Removal of Methylene Blue Dye from Aqueous Solution by Adsorption on Leonardite Char

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Abstract

The present investigation was studied the adsorption of MB dye from aqueous solution by using leonardite carbonized as adsorbent at various temperatures in a batch experiment. The prepared leonardite adsorbents were characterized by FTIR, BET, SEM and XRD. The BET results showed that LN700 gave highest micropores in the surface which is in agreement with adsorption efficiency study. The optimum parameters for MB adsorption onto LN700 such as pH of MB solution, contact time and adsorbent particle size were investigated. The optimum contact time for MB removal onto 45-75 μm LN700 was 30 min. at pH value of 10. The adsorption kinetic of MB onto LN700 shows linear plot of pseudo second-order model and the adsorption at equilibrium data fitted well to Langmuir isotherm model which the maximum adsorption capacity was 26.32 mg MB g^{-1}.

Keywords: Leonardite, Adsorption, Methylene blue

Introduction

Recently, many industries such as textile, leather tanning, paper production, food technology, printing and hair coloring product use dyes that produce highly colored waste effluents (Yamuna & Kamara, 2016; Guimarães Gusmão, Alves Gurgel, Sacramento Melo, & Gil, 2013). There is a report that more than 100,000 commercially dyes are produced over $7x10^5$ tones each year (Yamuna & Kamara, 2016; Olusegun & Ugba, 2013). Due to the large amount production of dyes, it can cause environmental pollution and a serious risk to human health (Guimarães Gusmão et al., 2013). Moreover, the removal of dyes in wastewater are difficult because dyes is stable to, heat, light and oxidizing agents (Hijazi et al., 2015). Even their degradation products can be toxic, carcinogenic and teratogenic for living organisms (He et al., 2013). Due to these problem, the removal of dyes before release into the environment has been widely studied. Methylene blue (MB) is one of a cationic dye which is generally used for dying cotton, wood and silk (Yamuna & Kamara, 2016). It could cause various harmful effects such as eye burns, irritation to the gastrointestinal tract and to the skin (Guimarães Gusmão et al., 2013; He et al., 2013). Therefore, many researchers interested to study removal of MB from wastewater. In several previous reports, natural low cost and modified biological materials adsorbents have been used to remove MB from aqueous solution such as pineapple peel (Yamuna & Kamara, 2016), sugarcane bagasse (Guimarães Gusmão et al., 2013), coconut shell (Olusegun & Ugba, 2013) and lebanese cymbopogon citratus (Hijazi et al., 2015). Leonardite is a low cost natural material containing a high content of humic acid (Zeledón-Toruño, Lao-Luque, de Las Heras, & Sole-Sardans, 2007). Humic materials contain oxygen functional groups (carbonyl, phenol and hydroxyl) which can be involved in chemical binding (Zeledón-Toruño et al., 2007). The organic substances can be converted to activated carbon during the carbonization process (Ausavasukhi, Kampoosaen, & Kengnok, 2016). Moreover, many researchers have studied and shown that leonardite or activated leonardite is an excellent adsorbent for removal of heavy metals

(Katanyoo, Naksata, Sooksamiti, Thiansem, & Arquero, 2012; Zengin, 2013; Chammui, Sooksamiti, Naksata, & Arqueropanyo, 2014), polycyclic aromatic hydrocarbon (PHAs) (Zeledón-Toruño et al., 2007) and Congo red (Ausavasukhi et al., 2016) Therefore, it is expected that leonardite char can be used as adsorbent for adsorption MB dye from aqueous solution. According to the state above, this research was aim to prepare leonardite char for removing MB from water. In this study, the temperature for preparing leonardite char has been investigated. Moreover, the adsorption of MB using leonardite char was tested in a series of batch experiments. The influence of parameters such as pH of MB solution, contact time, particle size of leonardite char and MB concentration that effect on the adsorption capacity of MB onto leonardite char were also studied.

Experimental

Preparation and characterization of leonardite char

The adsorbent used in this study was leonardite which obtained from Mae Moh lignite mine in Lampang province, Thailand. Samples were cleaned with deionized water to remove the surface dust, some acid and then dried in an oven at 105 °C for 24 hours. The adsorbent was ground and sieved through a grain size between <38 and 300 μm. The prepared leonardite samples were carbonized at 600, 700, 800 and 900 °C for an hour and store in desiccator. The leonardite char will be denoted as LN600, LN700, LN800 and LN900 corresponding to temperature usage.

