Decolorization of hydrolysate of coconut meal using activated carbon after subcritical water treatment

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Abstract

The hydrolysate obtained from subcritical water treatment of coconut meal exhibited dark brown color because of the degradation products from the treatment and hence interfered the purification process of the oligosaccharides from the hydrolysate. To solve this problem, the effectiveness of activated carbon for decolorizing the hydrolysate was studied. The activated carbon concentrations of 1–10% (w/v) and mixing times of 0–60 min were investigated. Color adsorption was determined by the change of an absorbance at 283 nm. The carbohydrate content was also measured after decolorization process. The results showed that the color adsorption increased as the activated carbon concentration was increased from 1 to 8% (w/v), but it was not significantly increased after 8% (w/v), indicated that 8% (w/v) was the optimal concentration for the decolorization. Additionally, the color adsorption did not change significantly after 20 min of mixing. The total carbohydrate content in the hydrolysate was not altered by the decolorization process. For the adsorption isotherm studies, three models (Langmuir, Freundlich, and Frumkin) were tested. The Langmuir model provided a better description of the process.

Keywords: Decolorization, Activated carbons, Adsorption, Coconut meal, Subcritical water

1. Introduction

Around 3600 tons of coconut meal was industrially produced each year (Khuwijitjaru *et al*., 2012). Coconut meal is a rich source of mannose polysaccharides which can be hydrolyzed into manno-oligosaccharides (Khuwijitjaru *et al*., 2012; Khuwijitjaru *et al*., 2014; Rungsatsamee *et al*., 2014). Several studies have showed that manno-oligosaccharides possessed good nutritional and biological activities, specifically due to its prebiotic properties (Salinardi et al., 2010)

Recently, we reported the method to efficiently produce oligosaccharides from coconut meal using subcritical water treatment (Khuwijitjaru *et al*., 2014). The hydrolysate of coconut meal obtained from the subcritical water treatment had dark brown color, which affected the color of oligosaccharides after purification. To remove brown color pigments, the activated carbon with a large internal surface area is widely used (Muduga *et al*., 2008; Zhao *et al*., 2010; Xiao *et al*., 2014).

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In this study, powdered activated carbon was used to decolorize the coconut meal hydrolysate and the adsorption process of the activated carbon was explained using appropriate adsorption isotherm models.

Isotherm model is used to describe the adsorption equilibrium. It is the relationship between concentration of the adsorbate in fluid phase and concentration of the adsorbate in the adsorbent particles (Koyucu *et al.*, 2007). A suitable model for a specific process is usually obtained by fitting the isotherm data using different isotherm models. Langmuir, Freundlich, and Frumkin isotherms are the most often used models for the system containing only one target component and the target component is adsorbed as a one molecular layer (Arslanglu *et al.*, 2005). The basis for the Langmuir isotherm is that all sites on the surface are similar, and that there are no interactions between adsorbed molecules. This is referred to as ideal adsorption (Agyei et al., 2000). The linear form of Langmuir model can be represented by equation (3) (Arslanglu *et al.*, 2005).

$$Ae/qe = 1/bQ0 + Ae/Q0 \qquad (3)$$

where Q0 ((a.u.)m3 hydrolysate/kg adsorbent) and b (1/a.u.) are the Langmuir constants related to adsorption capacity and rate of adsorption ,respectively. The decreasing absorbance value at equilibrium per adsorbent amount, qe ((a.u.)m3 hydrolysate/kg adsorbent), was calculated from equation (4):

$$qe = (A0 - Ae)V/m \qquad (4)$$

where A0 and Ae are the initial and equilibrium absorbance values, V is the volume of hydrolysate (m3), and m is the weight of adsorbent used (kg). The Freundlich model is an empirical equation employed to describe heterogeneous surface. It is non-ideal adsorption which predicts that adsorbate on the adsorbent will increase as there is an increased in the adsorbate concentration in the liquid phase (Hameed *et al.*, 2007). A linear form of Freundlich isotherm model is given by equation (5) (Arslanglu *et al.*, 2005).

