Adsorption of Methylene blue onto Cajeput Tree Bark: Isotherm and Kinetic Studies

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Abstract

Cajeput tree bark was used as a low-cost adsorbent for the removal of methylene blue from aqueous solutions. The effects of pH, contact time and initial methylene blue concentration on adsorption capacity were studied in batch experiments. The experimental results indicated that the optimum pH for methylene blue adsorption was 7 and the adsorption equilibrium was achieved within 90 minutes. Equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherms. The Langmuir isotherm fitted the equilibrium data better than the Freundlich isotherm. The maximum monolayer adsorption capacity of cajeput tree bark was found to be 64.43 mg/g. The pseudo-first-order and pseudo-second-order kinetic models were selected to describe the adsorption mechanism. Kinetic studies revealed that the adsorption kinetics of methylene blue followed the pseudo-second-order kinetic model. These results showed that cajeput tree bark can be used as an efficient low-cost adsorbent for the removal of methylene blue from aqueous solutions.

Keywords: Adsorption, Methylene blue, Cajeput tree bark, Langmuir isotherm, Freundlich isotherm, Adsorption kinetic

Introduction

Dyes have been used extensively in various industries such as cosmetics, paper, printing, textile, leather, rubber, and food. The discharge of dyes into water sources without treatment results in water pollution which is important environmental problems (Kumar, Chaudhary, & Verma, 2013; Vanaamudan, Chavada, & Padmaja, 2016). Most dyes are organic compounds which have complicated aromatic molecular structure (Achmad, Kassim, Suan, Amat, & Seey, 2012). Therefore, dyes are stable to sunlight, chemicals and microorganism and difficult to biodegrade (Seey & Kassim, 2012; Vijayakumar, Tamilarasan, & Dharmendirakumar, 2012; Dehvari, Ghaneian, Ebrahimi, Jamshidi, & Mootab, 2016). The presence of dyes in water sources reduces sunlight penetration affecting the photosynthetic process of aquatic life (Sun, Zhang, Wang, & Wu, 2013). Furthermore, many dyes are highly toxic and carcinogenic causing a danger to human and animal health (Yagub, Sen, Afroze, & Ang, 2014; Vital, Saibaba, Shaik, & Gopinath, 2016). Methylene blue is a cationic dye (basic dye) that is widely applied in the textile industry for dyeing materials such as silk, cotton, and wool. Even though methylene blue is not severely toxic, it can cause various harmful effects. The side effects of methylene blue include profuse sweating, nausea, chest pain, abdominal pain, headache, vomiting, diarrhea, dizziness and increased heart rate (Hameed, Mahmoud, & Ahmad, 2008; Fil, Özmetin, & Korkmaz, 2012; Afroze, Sen, Ang, & Nishioka, 2015). Thus, the removal of methylene blue from wastewater is important to the environment and living organisms.

The conventional techniques for the removal of dyes from wastewater include coagulation, chemical oxidation, chemical precipitation, adsorption, electrochemical, ozonation, membrane separation process, and biological treatment. Among these techniques, the adsorption process is the most commonly used because of its

low costs, easy operation, and high efficiency (Tichaona, Viola, Olindah, & Munyaradzi, 2013; Mahmoud et al., 2016). The characteristics of adsorbent resulting in the effective adsorption consist of high porosity, large specific surface area, and small particle size. At present, low-cost adsorbents, produced from industrial waste, agricultural waste and natural materials such as sawdust, corncob, rice husk, hazelnut shell, fly ash, red mud, wood, pine bark, cotton, peat, clay, etc., have been used for the removal of numerous dyes (Gupta & Suhas, 2009).

The cajeput tree (*Melaleuca cajuputi* Powell), also called paperbark tree, milk wood, or swamp tree, is a perennial tree of Myrtaceae family. Cajeput trees can be grown in swampy areas of the southeastern, southwestern and southern Thailand which commonly known as White Samet. The bark of cajeput tree is whitish or grayish brown, layered, papery, and spongy. The specific properties of cajeput tree bark are insulative, waterproof, and durable. Therefore, cajeput tree bark has already been used in several beneficial applications such as house wall material, caulking boat, and roofing material (Abdullah et al., 2001; Nuyim, 2002; Veeramani et al., 2015). Moreover, it is a good choice for use as a low-cost adsorbent due to its porous tree bark.