FTIR (Frontier, Perkin Elmer) data were recorded in the transmission mode at room temperature in the wavenumber range of 4000-500 cm^{-1}. The BET surface area and pore volume were carried out on Micromeritics model TriStar II 3020. The crystals morphologies of leonardite char at various temperature were determined by scanning electron microscope (SEM; LEO 1450, CARL ZEISS CO LTD). X-ray diffraction analysis (Bruker D8 Advance, Bruker BioSpin AG) was carried out in order to identify the mineral crystallography of the leonardite char.

Adsorption experiments

Batch adsorption experiments were carried out to determine the optimum conditions. The effect of pH was investigated using 100 mg L^{-1} MB (Ajax finechem, Autralia) in the range of 2-10. The pH values were adjusted using 2 mol L^{-1} HNO_3 (RCI Labscan, Thailand) or 2 mol L^{-1} NaOH (RCI Labscan, Thailand) solution. After the pH adjusted, the 0.20 g of leonardite char was added to 50 mL of 100 mg L^{-1} MB at room temperature and were stirred continuously for 30 minutes. Then, the aqueous solution was centrifuged and separated from leonardite char. The color of remaining methylene blue solution was determined by measuring the absorbance with a UV-Visible spectrophotometer (Specord plus 600, Germany) at λ_{max} 664 nm. The difference between the initial and final MB concentration was used to calculate the amount of MB adsorbed.

The adsorption time was evaluated at various stirring times between 5 and 120 min. using 50 mL of 100 mg L^{-1} MB with 0.20 g of leonardite char placed in several flasks. The leonardite particle size was carried out from less than 38 to 300 μm in 50 mL of 100 mg L^{-1} MB with 0.20 g of leonardite char.

Kinetic study

The sorption kinetic of MB onto leonardite char (0.20 g) was determined with 50 mL solution containing 100 mg L^{-1} MB concentration at appropriate pH. The solution was shaken at different time from 5 to 120 min at room temperature.

Adsorption isotherms

A 0.20 g of leonardite char was added to flasks containing 50 mL of MB solution from 25 to 250 mg L^{-1} at appropriate pH value. And the experiment was performed in the following procedure described above.

Results and Discussion

Characterisation of adsorbents

The FTIR spectra of leonardite and leonardite char at various temperatures were shown in Figure 1.

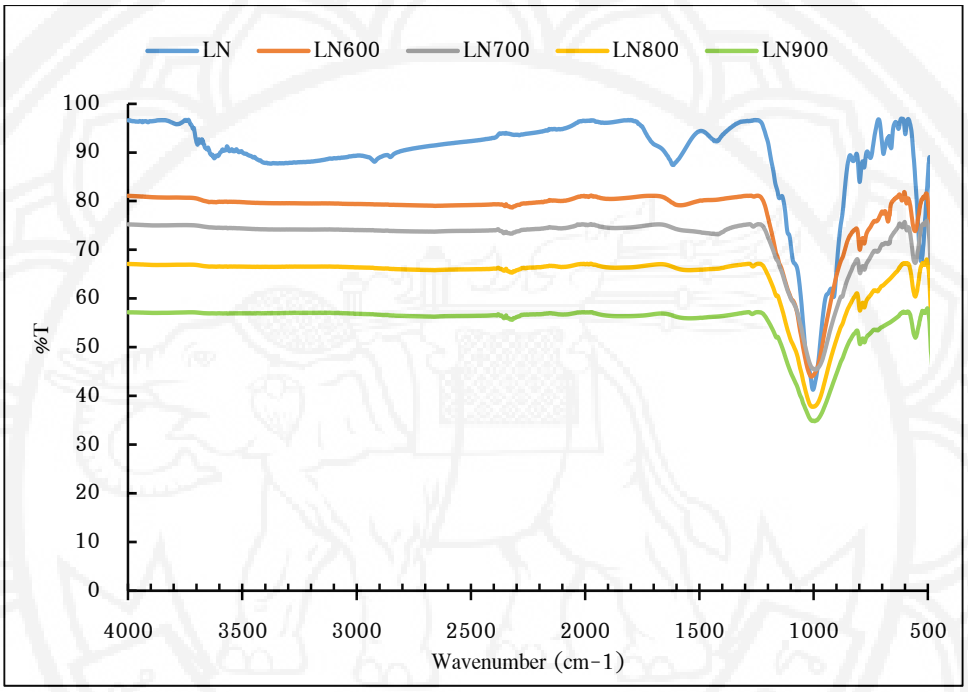

Figure 1 FTIR spectra of the leonardite (LN) and leonardite char at different thermal carbonized process

