The Potential of Activated Carbon Production from *Leucaena leucocephala* charcoal and Application in Melanoidin Removal

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Abstract

Melanoidins are brown recalcitrant compounds present in the effluents of ethanol production, and brewery industry. It is difficult to biodegrade by the conventional treatment processes. Adsorption process was reported to have achieved more than 90% of melanoidin removal. However, due to its high operating cost has limited its use for wastewater treatment, alternative low-cost adsorbents are finding from various materials such as plant waste. The *L. leucocephala* was reported as a potential material for adsorbent due to their properties. The aim of this work was to produce the low-cost adsorbent *L. leucocephala* activated carbon (LAC) derive from *L. leucocephala* char by CO_2 activation method. Batch experiments were carried out to determine the optimum conditions for melanoidin adsorbed on LAC samples. Kinetic data and adsorption equilibrium isotherm were done in the batch experiments. The results showed the LAC samples had the high surface areas in the range of 823.63-1,596.20 m^2/g. Maximum adsorption capacity of melanoidin on the LAC samples were found in the range of 588.24-1,666.67 mg/g. The optimum adsorption conditions of the LAC were obtained at the contact time of 480 min, the initial melanoidin concentration of 1,000 mg/L, the initial solution pH of 2, the agitation speed of 100 rpm and the temperature of 65° C. This finding is a useful tool for scale-up and design purposes to apply for wastewater treatment of industry. It can be concluded that the LAC is a potential material to produce as a low-cost adsorbent for the removal of melanoidin from wastewater.

Keywords: Melanoidin, Adsorption, *Leucocephala*, Activated carbon, Low-cost adsorbent

Introduction

Melanoidins are dark brown color compounds present in the effluents of sugar industry, ethanol production, bakery yeast processing and brewery industry (Ojijo, Onyango, Ochieng, & Otieno, 2010). Melanoidin is a nitrogenous brown polymer and is a major pollutant when it is discharged into water resource system. It prevents the penetration of sunlight that affects the photosynthetic activity of aquatic plants. Owing to their structural complexity, melanoidins are difficult to biodegrade and only 6-7% of melanoidins is biodegraded by the conventional treatment processes (Gonzalez et al., 2000; Kaushik, Basu, Singh, Batra, & Balakrishnan, 2017). Hence, alternative treatment processes have been explored to remove melanoidin. In previous works, adsorption process was reported to have achieved more than 90% of colour and melanoidin concentration reduction (Simaratanamongkol & Thiravetyan, 2010; Onyango, Kittinya, & Ojijo, 2011). However, commercially available activated carbon is expensive. Thus, researchers are interested to find cheaper adsorbents with high adsorption efficiency. Biological materials can be considered as cheap, especially if it is abundant in nature. The *Leucaena leucocephala* (*L. leucocephala*) is quick growing tree, abundant and available in large quantities in many areas of Thailand. It has potential properties to be a material for activated carbon production because it has high percentage of carbon (47.55) and fixed carbon (16.59) and low percentage of ash (1.78). It shows that *L. leucocephala* is a suitable resource material for preparation of activated carbon.

The objective of this study is to prepare activated carbon (AC) from *L. leucocephala* char by CO_2 activation method at various temperature and contact time and apply to remove melanoidin from aqueous solution. Their adsorption ability and effects of many variables, including solution pH, contact time, initial concentration, agitation speed and temperature were investigated. Langmuir and Freundlich adsorption models were used to describe adsorption isotherm, and in addition to investigate their adsorption kinetics. The results of this study will increase value of *L. leucocephala* to use as low cost activated carbon for application of melanoidin removal from wastewater of sugar industry, ethanol production, bakery yeast processing and brewery industry.

Methods and Materials

1. Raw materials

L. leucocephala charcoal was obtained from Suranaree University, Nakhon Ratchasima, Thailand. It was crushed and sieved by sieve analysis (ASTM, 2004) to obtain samples in the range of 1.7- 2.36 mm.