$$\ln(qe) = \ln(Kf) + 1/n \ln(Ae) \qquad (5)$$

where Kf ((a.u.)m3 hydrolysate/kg PAC) is a Freundlich constant related to adsorption capacity of the adsorbent to bind the adsorbate and the slope 1/n ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Another well-known isotherm model is Frumkin model which assumes that the surface of adsorbent is heterogeneous and there are interactions between the adsorbed molecules (Agyei *et al*., 2000). The Frumkin model expressed in equation (6) (Arslanglu *et al*., 2005).

$$qe = A + B\ln(Ae/\,qe) \qquad (6)$$

where A and B are adsorption constants or Frumkin constants.

2. Materials and Methods

2.1 Raw material

Coconut meal used in this study was a by-product from a coconut milk factory (Vara Food and Drink, Nakhon Pathom, Thailand). The obtained meal was dried in a hot air oven at 60°C for 12 h. The dried coconut meal was sieved to collect the sample with the particle size of 0.30–3.35 mm.

2.2 Adsorbent

A commercial powdered activated carbon (PAC), NORIT®SA2, was obtained from ACROS OrganicTM, Netherlands. Moisture content, ash content, volatile matter, and fixed carbon (by difference), was accomplished using the procedure described by Malik et al. (2007). All analyses were performed in triplicate. Table 1 shows important physical and chemical properties of this product.

Table 1 The physical and chemical characteristics of powdered activated carbon (PAC) used in this study.

Parameter	Quantity
Molasses number*	300
Total ash content (%)	10.96 ± 0.12
Moisture content (%)	11.74 ± 0.01
Volatile matter content (%)	6.58 ± 0.01
Fixed carbon content (%)**	70.72

Note: * data from product specification

** Calculated by 100 – (Total ash content + Moisture content + Volatile matter content)

2.3 Preparation of coconut meal hydrolysate

Dried coconut meal was treated with subcritical water in a bath-type stainless steel vessel with a net volume of 120 mL (Taiatsu Techno Corporation, Osaka, Japan) using the optimal condition, which efficiently produce oligosaccharides, reported by Khuwijitjaru *et al*. (2014). Eight gram of coconut meal and 80 g of distilled water were mixed and treated at 250°C for 14 min. After treatment, the vessel was rapidly cooled under running tap water. The liquid was separated by filtering through a Whatman no.1 paper and then centrifuge at 12000×g for 20 min at 4°C (Sorvall RC6, Thermo Scientific, Waltham, MA, USA). Finally, the resultant filtrates were pooled together and freeze-dried in order to increase the solid content as required. The freeze-dried hydrolysate was then stored in a plastic bag at -18°C for further analyses.

2.4 Equilibrium adsorption test

The freeze-dried hydrolysate was re-dissolved with distilled water at the concentration of 5% w/v. Adsorption experiments were carried out by adding different amounts of PAC (0.5, 1, 1.5, 2, 2.5, 4, and 5 g) in 50 mL of the hydrolysate in a 100 mL glass bottle. Then the mixture was well mixed by stirring at 700 rpm at room temperature using a magnetic stirrer. In each experiment, samples (3 mL) were collected at different time intervals (0, 5, 10, 15, 20, 30, 40, 50, and 60 min) during the adsorption process. Afterward, the samples were filtered through Whatman no.5 paper and an absorbance at a wavelength of 283 nm, which was taken from spectrophotometric scanning, was measured using a spectrophotometer (Genesys 10s UV, Thermo Fisher Scientific, USA). Appropriate dilutions were taken when absorbance exceed 1. Adsorption experiments were performed in triplicate.