The leonardite (LN) spectrum shows the very large band at ~1058 cm^{-1} which was related to the absorption of silicates (Olivella, Sole, Gorchs, Lao, & De Las Heras, 2011). The absorption band at ~1615 and ~1420 cm^{-1} were assigned to an aromatic ring of C-C stretching mode in polyaromatics (Ausavasukhi et al., 2016). The band at 2920 and 2850 cm^{-1} were attributed to the symmetric and asymmetric stretching modes of aromatic and aliphatic C-H bonding (Ausavasukhi et al., 2016) The band around 3700-3620 cm^{-1} was stretching O-H vibration of the OH-group (Ausavasukhi et al., 2016; Zengin, 2013). As can be seen from LN600, LN700, LN800 and LN900, the absorption band at around 3700-3620 cm^{-1} and 2920-2850 cm^{-1} were disappeared as a function of temperature. This is due to decompose of carbon from aromatic and aliphatic compounds at temperature higher than 600 °C. From Table 1, it can be seen that the BET surface area and pore volume of LN700 showed highest microspores in the surface. This is corresponding to SEM data in Figure 2.

Table 1 BET analysis of leonardite and leonardite char at different temperatures

	Surface area (m^2/g)	Pore Volume (cc/g)	pore size (nm)
LN	19.31	0.065	13.47
LN600	112.7	0.201	7.15
LN700	136.7	0.236	6.92
LN800	87.97	0.224	10.22
LN900	83.28	0.205	9.85

