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Adsorption of melanoidins by chitin nanofibers

Rujira Dolphen[a], Paitip Thiravetyan[b,*]

[a] Pilot Plant Development and Training Institute, King Mongkut's University of Technology Thonburi, Bangkok 10150, Thailand
[b] School of Bioresources and Technology, King Mongkut's University of Technology Thonburi, Bangkok 10150, Thailand

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ABSTRACT

Melanoidins, the complex bio-polymer of amino-carbonyl compounds are widely distributed in food, drinks but if it was discharged into a water resource system that affect as environmental pollutants. Adsorption is a potential method to remove the color from the food or environment. Therefore, this research studied on the adsorption of synthetic melanoidins by chitin nanofibers prepared from shrimp shell waste. The results showed that the adsorption of melanoidins with chitin nanofibers was increased when increasing temperature, giving values of 131, 331 and 353 mg/g at 20 °C, 40 °C and 60 °C, respectively, which were higher than other chitin-derived adsorbents. In addition, the *b* value of chitin nanofibers also had a high affinity and strength for melanoidins adsorption at low concentration higher than other chitin-derived adsorbents. The results from Fourier transform infrared (FT-IR) spectroscopy and elution studies confirmed that the interaction between melanoidins and chitin nanofibers involved both electrostatic and chemical adsorption. For application in the sugar industry, chitin nanofibers can be used for adsorption of melanoidins and other pigments from sugar syrup.

1. Introduction

Melanoidins, which are also known as Maillard reaction products, are polymeric and colored products that are formed by a condensation reaction involving sugars and amino acids [1]. Despite extensive investigations using techniques such as infrared (IR) spectroscopy, mass spectrometry and advanced multidimensional nuclear magnetic resonance (NMR) spectroscopy analyses [2], the structures of melanoidins are still not completely understood. Melanoidins occur extensively in food and biological material [3] and have significant effects on the quality of food; since colors and flavors are important food attributes and key factor in consumer's acceptance [1,4]. Food and drink having brown-colored melanoidins may offer substantial health promoting effects, but *in vitro* studies have also revealed some mutagenic, carcinogenic and cytotoxic properties [5,6].

Melanoidins in wastewaters released from distilleries and fermentation industries may cause aquatic pollution and several studies of the decolorization and degradation of melanoidins have been performed using techniques such as flocculation treatment [7], and physicochemical treatment [8]. Activated carbon adsorption is widely used as an adsorbent such as remove color from organic compounds from wastewater [9], the molasses' wastewater [10], melanoidin [11], and clarified juice in sugar refineries [12]. Biological decolorization of melanoidins has been successfully achieved [13–16], but it has limited environmental factors. In prior reports, chitin nanofibers have been successfully prepared from other materials based on methods described elsewhere for crab shells [17,18], squid pens [19], *Riftia* tubes [20] and shrimp shells [21]. However, there have not been prior reports the use of chitin nanofibers for adsorption of melanoidins. Moreover, a significant amount of shrimp waste is produced in Asia, primarily in Thailand, the main shrimp exporter [22] that large quantities of shrimp waste constitute a potential source of chitin production. The present study reports the alternative use of chitin nanofibers for adsorption of water containing melanoidins, the Langmuir adsorption isotherm and the interaction between melanoidins and chitin nanofibers studies by FTIR and elution study. In addition, the study of sugar syrup by using chitin nanofibers was also investigated.

2. Materials and methods

2.1. Chitin and chitosan

Chitin (48% DD) and chitosan (90% DD) from shrimp shell waste was supplied by Seafresh Chitosan (Lab) Co. Ltd., Thailand. The average particle sizes were 400 μm–1 mm.

2.2. Preparation of chitin nanofibers

The preparation of chitin nanofibers was adapted from the method reported in Nair and Dufresne [18]. The chitin was

* Corresponding author. Tel.: +66 2 470 7535; fax: +66 2 452 3455.
E-mail address: paitip.thi@kmutt.ac.th (P. Thiravetyan).

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hydrolyzed with 3 M HCl (the ratio of 3 M HCl to chitin was 10 g/L) at 80–90 °C under stirring to produce a protein-free product. After acid hydrolysis, the suspensions were centrifuged at 36,000 rpm for 15 min, and the process was repeated three times. Next, the suspensions were transferred to a dialysis bag, dialyzed in running distilled water for 2 h and then overnight in distilled water until a pH 3.5 was reached and then air dried. The size distribution is 150–800 nm length and 10–50 nm width.

2.3. Preparation of modified chitin

Chitin was bleached with 6% (w/v) sodium hypochlorite (ratio of 1:30 (w/v)); the mixture was being shaken at 150 rpm at 30 ± 2 °C for 1 h. The modified chitin was washed with an excess of distilled water until the pH was ~7, and then dried. The average particle size was 400 nm–1 mm.

2.4. Preparation of melanoidins

Melanoidins were prepared using a modification of a previous method [9] by mixing 4.5 g (0.025 M) of glucose, 1.88 g (0.025 M) of glycine and 0.42 g (0.005 M) of sodium bicarbonate ($NaHCO_3$) with 100 mL of distilled water, then heating overnight at 80 °C until dry. 100 mL of water was then added and the sample was dialyzed in 1 L of distilled water using 10 cm dialysis tubing, with a change of water every 8–10 h. The total dialysis time was 136 h. After dialysis, the samples were filtered through cotton wool and freeze-dried.