This study aims to investigate the ability of cajeput tree bark, as a low-cost adsorbent, for the removal of methylene blue from aqueous solutions. The effects of various parameters such as pH, contact time and initial concentration were examined by batch experiments. Besides, the isotherm and kinetics of methylene blue adsorption onto cajeput tree bark were also evaluated.

Methods and Materials

Adsorbent

Cajeput tree bark was obtained from Nakhon Si Thammarat province, Thailand. It was washed repeatedly with distilled water to remove impurities, and then oven-dried at 80°C to constant weight. The dried bark was crushed and sieved through 100 mesh sieve (0.149 mm). The bark powder was dried in an oven at 105°C for 24 h to get the dried adsorbent and stored in a well-sealed bottle for further use.

The characteristics of the cajeput tree bark were analyzed by standard methods. The specific surface area, total pore volume, and average pore diameter were measured by the Brunauer-Emmett-Teller (BET) method using surface area and pore size analyzer (Quadrasorb SI, Quantachrome instruments). The Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) was performed with JEOL JSM-6610LV, Oxford INCAx-act to determine the surface morphology and elemental compositions of the cajeput tree bark. In addition, the functional groups on the surface of cajeput tree bark were identified by the Fourier Transform Infrared (FTIR) spectrometer (Spectrum One, Perkin Elmer).

Adsorbate

Methylene blue used in this research was laboratory grade purchased from Asia Pacific Specialty Chemicals Limited. It has a chemical formula of $C_{16}H_{18}ClN_3S$ with a molecular weight of 319.85 g/mol. The structure of methylene blue is illustrated in Figure 1. The stock solution of 1,000 mg/L methylene blue was prepared by dissolving accurately weighed dye in distilled water. The different methylene blue concentrations in the range of 50-150 mg/L were obtained by diluting the stock solution.
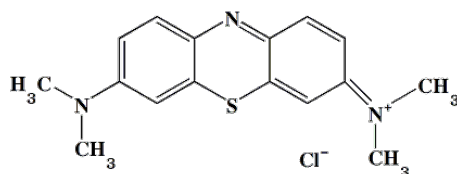
Figure 1 The structure of methylene blue

Adsorption studies

Batch adsorption experiments were performed in 125 mL Erlenmeyer flasks where 0.1 g of cajeput tree bark and 50 mL of methylene blue solution were added. The flasks were agitated in an orbital shaker at a speed of 150 rpm and a temperature of 25°C. The effect of pH was examined in the pH range of 2-10. The pH of 100 mg/L methylene blue solution was adjusted to the required pH value by addition of 0.1 M HCl and 0.1 M NaOH solutions. After 6 h of the adsorption process, the mixtures were filtered using Whatman filter paper. The concentration of residual methylene blue was analyzed by UV-Vis spectrophotometer (UV5100, Metash instruments) at a maximum wavelength of 665 nm.

The adsorption of methylene blue at different contact times (10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 240, 300 and 360 min) was conducted to study the effect of contact time. The experiments were carried out using initial methylene blue concentration of 100 mg/L at the optimum pH of 7. The mixtures were filtered and the concentration of residual methylene blue was measured using a UV-vis spectrophotometer at a maximum wavelength of 665 nm.

The effect of initial methylene blue concentration was studied by varying the initial concentrations from 50 to 150 mg/L under the optimum pH of 7 and contact time of 90 min. After equilibrium time, the mixtures were filtered and the concentration of residual methylene blue was measured using a UV-vis spectrophotometer at a maximum wavelength of 665 nm.

The percentage removal of dye was calculated as follows:

$$\% \text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

The amount of dye adsorbed, q_e, was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, C_0 (mg/L) is the initial dye concentration, C_e (mg/L) is the equilibrium dye concentration, V (L) is the volume of dye solution and W (g) is the mass of the adsorbent.