2. Preparation of melanoidin solution

Melanoidin was chosen in this study because it is dark brown color compounds present in the effluents of the fermentation processes that use molasses. Thus, this study has used melanoidin as a model color. The synthetic melanoidin stock solution was prepared by method that was reported in Kotsiopoulou, Liakos, and Lazaridis (2016) by mixing 4.5 g glucose, 1.88 g glycine and 0.42 g sodium bicarbonate in 100 mL of deionized water. The solution was heated in an oven for 7 hrs at 95 ° C. During heating various reactions were carried out leading to the formation of melanoidins that are responsible for the dark brown colour of the solution. After 7 hrs the mixture was removed from the oven, and was left to reach ambient temperature, then another 100 mL of deionized water was added (Liang, Wang, Zhou, & Liu, 2009). The resulting concentration of the melanoidin stock solution was 25,500 mg/L. Solutions were prepared by diluting the concentrated stock solutions. The wavelength of melanoidin concentration was determined by running a scan of melanoidin solution on UV-Visible spectrophotometer (GENESYSTM20, USA) and the maximum absorbance wavelengths (λ_{max}) was found at 291 nm.

3. Preparation of *L. leucocephala* activated carbon (LAC)

The *L. leucocephala* charcoal sample was loaded on a ceramic boat which was placed in a horizontal tubular furnace (CTF 12/75/700/201-Cabrbolite, UK) and then activation processes are influenced by activation with varies temperature 900 and 950 ° C, at a heating rate of 5 ° $C.min^{-1}$ under the flow of N_2 gas. When the desired activation temperature was reached, CO_2 gas was allowed to flow in the furnace. The activation time varied 60, 120 and 180 min. When the activation was completed, the sample was cooled to the room temperature under N_2 gas flow. In this study, the *L.leucocephala* activated carbon samples were named LAC-temperature.time which indicated activation conditions of the temperature and time, for example, LAC-900.180. In this study had selected to use CO_2 is selected as an activator in this study due to its widespread used as an activating agent and it′s lower reactivity at high temperature, which makes the activation process easier to control. In addition, CO_2 activation favors microporosity formation (Molina-Sabio, Gonzá lez, Rodriguez-Reinoso, & Sepú lveda-Escribano, 1996). And the *L. leucocephala* has lignin as major fraction; being that its decomposition is difficult. Indeed, it is known that the decomposition of lignin occurs slowly from 200- 900° C. (Hayashi, Horikawa, Takeda, Muroyama, & Nasir Ani, 2002; Cazetta, Vargas, & Nogami,

2011; Foo & Hameed, 2011). The lignin molecules require a broad range of temperature for degradation (Danish, Hashim, Ibrahim, Rafatullah, & Sulaiman, 2012). This implies that 900 °C is the beginning temperature for physical activation processes. Thus, in this study the activation temperature was started at 900 °C to 950 °C.

4. Characterization of the activated carbon

The porous properties of the LAC samples were characterized by a nitrogen adsorption isotherm with an accelerated surface area and a porosimetry system (the Brunauer-Emmett-Tellet (BET), Bet Sorp mini II, Bet-Japan). The BET surface area was calculated from the isotherms by using the BET equation. The Dubinin-Astakhov (DA) equation was used to calculate the micropore volume. The total volume was found from the amount of N_2 adsorbed at a relative pressure (P/P_0) of 0.99 and converted to N_2 volume in liquid state. The Point of Zero Charge (PZC) was determined using a potential titration method. The final pH was measured, and the pH_{PZC} was determined as the equilibrium converging pH value from the initial pH versus adsorbent mass curve.

5. Adsorption experiments

In order to investigate the effects of contact time, initial melanoidin concentration, initial solution pH, agitation speed and temperature on melanoidin adsorption, 0.2 g LAC samples were added into 100 mL melanoidin solutions. The contact time are in the range of 240-1,080 min, the initial melanoidin concentration in the range of 200-1000 mg/L, the initial solution pH in the range of 2-12, the agitation speed in the range of 100-350 rpm and the temperature in the range of 25-65 °C were varied in order to study these factors. The concentration of melanoidin in the supernatant solutions before and after the adsorption of melanoidin was analyzed. The optimum conditions of adsorption experiments were analyzed by mean and standard deviation (SD) and analysis of variance with One Way ANOVA and Paired Sample T-Test (SPSS version 23).

6. Adsorption isotherms and kinetics

The equilibrium isotherms of the melanoidin adsorption on the LAC samples were conducted through the batch experiments. Adsorption isotherms were performed by varying mass of LAC (0.1-0.5 g), and the 100 mL melanoidin solution with the initial melanoidin concentration of 1,000 mg/L was added to 250 Erlenmeyer flasks which were placed in the shaker (agitation speed of 100 rpm) at temperature 65 °C and pH 2 for 480 min. The initial and remaining concentrations of the melanoidin solution were measured. For comparison purposes, the similar batch adsorption experiments were also conducted for commercial activated carbon (AC). The AC which was used to compare with LAC samples was obtained from Cabot Corporation Ltd., Thailand. The AC has Iodine number 1,000 mg/g, moisture 5%, ash content 3.9%, bulk density 0.46-0.50 g/mL and methylene blue 185 cc/g. The adsorption kinetics studies were carried out, and the 200 mL melanoidin solution with the initial concentration of 1,000 mg/L was withdrawn at certain time intervals (15 min) until the equilibrium was reached.