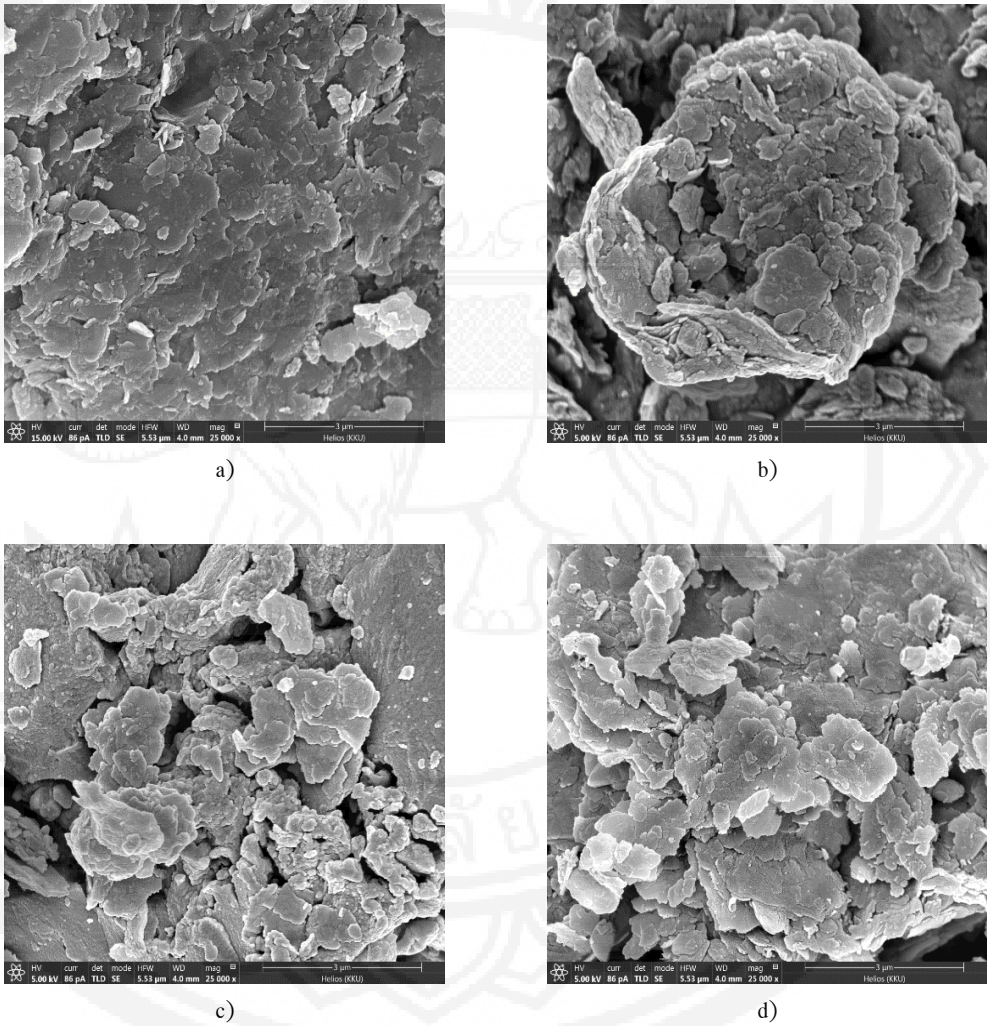

Figure 2 SEM micrograph of the a) LN600 b) LN700 c) LN800 and d) LN900

The XRD patterns of the leonardite char at different temperatures are shown in Figure 3. As can be seen from Figure 3, the major phases of leonardite char are quartz (SiO_2), hematite (Fe_2O_3), muscovite ($H_2KAl_3(SiO_4)_3$) and anhydrite ($CaSO_4$) (Ausavasukhi et al., 2016; Chammui et al., 2014). These mineral components correspond with

JCPDS file no. 00-046-1045, 01-073-0603, 00-001-1098 and 01-072-0503 15. (X Pert HighScore Plus software version 2.1.0. 2004), respectively.

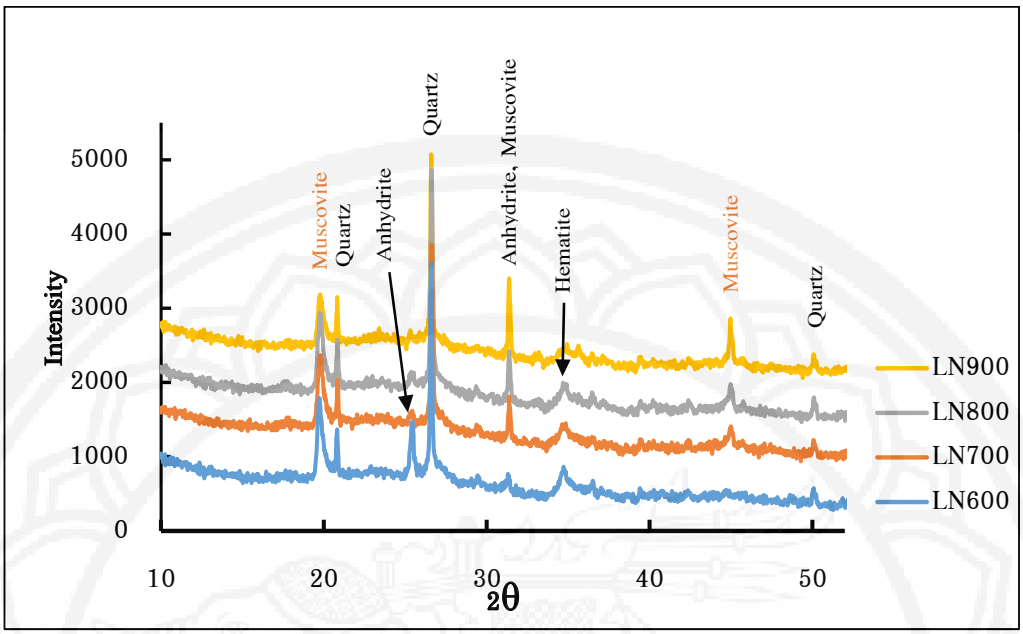

Figure 3 XRD pattern of leonardite char at different temperatures

Effect of carbonization temperature on MB adsorption

Leonardite was carbonized at different temperatures from 600 to 900 °C for an hour. The results in Figure 4 showed that the adsorption amount of MB on leonardite char raised until 700 °C then it decreased gradually. It is recognized that the surface of leonardite is as an acidic group (Ausavasukhi et al., 2016) which could be adsorbed MB via cation exchanger. After carbonization at 600°C, the adsorption amount decreased, it would be reduction in acidic groups. The adsorption efficiency increased at LN700. This could be due to changing in surface area and pore volume of the absorbent (Zeledón-Toruño et al., 2007). This is in agreement with BET results. BET surface area and pore volume of LN700 higher than other temperature of carbonization. Therefore, LN700 was chosen for adsorption study.

