.* 2012). Compared with conventional modified starch, porous starch displays large pore volume, high specific surface area, small particle density, and strong adsorption (Wang *et al.* 2012; Jiang *et al.* 2017; Xu *et al.* 2018). Due

to these characteristics, porous starch is widely used in the food (*e.g.*, flavor, oil, and probiotic carriers), chemical (*e.g.*, structure-directing agent), environmental (*e.g.*, typical organics and heavy metal pollutant adsorption), and pharmaceutical (*e.g.*, targeted drug delivery system) industries (Chang *et al.* 2011; Belingheri *et al.* 2012; Belingheri *et al.* 2015; Hu *et al.* 2015; Xu *et al.* 2017; Benavent-Gil *et al.* 2018; Lei *et al.* 2018; Zhu *et al.* 2018b).

Methods such as ball milling, acid hydrolysis, freeze-thawing, solvent exchange, and solvent treatment have been employed to prepare porous starch (Niemann and Whistler 1992; Chang *et al.* 2011; Qian *et al.* 2011; Wu *et al.* 2011; Mi *et al.* 2012; Zhao *et al.* 2018). In this regard, a green, non-chemical way to modify starch granules applying enzymatic treatment has captured the attention of the scientific community. The number, size, and depth of pores depend on the extent of enzyme action, the source of starch, the species and concentration of amylases, the treatment temperature, the reaction time, and the pH of the starch slurry (Benavent-Gil and Rosell 2017a,b; Jung *et al.* 2017; Lei *et al.* 2018). Most porous starches are produced through the enzymatic hydrolysis of corn, cassava, and rice starches. In this study, purple sweet potato (PSP) was chosen as the raw material because of its wide planting area, rich nutrition, and high dry matter contents. The effects of enzymatic treatment conditions on the production of purple sweet potato porous starch (PSP-PS) for the wall-forming material have not yet been comprehensively investigated. Thus, the experimental extraction conditions of purple sweet potato starch (PSP-S) derived from PSP were established first in this study.

An optimized method was introduced to prepare PSP-PS by using α -amylase and glucoamylase as hydrolysis enzymes. These enzymes were chosen because their synergistic action results in the rapid and effective hydrolysis of raw starch. Enzymatic hydrolysis using amylase and glucoamylase was employed to prepare porous starch by controlling the enzyme ratio, enzyme content, and substrate content. The hydrolysis conditions were optimized by using the Plackett–Burman design and response surface methodology. The surface morphology and microstructure of the samples were observed *via* scanning electron microscopy (SEM). The original starch and the porous starch were compared *via* Fourier-transform infrared (FTIR) and thermogravimetric analyses (TGA). The results showed that the molecular structure and thermal stability of the produced porous starch with a high oil adsorption capacity did not change. This study presents a simple yet efficient approach to produce food-based porous materials with a high adsorption capacity for potential applications in oil microencapsulation.

EXPERIMENTAL

Materials

The PSP was purchased from the local market. The α -amylase with an activity of 500 U/mg and glucoamylase with an activity of 100000 u/mL were provided by Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Food grade soybean oil was obtained from Yihai Jiali (Wuhan) Cereal and Oil Industry Co., Ltd (Wuhan, China). Citric acid and disodium hydrogen phosphate were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All other chemicals were of analytical grade.

Preparation of Purple Sweet Potato Starch

Fresh purple sweet potatoes (PSPs) (Fig. 1a) were artificially washed, peeled, and pulped by passing the slices of potatoes through a blender. The resulting slurry (20 g) was poured into a beaker containing 60 mL of 0.05 mol/L citric acid-sodium dihydrogen phosphate running buffer (pH adjusted with citric acid). After the reaction, the cooled slurry was filtered using a silk cloth, and the residue was repeatedly washed with water until the filtrate was no longer turbid. The obtained filtrate (Fig. 1b) was centrifuged at 3000 r/min for 10 min using a centrifugal machine (TGL16, Changsha Yingtai Co., Ltd., Hunan, China). The products were dried, crushed, and passed through a 100-mesh sieve to obtain the PSP-S. The effects of reaction temperature, pH, and treatment time on the yield were analyzed. Based on a single-factor experiment, L9 (3³) was selected as the orthogonal test table. The experimental results were used to optimize the starch yield, as calculated by Eq. 1,

$$\text{Yield (\%)} = \frac{M_1}{M_2} \times 100\% \quad (1)$$

where M_1 (g) is the mass of the PSP-S, and M_2 (g) is the mass of the dried PSP.