Results and Discussion

1. Yield and characterization of LAC

As for the properties, a pore structure (in terms of a surface area and a pore volume) is an important characteristic of activated carbon. In general, activated carbon with a high surface area, porosity and high percent

yield, allowing large capacity of adsorption, is desirable. In this study, the results of the porosity parameters calculated from nitrogen sorption isotherms and the percent yield are collected in Table 1. The percent yield of the samples are in the range of 18.06- 66.97% and surface area are in range of 823.63-1,596.20 m^2/g. The results showed LAC samples had good properties to be used as AC with high surface area, pore volume and high percent yield. These due to the activation of char with CO_2 must have involved the C-CO_2 reaction. This would lead to the removal of carbon atoms and also cause the burn-off, there by contributing to the development of micropore structure. Activating reaction rate ascended with the increasing temperature, which enhanced this process and produced lots of micropores. Consequently, BET Surface area increased and yields decreased. However, when the temperature exceeded 800 °C, the freshly formed micropores structure was destructed then some micropores developed into mesopores and macropores, which caused the decline of specific surface area and rise of external specific surface area (Rodr´ ı guez-Reinoso & Molina-Sabio, 1992). The pH_{pzc} of the LAC adsorbent was 9.32, where the net surface charge of the adsorbent is zero.

From the data presented in Table 1, the pore size distribution of the LAC samples illustrates that the mean pore diameter (D_{ap}) is in the range of 1.79-1.86 nm which is very near 2.0 nm. These indicated a great development of micropores based on the classification adopted by IUPAC: micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm). Pore size distribution is a very important property of absorbents because the differences in the pore sizes affect the adsorption capacity for molecules of different sizes and shapes, and this is also one of the criteria by which carbon adsorbents are selected for a particular application (Xiao et al., 2012). Activation of LAC chars with CO_2 was carried out as the temperature 900, 950 ° C. Varying activation times of 60, 120 and 180 min. Increase activation temperature increase surface area and pore volume, due to the removal of pyrolysis gaseous products within the pore walls leads to pore widening and formation of micropores. However, increase activation times with prolonged beyond 120 min, due to over gasification, hypothesized to be a result of the micropore structure collapse caused by the surplus CO_2 steam, causing particle sintering and reducing the surface area (Hou, Liu, & His, 2015). The activation temperature had a significant effect on the development of the porous structure (Ding et al., 2014; Kacan, 2016). As shown in Table 1, only the LAC-900.60 sample had low total volume of 189.23 cm^3/g and much different from the other sample. Therefore, five LAC samples (LAC-900.120, LAC-900.180, LAC-950.60, LAC-950.120 and LAC-950-180) with surface area and total volume in range of 986.44 -1,596.20 m^2/g and 223.34-366.73 cm^3/g respectively were selected to further investigate the effects of the factors on the adsorption, isotherm and kinetic experiments.

Table 1 Percent yield and parameters of porous structure of LAC samples

Activation conditions		Yield (%)	S_{BET} (m^2/g)	V_T (cm^3/g)	D_{ap} (nm)
Temp (° C)	Time (min)				
900	60	66.97	823.63	189.23	1.7949
	120	51.45	986.44	226.64	1.825
	180	41.39	972.09	223.34	1.852
950	60	61.70	1,596.20	366.73	1.793
	120	39.39	1,081.20	248.41	1.852
	180	18.06	1,270.00	291.80	1.859

2. Effects of factors on melanoidin adsorption onto LAC

2.1 Effect of contact time: The results of different contact time versus amount of melanoidin absorbed per gram of LAC (q_e) was shown in Figure 1 to study their effect on adsorption capacity. Adsorption of melanoidin was rapid in first of 360 minutes and after 480 minutes, amount melanoidin absorbed was gradually increased with the prolongation of contact time and almost constant. Therefore, for batch experiments 480 minutes equilibrium time was used for adsorption isotherm studies. The rapid adsorption at the beginning may be attributed to the rapid attachment of the melanoidin molecules to the surface of the LAC and the following slower sorption to intra particle diffusion. The initial rapid phase may also be due to the increased number of vacant sites available at the initial rapid stage, consequently exist an increase in driving force of the concentration gradient between adsorbate in solution and adsorbate in the adsorbent (Patil & Shrivastava, 2012; Namasivayam & Kavitha, 2002). At the end of the process, the adsorption capacities become slower due to the saturation of active sites (Li & Wang, 2009).