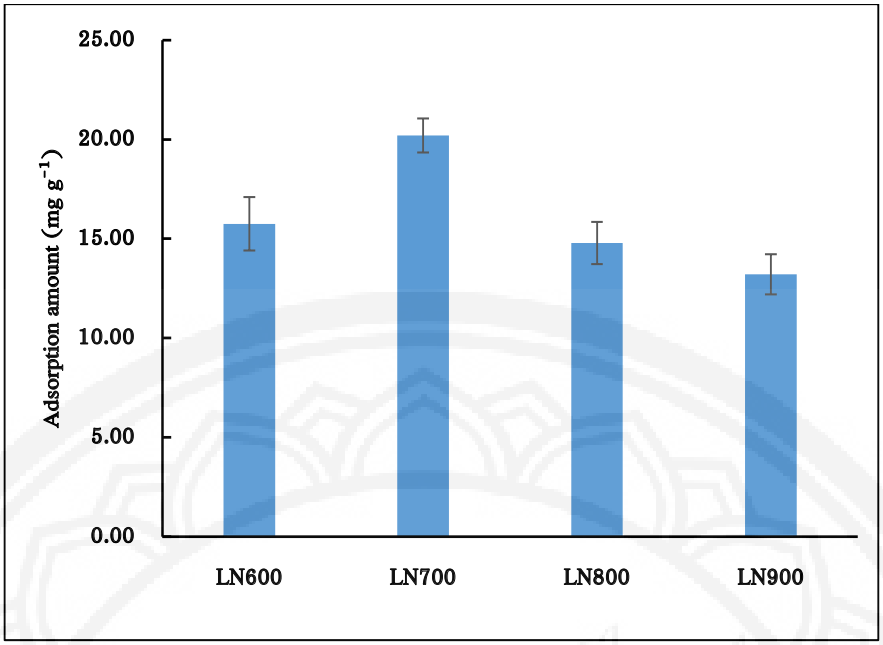

Figure 4 Adsorption efficiency of MB onto leonardite char at different temperatures. Adsorption condition: [MB] = 100 mg L^{-1}, Volume of MB = 50.00 mL, Adsorbent = 0.20xx g, contact time = 30 min, no adjust pH

Effect of pH

The initial pH of the MB solution was studied in the range 2-10. The results showed that the adsorption amount of MB was 16.87 mg g^{-1} at pH 2 and slightly increased to 20.07 mg g^{-1} with the increase pH up to 10. This indicated that surface area of LN700 no effect the pH value. Therefore, the investigation of contact time was carried out at pH 10 because this pH is identical with pH of LN700.

Effect of contact time

The contact time between leonardite char and MB solution was investigated to evaluate the time needed to reach equilibrium. 100 mg L^{-1} MB solution at pH 10 was added to flask containing 0.20 g LN700 and stirred as a function of time. The results are shown in Figure 5.

As can be seen from Figure 5, adsorption was increase rapidly in the first 5 min and reach the steady state at 10 min. These results show that the available sites of the adsorbent surface are most effective to MB during this time. So, 30 min contact time was a suitable time for another parameters investigation.