Preparation of Porous Starch Derived from Purple Sweet Potato Starch

Porous starch was prepared as previously described with some modifications (Zhang *et al.* 2012; Lei *et al.* 2018). A certain amount of PSP and 60 mL of disodium hydrogen phosphate-citric acid buffer solution with a pH of 5.0 were mixed in a 250 mL three-necked flask and then mechanically stirred for 5 min in a constant-temperature water bath using a turbine stirrer (JJ-1, Changzhou Guohua Electric Appliance Co., Ltd., Jiangsu, China). A predetermined amount of α -amylase and glucoamylase was subsequently added. After a certain period of reaction at 45 °C, 1.0 w/v% NaOH solution was added, and the pH was adjusted to neutral to inhibit enzyme activity. The resulting suspension was centrifuged to separate the hydrolyzed starch. The starch was then washed with distilled water several times by suction filtration in Buchner funnel, and the substrate was dried a constant weight in the oven at 40 °C. Finally, the product was ground into fine particles to yield PSP-PS (Fig. 1c). The mass ratio (w/w) of glucoamylase to α -amylase, the enzyme content, and the substrate content were analyzed using response surface methodology to obtain the optimum preparation conditions for porous starch. The oil adsorption ratio of porous starch, which was used as the index, was calculated using Eq. 2,

$$\text{Adsorption Ratio (\%)} = \frac{m_2 - m_1 - m_0}{m_0} \quad (2)$$

where m_0 (g) is the mass of starch samples, and $(m_2 - m_1)$ (g) is the mass of the funnel before and after the experiment.

Characterization of Materials

The morphology of the starches was observed using a scanning electron microscope (Hitachi, S-3000N SEM, Tokyo, Japan). Before examination, all samples were sputter-coated with a thin layer of gold. Thermogravimetric analysis (TGA) was conducted on a METTLER TOLEDO TGA-S1100SF device (Columbus, OH, USA) in N₂ atmosphere with a heating rate of 10 °C/min and a temperature range of 30 °C to 800 °C. Fourier-

transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet NEXUS670 spectrometer (Madison, WI, USA) using KBr pellets.

RESULTS AND DISCUSSION

Preparation of Purple Sweet Potato Starch

The effects of treatment temperature, pH, and treatment time on the starch yield were studied to establish the processing technology for producing PSP-S. The extent of the effect of each factor was determined based on the results of the single-factor experiment. Figure 1d shows the plot of treatment temperature against the PSP-S yield. The starch yield increased at temperatures below 40 °C and decreased at temperatures above 40 °C. The starch was insoluble in water at a low temperature, whereas an elevated temperature was conducive for starch extraction. However, at a high temperature, the viscosity of the mixture increased, and the starch structure was destroyed. Therefore, 40 °C was deemed as the optimum temperature for starch extraction. The solubility of starch was high under slightly acidic conditions, although the starch molecules were destroyed in a peracid environment. The effect of pH is depicted in Fig. 1e, which shows that the yield of the PSP-S increased at a pH lower than 4.5. The starch could be dissolved and dispersed better at a pH below 4.5. The yield of PSP-S decreased at a pH higher than 4.5. These results demonstrate that 4.5 is the optimal pH for starch extraction. Figure 1f shows the effect of the treatment time on the starch yield. The starch yield increased when the treatment time was less than 3 h and slightly decreased when the treatment time exceeded 3 h. Therefore, 3 h was deemed the optimum treatment time for starch extraction.