2.2 Effect of initial concentration: The result of different initial concentration of melanoidin versus amount of q_e was shown in Figure 2 to study their effect on adsorption capacity. It is clear that increasing the initial concentration, causes an increasing of q_e and decolourization of solution because of the greater number adsorption sites of LAC samples. This indicated that the initial melanoidin concentration plays an important role which provided the necessary driving force to overcome the resistances to the mass transfer of melanoidin between the aqueous and the solid phases (Attia, Girgis, & Fathy, 2008). The interaction between adsorbate and adsorbent was also found to enhance with the increase in the initial concentration. Thus, it can be concluded that higher initial concentration enhances the adsorption uptake of melanoidin. Therefore, for batch experiments equilibrium initial melanoidin concentration 1,000 mg/L was used for adsorption isotherm studies.

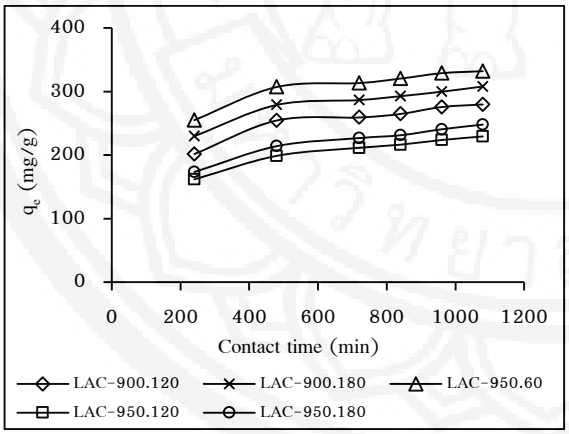

Figure 1 Effect of Contact time on the adsorption of melanoidin on LAC

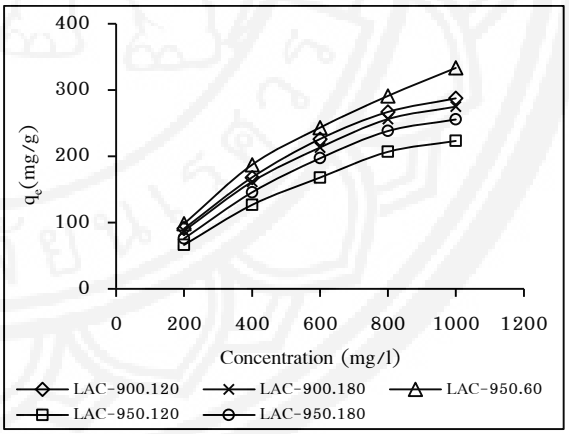

Figure 2 Effect of initial melanoidin concentration on the adsorption of melanoidin on LAC

2.3 Effect of initial pH solution: The results of different pH values versus amount of q_e was shown in Figure 3 to study their effect on adsorption capacity. The maximum q_e of all LAC samples were found to be at pH 2 in range of 323-436 mg/g. The increasing of pH from 2.0 to 13.0 causes a strong decrease in the adsorption capacity and decolourization of solution. The pH of solution is one of the most important parameters in the adsorption investigations. As previous mentioned, the pH_{pzc} of the LAC adsorbent was 9.32. The pH value

below pH_{pzc} and it indicates the surface of the LAC has positive charge. On the other hand, the melanoidin molecule has a negative charge, because of carboxyl groups which have a high density of electrons. Therefore, the melanoidin adsorption in acidic pHs will perform better than the alkaline, which is in agreement with the obtained results. Thus, as shown in the results of this study indicated that the increase of pH hampers the interaction between the negatively charged LAC with the negatively charged melanoidin. The adsorption mechanism of melanoidin onto activated carbon involves mainly physical adsorption by electrostatic interactions and is favored in acidic pH (Liakos & Lazaridis, 2016). Therefore, further experiments were carried out keeping the initial pH solution of 2.