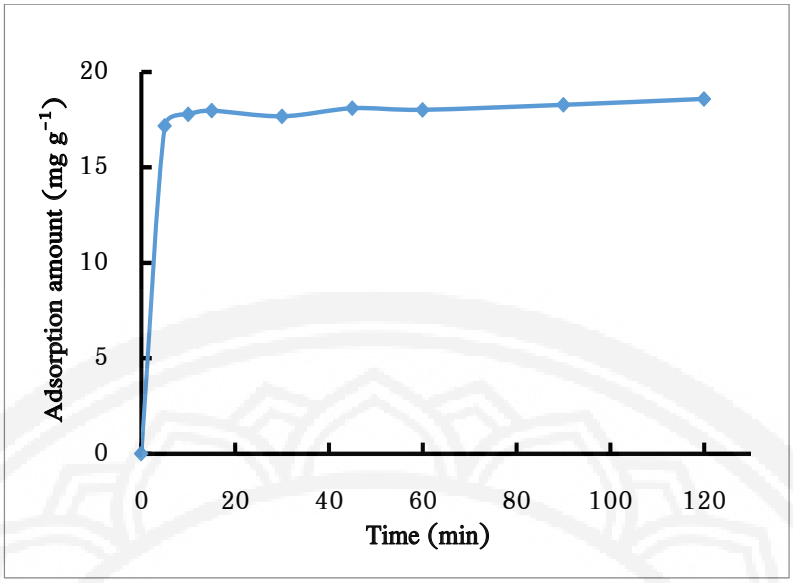

Figure 5 Adsorption efficiency of MB on LN700 at different contact time. Adsorption condition: [MB] = 100 mg L^{-1}, Volume of MB= 50.00 mL, Adsorbent = 0.20xx g, pH = 10.

Effect of particle size

The particle size of adsorbent has a significant effect on the kinetic of adsorption. This is corresponding to the adsorption amount of MB on LN700 surface which varied with surface area of adsorbent at a constant weight. Figure 6 shows the absorption amount of MB on the different particle size of LN700 from less than 38 μm to 300 μm. It can be seen that the adsorption amount increased with particle size decreased. The reason for this result could be the small particles give the large external surface area to adsorb MB in the solution (Weber & Morris, 1963). The 45-75 μm particle size of LN700 was suitable for further experiment because this size gave a good adsorption and readily separated from the MB solution.

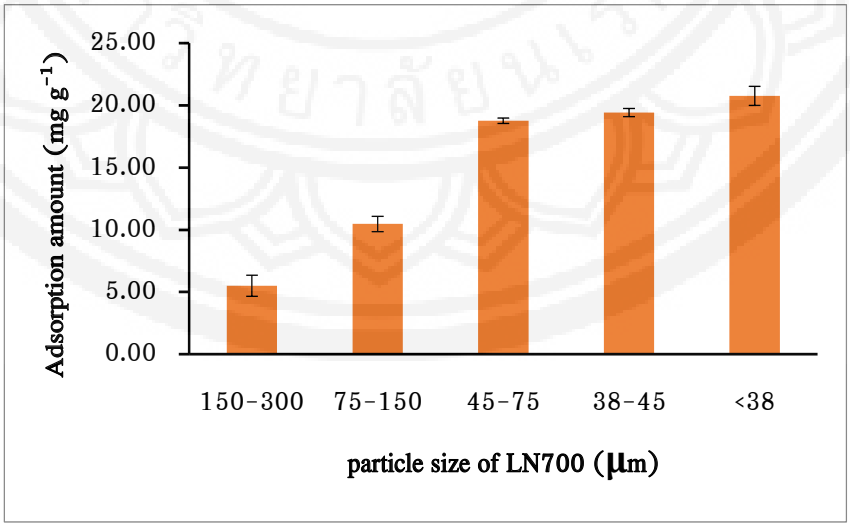

Figure 6 Adsorption efficiency of MB on LN700 at different particle size. Adsorption condition: [MB] = 100 mg L^{-1}, Volume of MB= 50.00 mL, Adsorbent = 0.20xx g, pH = 10 contact time 30 min.

Adsorption Kinetics

The pseudo-first-order and pseudo-second-order models were used to study the adsorption kinetics of MB. The pseudo-first-order kinetic equation in the linear form is represented as follows: (Guimarães Gusmão et al., 2013; Zengin, 2013)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (1)$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) are amount at equilibrium and at given time t of MB adsorbed on the adsorbent, respectively, and k_1 (min^{-1}) is the rate constant. The pseudo second-order kinetic was proposed by Ho and McKay (Guimarães Gusmão et al., 2013; Zengin, 2013), whose linear equation form is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (2)$$

Where k_2 (g mg^{-1} min^{-1}) is the pseudo second-order rate constant of adsorption. The results in Table 2 showed that the R^2 value for pseudo second-order model are closer to 1 than pseudo first-order model. Thus, the adsorption kinetic of MB was fitted with pseudo second-order model. This could be the absorption of MB on LN700 is due to chemisorption (Zengin, 2013; Ćurković, Cerjan-Stefanović, & Filipan, 1997). Moreover, the $q_{e,cal}$ values calculate from pseudo second-order equation were more consistent with $q_{e,exp}$ than those calculated from pseudo first-order equation. The q_e of MB calculated and experimental values were found to be 18.59 and 18.32 mg/g, respectively. The pseudo second-order plot of MB represented in Figure 7.