2.5. Determination of surface area

The BET surface area, total pore volume and average pore volume of adsorbents were determined using a surface area analyzer (Autosorb-1, Quantachrome, USA).

2.6. IR analysis

Functional groups of adsorbents before and after melanoidins adsorption were measured by Fourier transform infrared (FT-IR) spectroscopy (Bruker, ALPHA, Germany). The sample was mixed with dry KBr in a ratio of 2 mg:200 mg and then the mixture was ground and compressed. The FT-IR spectra of samples were taken at 400–4000 cm^{-1} wavenumber range.

2.7. Microscopic analysis

For the analysis of chitin nanofibers by transmission electron microscopy (TEM) (JEM-2100, Japan), a droplet of a dilute suspension of nano-chitin was deposited on a carbon-coated grid and allowed to dry. The accelerating voltage was 80 kV.

2.8. Adsorption study

Adsorption experiments were performed in a 15 mL vial using 0.05 g of adsorbents with 10 mL of melanoidins at various concentrations in the range of 20–3000 mg/L. The mixtures were shaken at 150 rpm at 20 °C, 40 °C or 60 °C at an equilibrium time for 1 h and then centrifuged at 4500 rpm for 10 min. The pH of the supernatant was measured using a pH meter (Mettler Delta 340, England) and the color was measured for absorbance at a maximum wavelength at 420 nm by spectrophotometer (UNICO-2100, USA). Melanoidins adsorption was analyzed using the Langmuir isotherm Eq. (1).

$$q_e = \frac{q_{max}\ bC_e}{1 + bC_e} \quad (1)$$

where q_e is the amount of melanoidins adsorbed at equilibrium (mg/g); C_e is the concentration of melanoidins at equilibrium (mg/L); q_{max} is the maximum adsorption capacity of melanoidins per g of adsorbent (mg/g); and b is the Langmuir constant related to the energy of adsorption (L/mg)

Sugar syrup was passed through packed columns containing chitin nanofibers at 1%, 5% and 10% dosage at a controlled flow rate of 10 mL/min for 1 h. Samples were then analyzed for pH, ICUMSA color remaining [23] and decolorization efficiency using Eqs. (2)–(4). All experiments were conducted twice.

$$\text{Concentration (g/100 mL)} = 0.00002\ (\text{Brix}^3) + 0.0036\ (\text{Brix}^2) + 1.0013\ (\text{Brix}) \quad (2)$$

$$\text{ICUMSA color} = \frac{\text{Abs (420 nm) } 100,000}{\text{Cell length (1 cm) Concentration (g/100 mL)}} \quad (3)$$

$$\text{Decolorization efficiency (\%)} = \left(1 - \frac{OD_{420}\ \text{color of permeate}}{OD_{420}\ \text{color of sugar syrup}}\right) \times 100 \quad (4)$$

2.9. Elution study

Suspensions of 1% (w/v) of melanoidin-adsorbed adsorbents were added to a syringe, which was connected to a peristaltic pump with a flow rate of 2.0 mL/min, and eluted with distilled water until no color appeared in the solution. 0.5 M NaOH was then used as a second eluent followed by 80% methanol, and the color was analyzed by spectrophotometer at 420 nm.

3. Results and discussion

3.1. Physical properties of chitin nanofibers

Table 1 shows the surface area, total pore volume and average pore diameter of chitin and chitin nanofibers measured by surface area analysis. The surface area of chitin nanofibers is slightly higher than chitin, but the average pore diameters of both chitin and chitin nanofibers are in the mesopore range (2–50 nm).

Table 1
Surface area, pore volume and pore size of chitin. chitin nanofibers, modified chitin and chitosan.

Sample types	Multipoint BET (m^2/g)	Total pore volume (cc/g)	Average pore diameter (nm)
Chitin	6.04	0.0209	13.82
Chitin nanofibers	8.76	0.0220	10.03
Modified chitin	3 01	0.0052	6.98
Chitosan	6.86	0.0078	4.57

After hydrolysis with 3 M HCl, the morphology of chitin nanofibers was observed by transmission electron microscopy (TEM) (Fig. 1). The results show that these chitin fragments consist of slender rods with sharp points and a broad size distribution with lengths and widths of 150–800 nm and 10–50 nm, respectively.

The FT-IR spectrum of chitin (Fig. 2a) is typical of chitin, with characteristic peaks at 3449 cm^{-1} (N–H), 1651 cm^{-1} for amide I (C=O), 1379 cm^{-1} (OH), 1255 cm^{-1} (CNH) and 1083 cm^{-1} (C–O). Accordingly, sodium hypochlorite affected the alcohol group (CH_2OH) of chitin and transformed it to CH_2OCl [24], modified chitin (Fig. 2b) shows a significant increase peaks at 1649 cm^{-1} and 1561 cm^{-1} and a new peak at 698 cm^{-1} (Cl) appeared. Chitosan (Fig. 2c) shows peaks at 1655 cm^{-1} (amide I, C=O) and 1560 cm^{-1} (combination amide II, combination of C–N STR and N–H bend).