2.4 Effect of agitation speed: The effect of the agitation speed on the melanoidin adsorption of the LAC samples was investigated and the results are shown in Figure 4 as the amount of melanoidin adsorbed per gram of LAC (q_e) versus agitation speed. The q_e increased with an increase of the agitation speed. It was observed that the q_e of all LAC samples was not significantly different between the agitation speeds of 100-300 rpm and the q_e was in the range of 341-484 mg/g. Beyond that, the q_e gradually decreased. The effect of the agitation speed is one of the important factors which plays the key role to control the solid-liquid mass transfer mechanism while affecting the external boundary film as well as the distribution of the solute in the bulk solution (Priyadarshini et al., 2018). Therefore, further experiments were carried out keeping the agitation speed at 100 rpm.

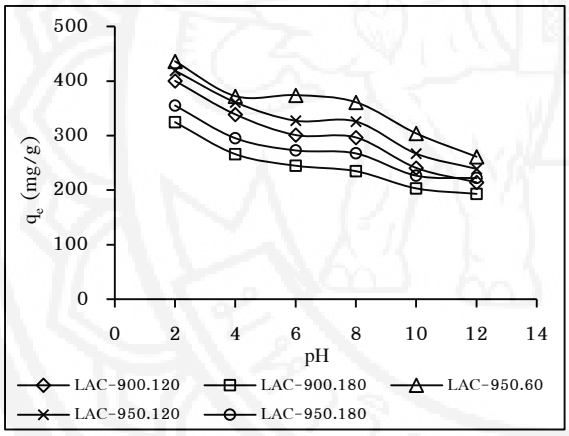

Figure 3 Effect of pH on the adsorption of melanoidin on LAC

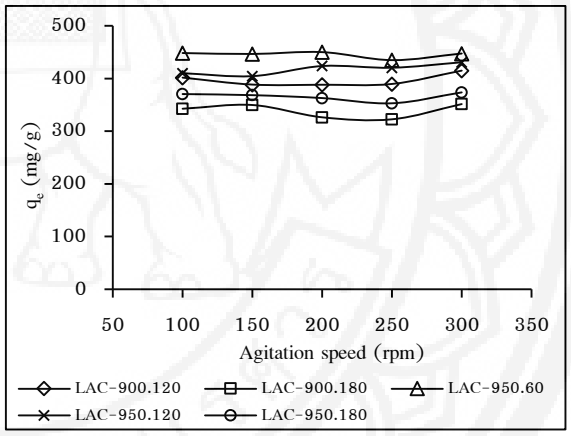

Figure 4 Effect of agitation speed on the adsorption of melanoidin on LAC

2.5 Effect of temperature: Variation of adsorption of melanoidin on the LAC with temperature is shown in Figure 5. The amount of the adsorbed melanoidin increased with increasing temperature, indicating an endothermic process. This might be due to increasing mobility of the melanoidin molecules and an increase in the number of active sites for the adsorption with increasing temperature (Yagub et al., 2014). This was comparable with the results obtained during various studies reported in the literature (Karacetin, Sivrikaya, & Imamoglu, 2014; Dural, Cavas, Papageorgiou, & Katsaros, 2011). Therefore, further experiments were carried out keeping the temperature at 65 ° C.

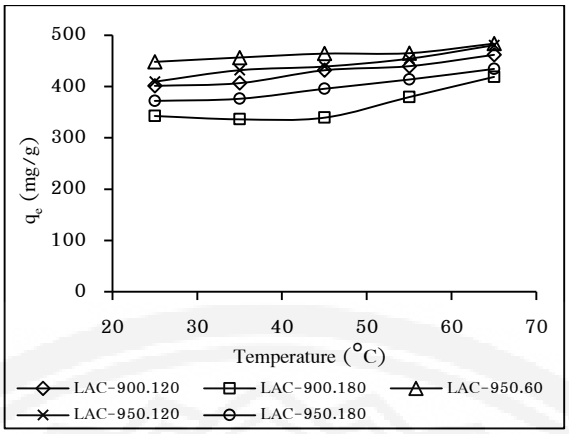

Figure 5 Effect of temperature on the adsorption of melanoidin on LAC

3. Adsorption isotherms and kinetics

3.1 Adsorption kinetic study: Adsorption kinetics is a critical tool in the investigation of adsorption mechanism. Therefore, to utilize the commonly used kinetic models, zero order, first order and second order were used to describe the adsorption process. The best fitted model was considered based on the correlation coefficient (R^2). The constants obtained from the three kinetic models are shown in Figure 6 and Table 2. It was apparent that coefficients of the second order (0.9783-0. 0.9934) were higher and closer to unity. Thus, it was concluded that the melanoidin adsorption on the LAC was described by the second order model. The kinetics of the melanoidin adsorption onto the LAC adsorbents were prerequisite for choosing the best operating conditions for the full-scale batch process to treat melanoidin from wastewater.