Table 2 Kinetic parameters for MB adsorption onto LN700

Pseudo first-order model		Pseudo second-order model	
		$q_{e,exp}$ (mg g^{-1})	18.59
k_1 (min^{-1})	-0.0136	k_2 (g/ mg min)	0.1100
$q_{e,cal}$ (mg g^{-1})	0.0919	$q_{e,cal}$ (mg g^{-1})	18.32
R^2	0.7385	R^2	0.9999

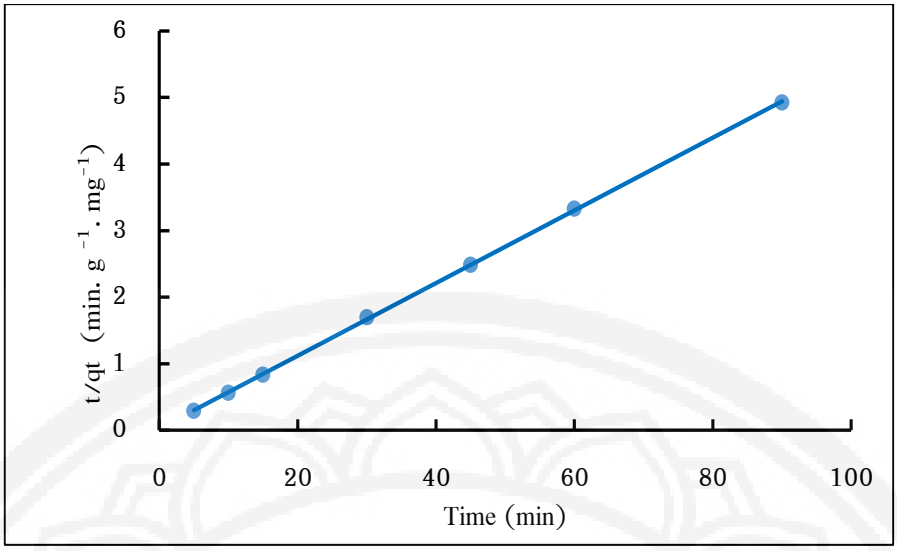

Figure 7 Adsorption kinetic data obtained by pseudo second-order model for the adsorption of MB

Adsorption Isotherm

The adsorption capacity of LN700 for removal MB was determined by Langmuir and Freundlich isotherms. Langmuir isotherm theory assumes that adsorption of adsorbate on adsorbent is a homogeneous surface (Guimarães Gusmão et al., 2013; Langmuir, 1918). This model explains that there is no interaction between the adsorbed molecules (Idris, Ndamitso, Iyaka, & Mhhammad, 2012). The Langmuir isotherm is represented by the following equation (Guimarães Gusmão et al., 2013):

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}} \qquad (3)$$

Where C_e is the equilibrium solution concentration of MB (mg L^{-1}), q_e is the amount of MB adsorbed at equilibrium (mg g^{-1}), Q_{max} is the adsorption capacity (mg g^{-1}) corresponding to complete monolayer coverage, b is the Langmuir constant (L mg^{-1}). The values of Q_{max} and b can be determined from the linear plot between $\frac{C_e}{q_e}$ and C_e (Guimarães Gusmão et al., 2013).

On the other hand, the Freundlich isotherm is an empirical equation which is applicable to equilibrium adsorption on the heterogeneous. The Freundlich isotherm can be expressed in its linear form as follows (Guimarães Gusmão et al., 2013; Said et al., 2012):

$$\text{Log } q_e = \text{Log } K_F + 1/n \text{ Log } C_e \qquad (4)$$

Where K_F indicates the Freundlich constant and n is the intensity of adsorption. If the value of 1/n falls in the range from 0 to 1 it indicated that the adsorption is favorable. The value of K_F and 1/n are calculated from the intercept and slope of the plot between log q_e and log C_e (Guimarães Gusmão et al., 2013).

Fitting of MB adsorption data to both Langmuir and Freundlich isotherms are presented in Figure 8 and 9.