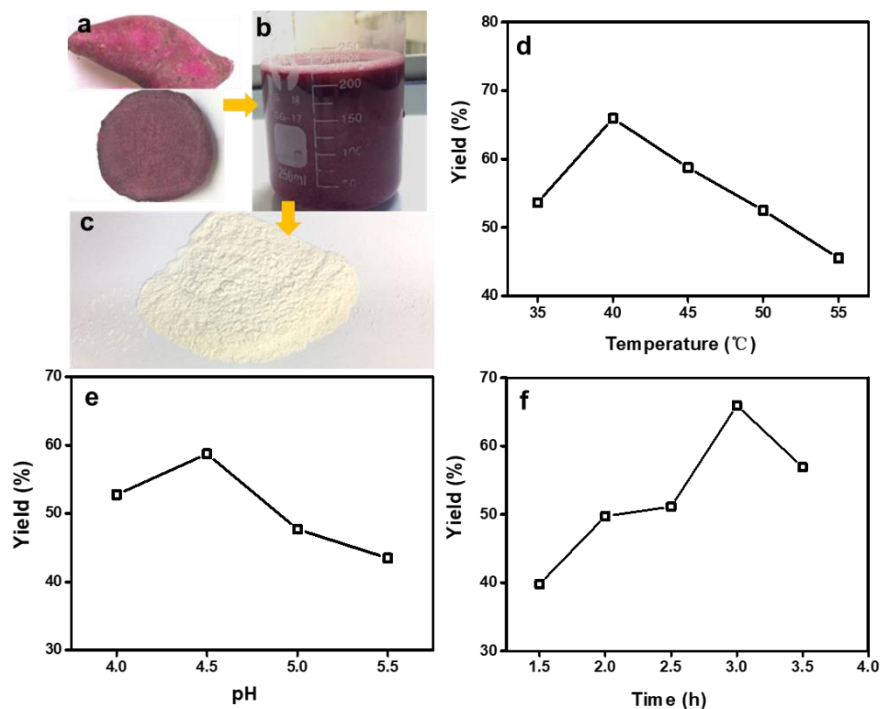


Fig. 1. Digital images of the PSP (a), filtrate (b), and porous starch (c) and the effect of extraction temperature (d), pH value of the reaction solution (e), and extraction time (f) on the yield of the PSP-S

The optimum process conditions for starch extraction were determined using the orthogonal test (Table 1), and the results are shown in Table 2. The degree of influence of the factors followed the sequence of B > A > C (time > pH > temperature). The best combination was A₁B₂C₃. Given the low effect of temperature on extraction and the problem with energy consumption, the optimum extraction conditions were as follows: pH of 4, extraction time of 3 h, and temperature of 45 °C.

Table 1. Results of Orthogonal Experiment

No.	A pH	B Time/h	C Temperature/°C	Yield/%(w/w)
1	4	2.5	35	58.02
2	4	3	40	59.55
3	4	3.5	45	57.94
4	4.5	2.5	40	56.54
5	4.5	3	45	58.23
6	4.5	3.5	35	53.4
7	5	2.5	45	57.33
8	5	3	35	59.33
9	5	3.5	40	55.42

Table 2. Range Analysis Data of the Starch Product Yield

Value name	A pH	B Time/h	C Temperature/°C
K1	175.51	171.89	170.75
K2	168.17	177.11	171.51
K3	172.08	166.76	173.5
k1	58.5	57.3	56.92
k2	56.06	59.04	57.17
k3	57.36	55.59	57.83
R	7.34	10.35	2.75

Preparation of Porous Starch Derived from Purple Sweet Potato Starch

Porous starch has been obtained by using physical, chemical, and biological methods. Among these methods, enzymatic hydrolysis treatment is considered a facile and green method for preparing porous starch. Herein, porous starch from PSP-S was produced through enzymatic hydrolysis using α -amylase, glucoamylase, and their complex as hydrolysis enzymes. The adsorption capacity of porous starch, an important parameter influencing its application, is advisable as the measuring standard.

The effect of α -amylase, glucoamylase, and their complex on the preparation of PSP-PS was examined (Fig. 2). As shown in Fig. 2, the starch treated with the complex enzymatic system displayed a higher adsorption capacity for water and oil compared with those treated with glucoamylase or α -amylase alone. During enzymatic hydrolysis, α -

amylase mainly hydrolyzed the α -1,4 glycosidic bonds of the starch molecules, whereas glucoamylase not only acted on the α -1,4 glycosidic bond, but also the α -1, 6 glycosidic bonds starting from the non-reducing end (Zhang *et al.* 2012). The former exposed the sugar chain of the starch contributing to the starch hydrolysis under the action of glucoamylase. Therefore, the adsorption capacity of the porous starch prepared using the complex of α -amylase and glucoamylase was superior to that of the porous starch prepared using a single enzyme. However, the porous starch yield (the mass ratio (m/m) of samples before and after enzymatic hydrolysis reaction) in the latter was slightly lower than that in the former. To obtain porous starch with optimum adsorption capacity, this study optimized the reaction parameters, such as the amount of reactants (PSP-S), mass ratio of α -amylase to glucoamylase, and mass ratio of total amount of enzymes to starch, as described below.