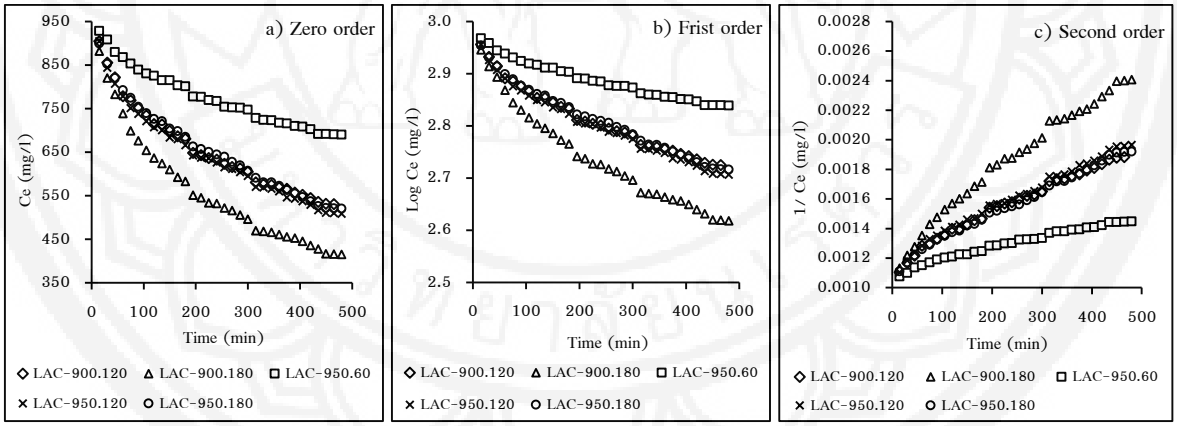

Figure 6 The kinetic models for melanoidin adsorption on LAC samples a) zero order kinetic; b) first order kinetic and c) second order kinetic

Table 2 Kinetic parameters for melanoidin adsorption on LAC

LAC sample	Zero Order		First Order		Second Order	
	k	R^2	k_1	R^2	k_2	R^2
LAC-900.60	0.7094	0.9264	0.0005	0.9600	$2x10^{-6}$	0.9823
LAC-900.120	0.8432	0.8969	0.0006	0.9511	$3x10^{-6}$	0.9840
LAC-950.60	0.4661	0.9509	0.0003	0.9664	$8x10^{-7}$	0.9783
LAC-950.120	0.7117	0.9328	0.0005	0.9674	$2x10^{-6}$	0.9875
LAC-950.180	0.7184	0.9545	0.0005	0.9802	$2x10^{-6}$	0.9934

3.2 Adsorption isotherm study: Langmuir and Freundlich isotherms are widely recognized and have been successfully applied to defining many adsorption equilibriums and evaluating adsorption equilibrium of melanoidin from aqueous solutions. Therefore, melanoidin adsorption data were analyzed by Langmuir and Freundlich equations 1 and 2 respectively:

$$\frac{C_e}{X} = \frac{C_e}{X_m} + \frac{1}{KX_m} \quad (1)$$

$$\log X = \log K_f + \frac{1}{n}\log C_e \quad (2)$$

Where K and q_m are Langmuir constants (L/mg) and maximum monolayer adsorption capacity (mg/g) respectively, and Freundlich coefficients n and K_f are related to adsorption intensity and adsorption capacity respectively. As for the previous finding of optimum conditions in this study, the experiment was carried out to investigate the adsorption isotherm with the initial concentration of melanoidin of 1,000 mg/L, the contact time of 480 min, the agitation speed of 100 rpm, the initial solution pH of 2 and keeping temperature at 65 °C in order to understand the mechanism of adsorption. The constants obtained from the Langmuir and Freundlich isotherm equations are shown in Figure 7 and Table 3. The best isotherm model was determined based on the linear square regression correlation coefficient, R^2. By comparing these two isotherm models, it can be seen that the data fitted both of isotherms with a high correlation coefficient (R^2) value of Langmuir and Freundlich model were in the range of 0.9583-0.9925 and in range of 0.9335-0.9932 respectively.