According to equation (1) (Zhao *et al*., 2011), the color adsorption (%) was calculated.

$$\text{Color adsorption (\%)} = [(A0 - At)/A0] \times 100 \qquad (1)$$

where A0 is the initial absorbance of hydrolysate before mixing with PAC and At is the absorbance of hydrolysate after mixing with PAC at time t min.

Three adsorption isotherm models, i.e. Langmuir, Freundlich, and Frumkin isotherms were used to describe the adsorption behavior. (El Qada, *et al*., 2006).

3. Results and Discussion

3.1 Effect of mixing time

Spectrophotometric scanning indicated that the hydrolysate had an maximum absorbance peak at 283 nm (Figure 1) which is a characteristic maximum absorbance of intermediate compounds from Maillard reaction and sugar degradation such as furfural and hydroxymethylfurfural (HMF) (Buedo *et al*., 2001), and therefore this absorbance was used for investigating the effectiveness of PAC on decolorization process.

The effect of the mixing time on the adsorption by PAC was examined at different concentrations of PAC for 60 min. The changes of color adsorption with mixing time at different concentrations of PAC are presented in Figure 2. The adsorptions increased sharply from 0 to 5 min of mixing but only slightly increase afterward. The equilibrium time required for the adsorption by PAC was estimated to be 20 min. The dark brown colored compounds uptake tended to saturation, which suggested that monolayer surface of PAC was totally covered with those compounds (Arslanglu *et al*., 2005).