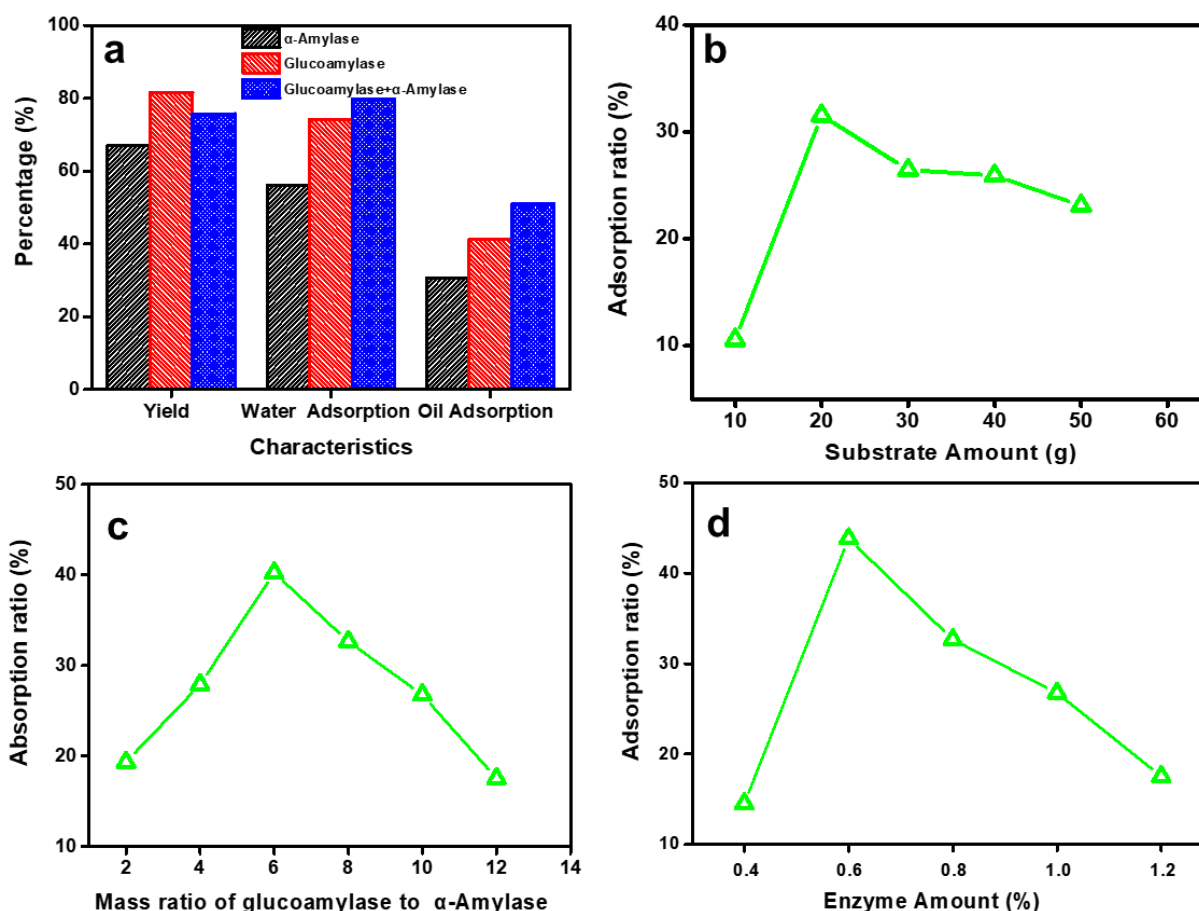


Fig. 2. (a) Performance comparison for porous starch products using various combinations enzymatic system, and (b-d) effect of amount of substrate (b), mass ratio of glucoamylase to α -amylase (c), and amount of enzymes (d) on adsorption ratio