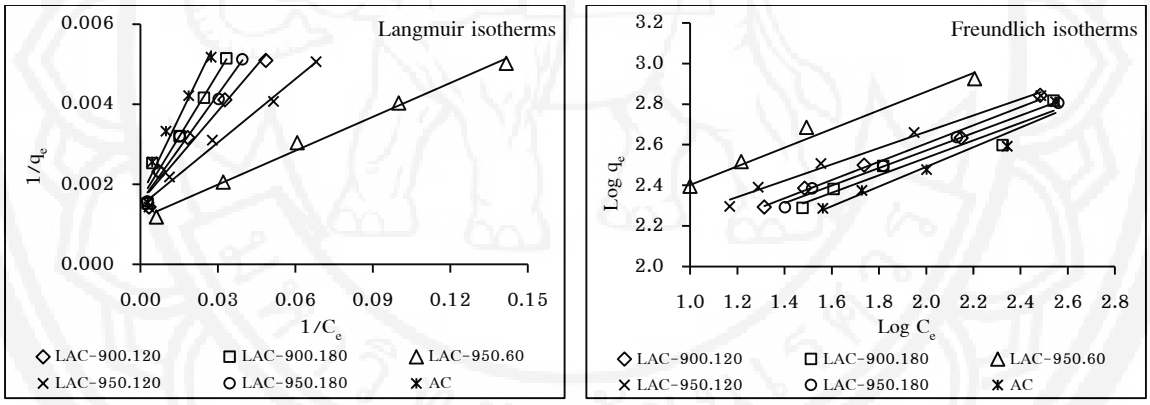

Figure 7 a) Langmuir and b) Freundlich isotherm plot for adsorption on LAC samples under optimum adsorption conditions

Table 3 Parameter values of LAC samples calculated using Langmuir and Freundlich adsorption models

Activation condition		S_{BET}	Langmuir constants			Freundlich constants		
Temp (°C)	Time (min)	(m^2g^{-1})	q_{max} (mg g^{-1})	K_L (L mg^{-1})	r^2	K_f (mg g^{-1})	n	r^2
900	120	986.44	641.03	0.0206	0.9677	51.18	2.23	0.9885
900	180	972.09	625.00	0.0151	0.9583	47.31	2.32	0.9375
950	60	1,596.2	869.57	0.0408	0.9925	87.86	2.18	0.9771
950	120	1,081.2	684.93	0.0276	0.9882	72.49	2.49	0.9874
950	180	1,270.0	645.16	0.0172	0.9788	51.22	2.32	0.9932
AC		*	500.00	0.0126	0.9411	33.19	2.06	0.9335

*AC: Iodine number 1,000 mg/g

In Table 4 presented summary of maximum adsorption capacities (q_{max}) of the various adsorbents for melanoidin. Recorded in this work, the q_{max} of this study was found in range of 625.00-869.57 mg/g and were higher than found in AC (q_{max} = 500 mg/g) which was determined in t the same condition of this study. A comparison with other reported adsorbents showed that the q_{max} value for the LAC is the higher than the other adsorbent (Table 4). This due to mean pore diameter of LAC samples are mainly micropore. The micropore and mesopore have a good adsorption efficiency for compounds such as tannic acid and melanoidin. This indicated LAC is a good candidate adsorbent for melanoidin compounds from wastewater, which represents a large source of the aqueous pollution in sugar cane industries (Figaro et al., 2006).

Table 4 Isotherm constants reported for the adsorption of melanoidin

No.	Adsorbent	Adsorbate	q_{max} (mg g^{-1})	Ref.
1	LAC	Melanoidin	869.57	This study
2	AC[1]	Melanoidin	500	This study
3	BBA-AC[2]	Melanoidin	208	Simaratanamongkol & Thiravetyan, (2010)
4	AC	Melanoidin	232.08	Figaro, Avril, Brouers, Ouensanga, and Gaspard
5	Chitin nanofibers	Melanoidin	131	Dolphen & Thiravetyan, (2011)

Notes: [1] BBA-AC: Activated carbon from bagasse bottom ash; [2] AC: Iodine number 1,000 mg/g

4. Thermodynamics of adsorption study

In adsorption studies, temperature plays an important role. The temperature results show that with increasing melanoidin solution temperature, the q_e value of LAC increased (Figure 5). The thermodynamic parameters for melanoidin adsorption onto LAC, including the Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated to analyze the feasibility of melanoidin adsorption via thermodynamic scrutiny by using the following equations 3- 4 respectively:

$$\Delta G = -RT \ln(K_c) \quad (3)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

where K_c is the Langmuir constant related to energy of adsorption, T is the temperature (K) and R is the universal gas constant (8.314 J mol^{-1} K^{-1}) (Barrett et al., 1951; Lippens and de Boer, 1965; Mall et al., 2005). ΔH was determined graphically from the linear plot of ln K_c versus 1/T (Figure 8), and the values of ΔG and ΔS computed numerically, are presented in Table 5.