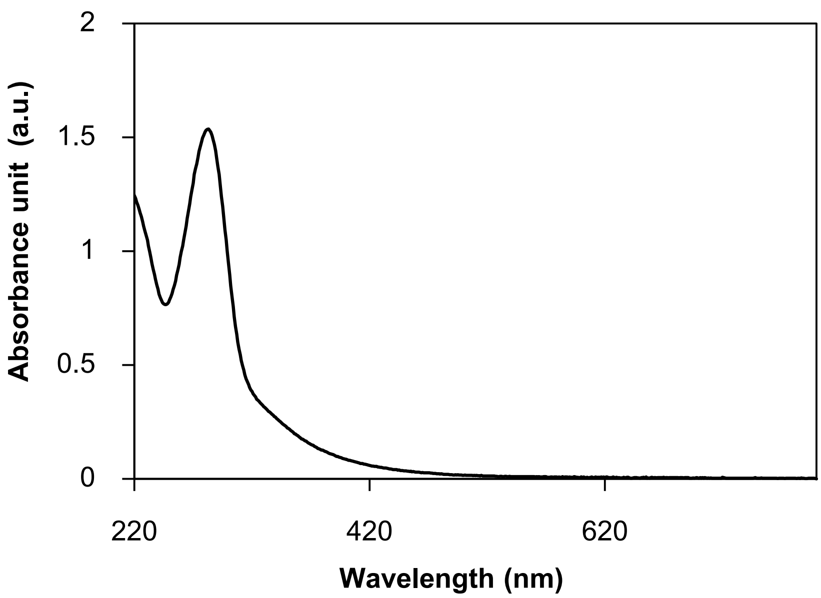

Figure 1 UV absorption spectra of coconut meal hydrolysate

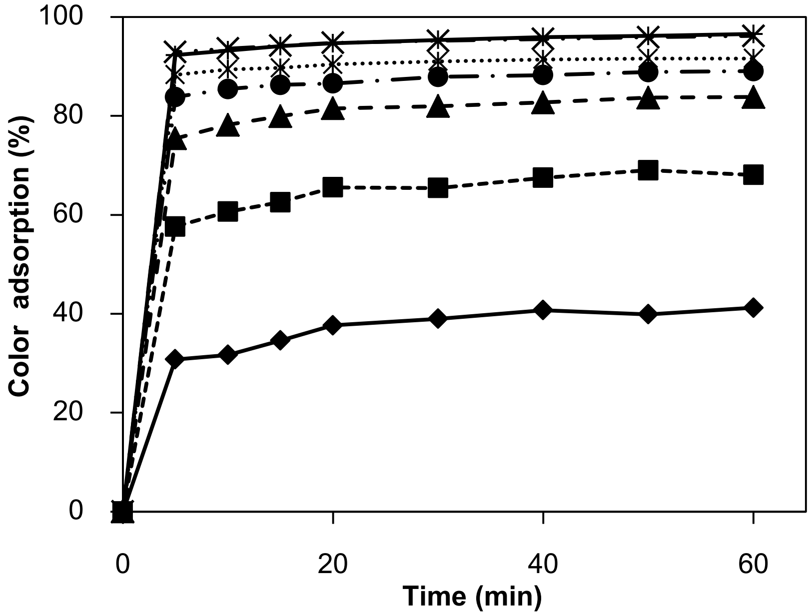

Figure 2 Effect of mixing time on the adsorption of dark colored compounds from coconut meal hydrolysate (PAC concentration: (◆) 1, (■) 2, (▲) 3, (●) 4, (✳) 5, (✕) 8, and (+) 10% (w/v)).

3.2 Effect of powdered activated carbon concentration

The adsorption was studied by increasing PAC concentration from 1 to 10% (w/v). Figure 3 shows that the color adsorption significantly increased as the concentrations of PAC added was increased ($p<0.05$) because more available surface area at higher PAC concentration (Arslanoglu *et al*., 2005). Similar result was reported by Nasehi *et al*. (2012) for the adsorption of dark colored compounds from date syrup using activated carbon. At the concentration of PAC higher than 8% (w/v), however, it was not detected a significant increase in the adsorption, which indicated that 8% (w/v) was the optimal concentration of PAC for the decolorization of the hydrolysate. The maximum color adsorption was about 95%. To investigate whether the PAC affected the carbohydrate in hydrolysate, phenol-sulfuric method was used to quantify the carbohydrate content. The results showed that the total carbohydrate content in all hydrolysates was not altered after decolorization for all treatments tested (data not shown).

3.3 Adsorption isotherm studies

The data obtained from adsorption studies in part 3.1 and 3.2 were fitted with 3 adsorption isotherm models, namely Langmuir, Freundlich and Frumkin isotherms. Table 2 summarizes the values of the parameters for each model, which were estimated from the best-fit line using linear regression. The adsorption isotherm according to Langmuir model is shown in Figure 4. The criteria used for model selection were the magnitudes of coefficient of determination (R2) and root mean square error (RMS). The higher values of R2 and the lower value of RMS, the better will be the goodness fitfit is obtained. As shown in Table 2, the values of RMS for Langmuir and Freundlich model are 0.0465 and 0.0426, respectively and were lower than that of Frumkin model (0.0699). Additionally, the value of R2 shows that the Freundlich model is less fitted to the data compared to the Langmuir model. The adsorption behavior could be explained by Langmuir models. This behavior indicated a monolayer adsorption of dark colored compounds at the outer surface of powdered activated carbon (Nasehi et al., 2012).

This adsorption behavior was similar to Arslanoglu et al. (2005) who used powered activated carbon to adsorb dark colored compounds from peach pulp and Simaratanamongkol and Thiravetyan (2010) who used activated carbon obtained from bagasse bottom ash for adsorbing melanoidin.

Table 2 Model parameters of different isotherm equations for the adsorption of dark brown colored compounds on PAC and statistical parameters (R2 and RMS) from model fitting.