Figure 2b shows the effect of the amount of starch reactants on the oil adsorption of porous starch. Oil adsorption was remarkably increased as the amount of reactants increased from 10 g to 20 g and then slightly decreased when the starch granules were continuously added into the reaction system. When the amount of substrates was relatively low, the starch could have dispersed in the reaction system uniformly and established contact with the enzyme efficiently, which consequently increased oil adsorption capacity. A continuous increase in the amount of starch substrates resulted in a high concentration

of the reaction system and a high viscosity of the solution. The dispersion of starch granules in the system was very uneven, which avoided close contact between the enzyme and substrates. Therefore, the oil adsorption capacity of the produced porous starch decreased.

Figure 2c shows that the oil adsorption ratio of the porous starch products was highest when the mass ratio of glucoamylase to α -amylase was 6:1. This result indicated it got the best synergistic effect of two enzymes. When the proportion of the glucoamylase was further increased, the synergistic effect of the enzymes was weakened and the oil adsorption ratio of the products decreased.

As shown in Fig. 2d, enzyme concentration considerably affected the enzymatic reaction. When a small quantity of enzyme was added, the oil adsorption ratio of products sharply increased. The substrates were combined with the enzyme and the surface of the starch granules began to form pores. Pore adsorption of the forming porous starch occurred as the primary adsorption manner (Zhang *et al.* 2012). Moreover, starch granules were hydrolyzed into smaller particles or glucose with the further increasing enzyme amount in the reaction system, resulting in the reduced adsorption ratio. The oil adsorption capacity of the products was the highest when the enzyme content was 0.6 w/w% (with respect to the mass of starch).

The Box-Behnken design was further used to analyze the effect of the three variables (mass ratio of glucoamylase to α -amylase (A), enzyme content (B), and substrate content (C)) on the oil adsorption ratio of the products (Table 3). The results of the regression analysis are shown in Table 4. The mathematical model equations were developed by using Design-Expert 8.0.6. software as follows:

$$\text{Oil adsorption} = 29.61 + 0.97A - 0.90B - 0.21C - 0.92AB + 0.20AC - 2.81A^2 - 1.35B^2 - 0.68C^2 + 1.16AB^2 \quad (3)$$

Table 3. Response Surface Box-Behnken Arrangement and Experimental Results

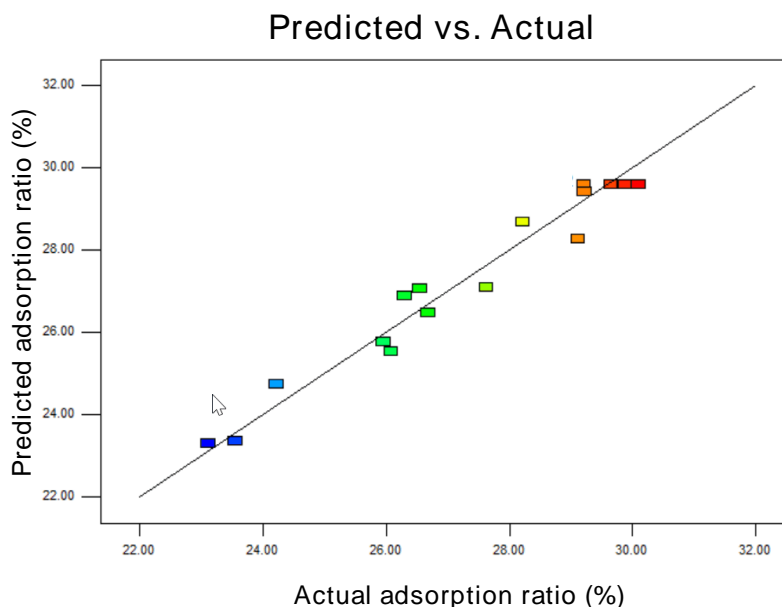
NO.	Mass Ratio (w/w) of glucoamylase to α -amylase	Enzyme Amount (%)	Substrate Amount (g)	Adsorption ratio (%)
1	6.00	0.50	15.00	28.22
2	6.00	0.60	20.00	29.21
3	6.00	0.60	20.00	30.1
4	6.00	0.60	20.00	29.21
5	7.00	0.60	15.00	27.63
6	6.00	0.70	15.00	26.3
7	6.00	0.70	25.00	26.68
8	7.00	0.50	20.00	29.22
9	5.00	0.60	15.00	26.08
10	6.00	0.60	20.00	29.88
11	5.00	0.70	20.00	23.55
12	5.00	0.60	25.00	24.22
13	6.00	0.60	20.00	29.65
14	7.00	0.70	20.00	25.96
15	7.00	0.60	25.00	26.55
16	5.00	0.50	20.00	23.11
17	6.00	0.50	25.00	29.12