Table 5 Thermodynamic parameters for synthetic melanoidin adsorption on LAC at various temperatures

Adsorbent	Temperature (° K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})
LAC-900.120	298.15-338.15	22.64	80.52	-23.98 -(-27.20)
LAC-900.180	298.15-338.15	17.84	58.64	-17.47 -(-19.81)
LAC-950.60	298.15-338.15	22.22	85.26	-25.40 -(-28.81)
LAC-950.120	298.15-338.15	29.05	103.29	-30.77 -(-34.90)
LAC-950.180	298.15-338.15	17.08	59.47	-17.71 -(-20.09)

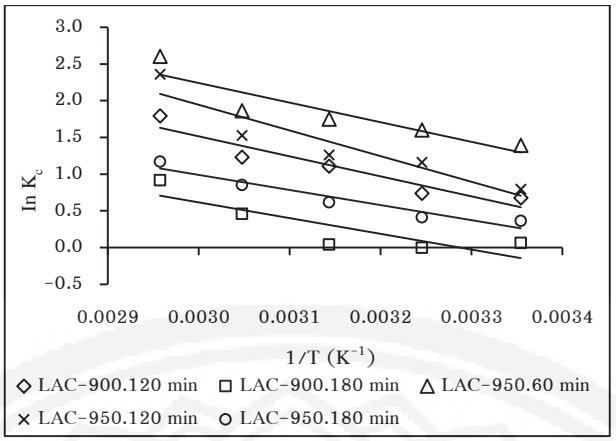

Figure 8 Plot of ln Kc vs 1/T for melanoidin for adsorption on LAC

The results show the positive value of the enthalpy (ΔH) in range of 17.08-29.05 kJ/mol indicated the adsorption of melanoidin on LAC are endothermic. And the results of Gibbs free energy (ΔG) show the negative values that indicative the adsorption process is spontaneous in nature and that the degree of spontaneity of the reaction increases with increasing temperature (Argun & Dursun, 2008). In addition, the magnitude of ΔH denotes the type of adsorption process, whether it belongs to the physical adsorption or chemical adsorption. It has been reported that the magnitude of ΔH for the physisorption reaction is < 20 kJ/mol, whilst for the chemical adsorption, the value is within 80-200 kJ/mol (Chowdhury, Zain, & Khan, 2012; Zhao et al., 2015). Therefore, the calculated (ΔH) of this study is about in range of 17.08-29.05 kJ/mol suggests that the adsorption of melanoidin is physisorption, and consistent with the reduction in amount of melanoidin adsorbed at an elevated temperature. And the results of the entropy (ΔS) show the positive values in range of 58.64-103.29 J mol^{-1} K^{-1} were indicative the increased randomness at the solid/solution interface during the adsorption process. It could be concluded that adsorption mechanism between LAC and melanoidin, is physisorption and could occur at room temperature so it was spontaneous in nature. When the environmental temperature increased, the probability of molecule of melanoidin increased for attack each other and movement. Hence, higher adsorption efficiency increased when increasing temperature. This explanation supported endothermic and freedom of molecule of melanoidin for random adsorbed on LAC.

Conclusion and Suggestions

The activated carbon that was produced from *L. leucocephala* charcoal by CO_2 activation method at temperature 900-950 °C and activation time in range of 60-180 min, had surface area in range of 823.63-1,596.20 m^2/g and mainly micropore. These results indicate that the *L. leucocephala* tree has potential material for production as low cost activated carbon. According to *L. leucocephala* charcoal has lower price than coconut shell and coal which are material for commercial activated carbon. The study of melanoidin adsorption on LAC can be deduced from the experimental data as following conclusion; the optimum conditions for melanoidin adsorption was favored at pH 2, contact time 480 min, agitation speed 100 rpm, temperature 65 °C and initial melanoidin concentration 1,000 mg/L. The kinetics of the adsorption process was found to follow the second model and the equilibrium data were better described by both Langmuir and Freundlich isotherm model with

maximum adsorption capacity of 625.00-869.57 mg/g. And the result of thermodynamic study supported melanoidin adsorption on LAC was physisorption and endothermic. In conclusion of this study, the LAC proved to be an efficient and economical adsorbent for using in wastewater treatment application to remove melanoidin. These finding is good to increase the value of *L. leucocephala* tree for using more application.

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