Langmuir isotherm		Freundlich isotherm		Frumkin isotherm	
parameters	value	parameters	value	parameters	value
b	0.0201	Kf	0.8453	A	-6.1905
Q0	15.2475	(1/n)	0.5393	B	7.0147
R2	0.9942	R2	0.9839	R2	0.9859
RMS	0.0465	RMS	0.0426	RMS	0.0699

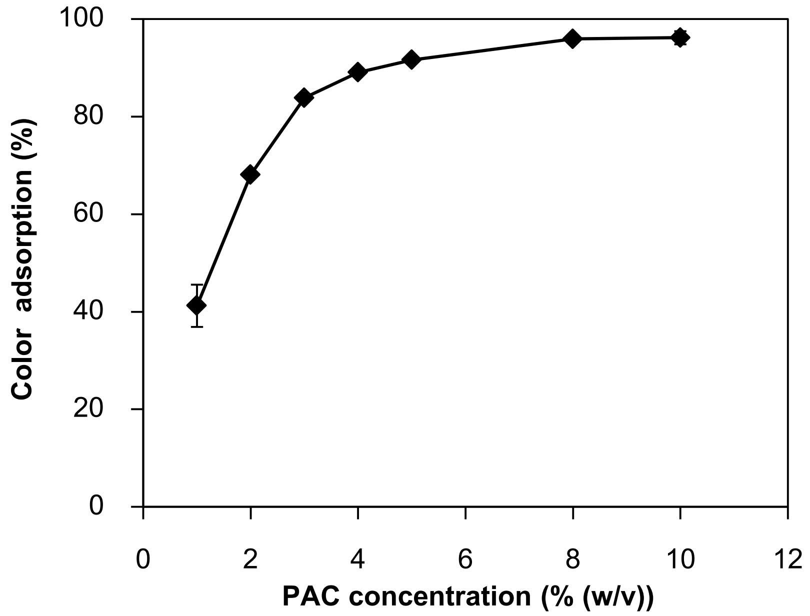

Figure 3 Color adsorption from coconut meal hydrolysate at different PAC concentrations after mixing for 60 min.

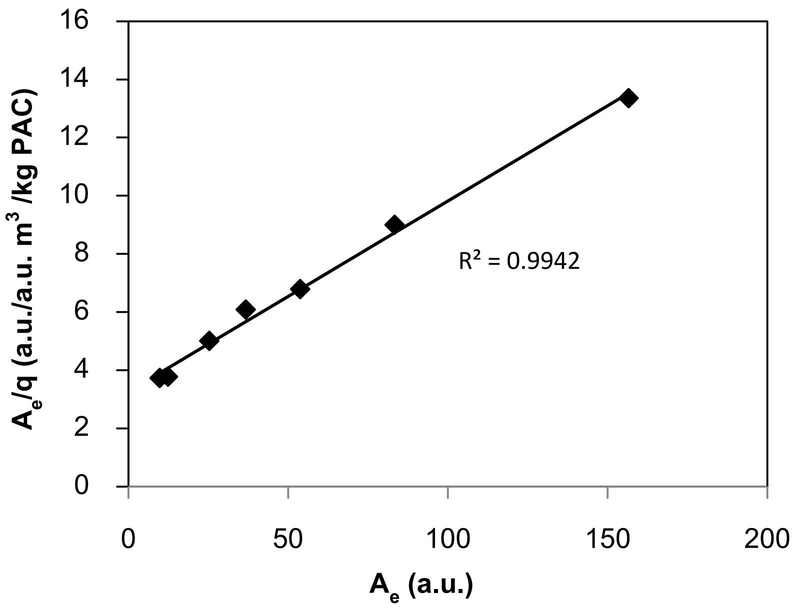

Figure 4 Langmuir adsorption isotherm for the adsorption of dark brown colored compounds from coconut meal hydrolysate with PAC (equilibrium time = 20 min, (-) predicted).

4. Conclusion

The results of the present investigation showed that powered activated carbon is an effective adsorbent for the removal of dark brown colored compounds from coconut meal hydrolysate. Using an adsorbent concentration of 8% (w/v) and mixing time of 20 min resulted in 95% of color adsorption. The adsorption behavior could be explained by Langmuir models.

Acknowledgements

This research was supported by the Research and Creative Fund from Faculty of Engineering and Industrial Technology, Silpakorn University.

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