Table 4. Analysis of Variance for the Model ^a

Source	Sum of Squares	df	Mean Square	F Value	P-value Prob > F	
Model	78.36	9	8.71	18.90	0.0004	Significant
A-Mass Ratio of	3.76	1	3.76	8.17	0.0244	
B-The Amount of	6.44	1	6.44	13.99	0.0073	
C- the Amount of	0.34	1	0.34	0.75	0.4158	
AB	3.42	1	3.42	7.43	0.0295	
AC	0.15	1	0.15	0.33	0.5835	
A ²	33.13	1	33.13	71.91	< 0.0001	
B ²	7.62	1	7.62	16.53	0.0048	
C ²	1.98	1	1.98	4.29	0.0771	
AB ²	2.69	1	2.69	5.84	0.0463	
Residual (error)	3.22	7	0.46			
Lack of Fit (LOF)	2.59	3	0.86	5.44	0.0677	
Pure Error	0.63	4	0.16			
Total	81.58	16				

^a Coefficient of determination (R^2)=0.9605; adjusted R^2 =0.9097; coefficient of variation (CV)=2.48%.

The P-values were used to check the significance of each coefficient. The model terms having values of “Prob > F” less than 0.05 were considered significant. As shown in Table 4, the model F-value of 18.90 with a “Prob > F” value of 0.0004 ($P < 0.01$) indicated that the model was significant. The lack of fit (LOF) was found to be insignificant in the present research study and, hence, the developed model may be accepted (Puri *et al.* 2005). The fits of the models were evaluated by coefficients of determination (R^2), which indicates the fraction of the variation of the response explained by the model (Kim and Akoh 2007).

**Fig. 3.** Comparison between predicted and observed adsorption ratio

The predicted versus actual plot for adsorption ratio of porous starch is shown in Fig. 3. The observed points on the plot demonstrate that the actual values are distributed relatively near to the straight line, which implied that the predicted data of the response from the empirical model were in good agreement with the observed ones in the range of the operating variables. The relationship between the variables and responses was depicted by the 3D surface response plots (Fig. 4), which were generated to show the response for any two independent variables in keeping the others at their central point. Figure 4 shows that the mass ratio of glucoamylase to α -amylase exerted significant effects ($P = 0.0244$). Moreover, the enzyme content significantly influenced the results ($P = 0.0073$). Furthermore, the analysis showed that a significant interaction occurred between the mass ratio of glucoamylase to α -amylase and enzyme content ($P = 0.0295$). The mass ratio of glucoamylase to α -amylase (A) and enzyme content (B) produced the best response in the selected range, indicating that the choice of the factor and the range of the test were reasonable. From the RSM result, it can be concluded that optimal conditions for fabrication of porous starch: amount of substrate 19.5 g, mass ratio (w/w) of glucoamylase to α -amylase 6.39 (w/w), and amount of enzymes 0.53%.