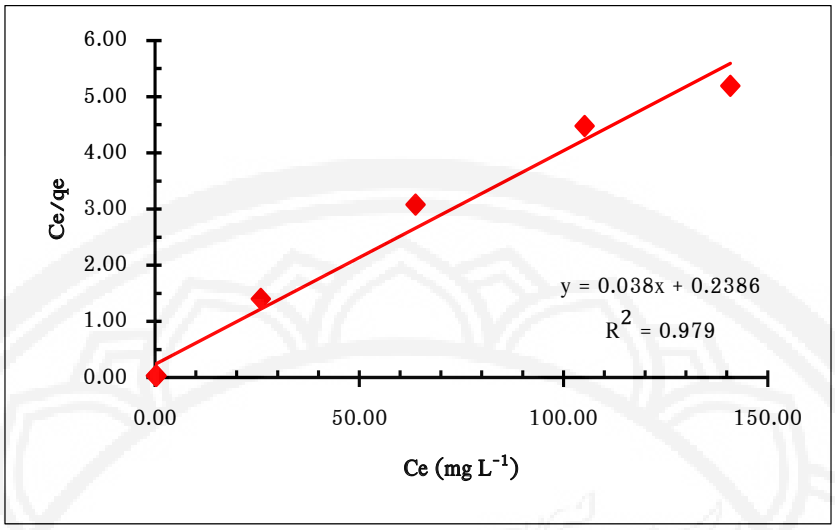

Figure 8 The Langmuir adsorption isotherm of MB on LN700

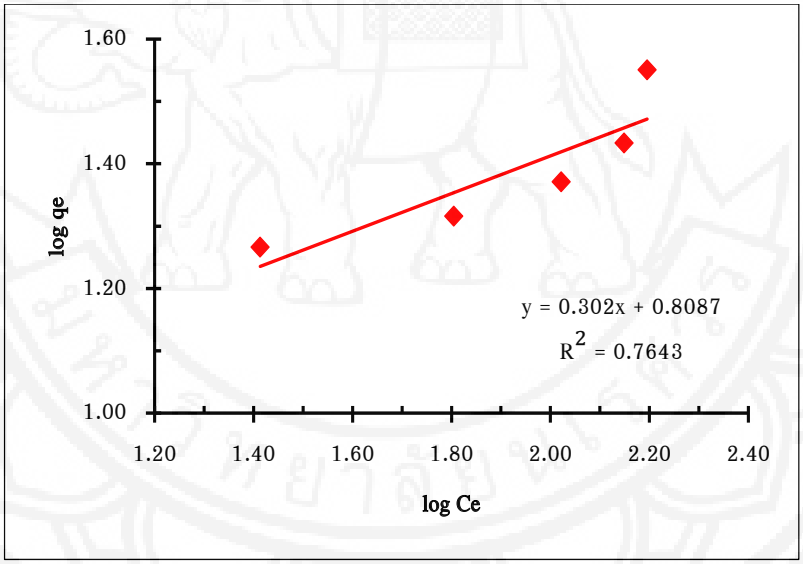

Figure 9 The Freundlich isotherm of MB on LN700

As can be seen in Figure 8 and 9, the adsorption isotherm data for the adsorption of MB on the LN700 was fitted with Langmuir model (r^2 = 0.973). This implies that the formation of monolayer coverage of MB on the surface of LN700 (Guimarães Gusmão et al., 2013). The coefficients isotherm parameters of the Langmuir and Freundlich isotherms are listed in Table 3 together with the correlation coefficients.

Table 3 Langmuir and Freundlich parameters for removal of MB onto LN700

	Langmuir			Freundlich		
	r^2	Q_{max} (mg g^{-1})	b (L^{-1} mg)	r^2	n	K_F (L^{-1} mg)
MB	0.979	26.32	0.159	0.764	3.31	6.437

Conclusion

The removal of MB using leonardite char by a prepared leonardite carbonized at 600, 700, 800 and 900 °C as adsorbent was investigated. The BET surface area and pore volume showed that LN700 has highest micropores in the surface which is in agreement with SEM data and MB adsorption. The experimental parameters including pH, contact time and particle size were determined and the optimum parameters were pH 10, 30 min contact time and 45-75 μm particle size. The kinetic data of MB were fitted to the pseudo second-order model which suggested that adsorption of MB on LN700 is due to chemisorption. The equilibrium data were fitted well with the Langmuir isotherms, suggesting the adsorption occurs in a monolayer (Guimarães Gusmão et al., 2013). The maximum adsorption capacity of MB onto LN700 was 26.32 mg g^{-1}.

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