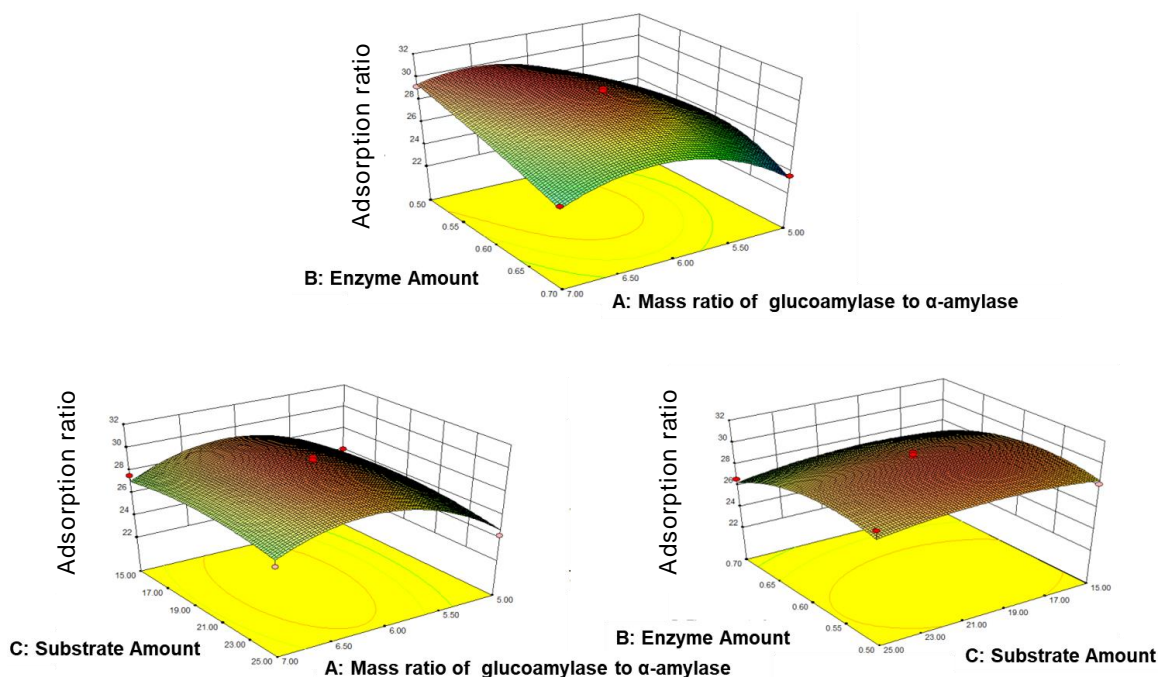


Fig. 4. Response surface plots for oil adsorption ratio showing the combined effects of process variables: mass ratio of glucoamylase to α -amylase, enzyme content, and substrate content

Figures 5a and 5b show SEM micrographs of the PSP-S and PSP-PS, respectively. The surface of the PSP-PS was rougher than that of the original starch because pores were formed on the starch granules. From this result, the porous starch can be assumed to have a stable adsorption capacity, which was evaluated based on its oil adsorption ratio as above. The relative high adsorption capacity of our samples is comparable to the values reported by other studies (Zhang *et al.* 2012; Li *et al.* 2013). The FTIR spectra of the PSP-S and PSP-PS were obtained, and the results are shown in Fig. 5c. The spectra of the porous starches produced were similar to those of the native starch, and no obvious difference was found in their characteristic absorption peaks. The intensity of the characteristic absorption

peaks of the porous starch slightly declined due to the reduced density of starch granules. These results indicated that the enzymatic hydrolysis of starch did not affect the basic chemical structures of the starches. However, this process resulted in the hydrolysis of large particles into small ones and in the formation of pores, as indicated by the SEM results. Figure 5d shows the TGA curves of the original starch and the porous starch. At temperatures below 100 °C, the water loss in the samples was the main cause of weight loss. When the decomposition temperature of the samples was reached, the weight decreased rapidly with the increasing temperature and then tended to stabilize. The highest reduction in the mass of samples was at 250 to 350 °C due to the decomposition of the starch backbone. The reduction rate was slightly higher in the porous starch than in the original starch corresponding to the increased sensitivity of thermal decomposition for porous structure. In summary, the masses of the original starch and porous starch were approximately the same under the same temperature, indicating that the thermal stability of the porous starch was basically the same as that of the original starch. This finding indicated that the structure of the porous starch was not destroyed.

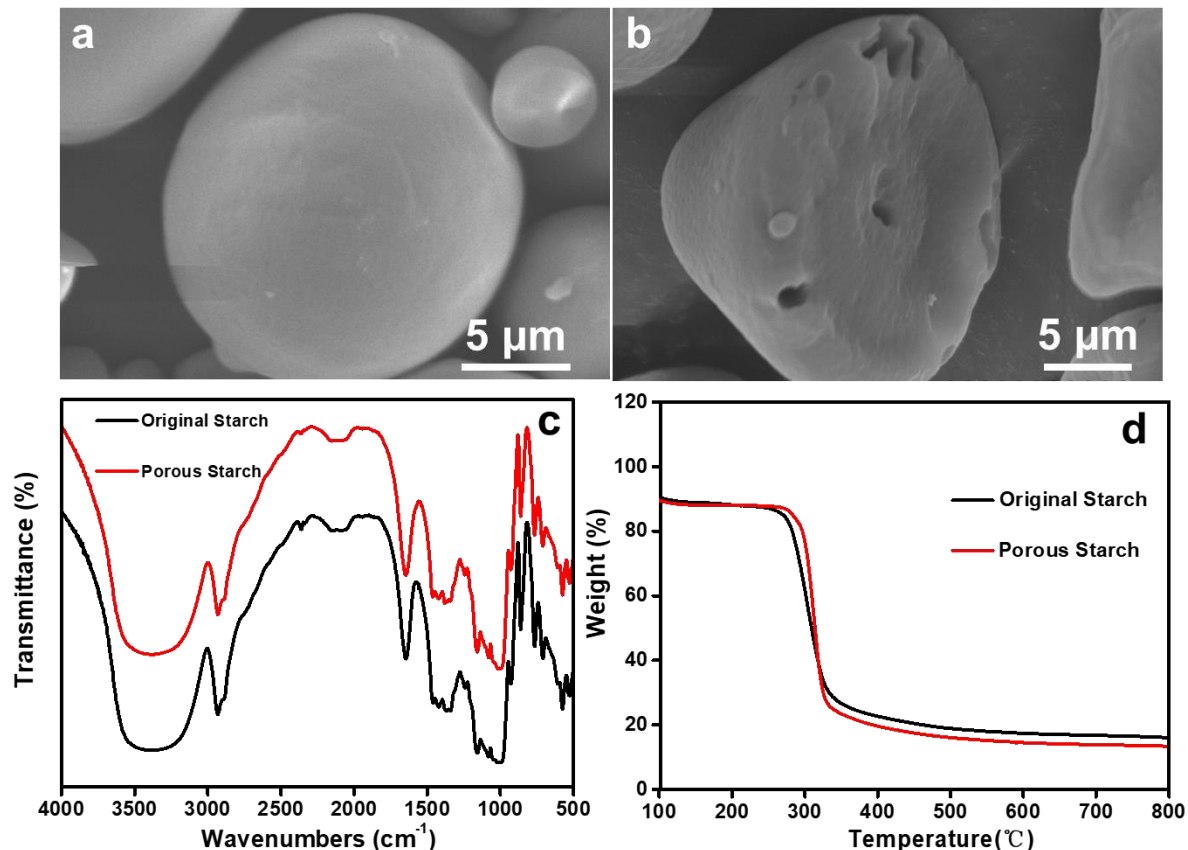


Fig. 5. (a-b) SEM images of the PSP-S before (a) and after (b) enzymatic treatment, (c) FTIR spectra of original starch and porous starch, and (d) TGA curves of original starch and porous starch.

CONCLUSIONS

1. In this study, purple sweet potato starch (PSP-S)-based porous materials were produced by extracting starch from purple sweet potato (PSP) followed by complex enzymatic hydrolysis with α -amylase and glucoamylase.
2. The results of the single-factor test and orthogonal analysis indicated that the optimal conditions for PSP-S extraction are as follows: pH of 4, treatment time of 3 h, and reaction temperature of 45 °C. The degree of influence of these factors affecting the extraction rate of PSP-S is as follows: time > pH > temperature.
3. The complex enzymatic hydrolysis technology was further used to PSP-PS. On the basis of the results of the single-factor test and response surface analysis, the optimal reaction conditions for preparing porous starch are as follows: a mass ratio of glucoamylase to α -amylase of 6.39, an enzyme content of 0.53%, and a substrate content of 19.5 g.
4. The surface morphology, microstructure, and thermal stability of the samples were analyzed through characterization. The results showed that the molecular structure of the produced porous starch with a high oil adsorption capacity did not change, demonstrating thermal stability.
5. The findings of the present work may provide a simple processing route to produce fully biodegradable and environmentally friendly food-based porous materials for adsorbents in the agriculture, medicine, and chemical industries.

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