Adsorption isotherms

Adsorption isotherms represent the relationship between the amount of dye adsorbed and the equilibrium concentration of dye at constant temperature. The Langmuir and Freundlich isotherms as the basic model are commonly used to describe adsorption data.

The Langmuir isotherm assumes that adsorption occurs on the homogeneous surface of adsorbent which is covered by only one layer of adsorbate molecules, i.e. monolayer adsorption. There is no interaction between the adsorbed molecules. The surface of adsorbent has a finite number of active sites, therefore each site can

hold one adsorbed molecule. All the active sites are energetically equivalent (Fil et al., 2012; Sukpreabprom, Arquero, Naksata, Sooksamiti, & Janhom, 2014). The Langmuir isotherm equation is expressed in the linear form as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{3}$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, C_e (mg/L) is the equilibrium dye concentration, q_m (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the Langmuir constant related to the energy of adsorption. The values of q_m and K_L are calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e.

The Freundlich isotherm is based on the assumption that the adsorbent surface is heterogeneous. There is an interaction between the adsorbed molecules. The adsorption energy exponentially distributes over the adsorbent surface (Zhang & Ou, 2013; Sukpreabprom et al., 2014). The Freundlich isotherm equation is represented as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where K_F and n are the Freundlich constants indicating adsorption capacity and adsorption intensity, respectively. The constant values of K_F and n can be calculated from the intercept and slope of the linear plot of $\log q_e$ versus $\log C_e$. Also, the value of n > 1 represents favorable adsorption (Hameed et al., 2008; Dawood, Sen, & Phan, 2016).

Adsorption kinetics

Adsorption kinetics are used to explain the adsorption mechanism. The adsorption mechanism of methylene blue onto cajeput tree bark was investigated using the pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order kinetic equation can be expressed as:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

where q_e and q_t (mg/g) are the amount of dye adsorbed at equilibrium and time t (min), respectively and k_1 (min^{-1}) is the pseudo-first-order rate constant. The plot of $\log(q_e - q_t)$ versus t gives a straight line from which k_1 and q_e can be determined from the slope and intercept, respectively (Ertugay & Malkoc, 2014; Radaei, Moghaddam, & Arami, 2014).

For the pseudo-second-order kinetic model, a linear equation is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_2 (g/mg.min) is the pseudo-second-order rate constant. The slope and intercept of the plot of t/q_t versus t use to evaluate the values of q_e and k_2, respectively (Budsaereechai, Kamwialisak, & Ngernyen, 2012; Radaei et al., 2014).

Besides, the initial adsorption rate, h (mg/g.min) can be determined from the pseudo-second-order kinetic model by the following equation (Ertugay & Malkoc, 2014; Afroze et al., 2015):

$$h = k_2 q_e^2 \tag{7}$$

Results and Discussion

Characterization of Adsorbent

The physical properties of cajeput tree bark such as total pore volume, average pore diameter, and specific surface area are presented in Table 1. The result of the BET method showed that the specific surface area of cajeput tree bark was very low compared to commercial activated carbons. Typical values of specific surface area for commercial activated carbons are usually in the range of 600-1500 m^2/g (Aznar, 2011). According to the classification of the International Union of Pure and Applied Chemistry (IUPAC), it can be seen that the pore size of cajeput tree bark was mesopore with the pore diameter in the range of 2-50 nm (Mays, 2007).

Table 1 Physical properties of cajeput tree bark

Parameter	Value
Total pore volume (cm^3/g)	3.67×10^{-2}
Average pore diameter (nm)	29.08
Specific surface area (m^2/g)	5.043

Cajeput tree bark was characterized by Scanning Electron Microscope (SEM)-Energy Dispersive X-Ray Spectroscopy (EDS). The SEM images of cajeput tree bark are shown in Figure 2. These images reveal that the cajeput tree bark exhibits the irregular and rough surface morphology. It also shows the porous and fibrous texture of cajeput tree bark which are main factors for the adsorption of adsorbent. EDS analysis was performed to determine the elemental compositions of cajeput tree bark. Table 2 shows the percentage weight of elemental compositions available on the adsorbent surface. The major component of cajeput tree bark was carbon (72.96%) and oxygen (24.34%).
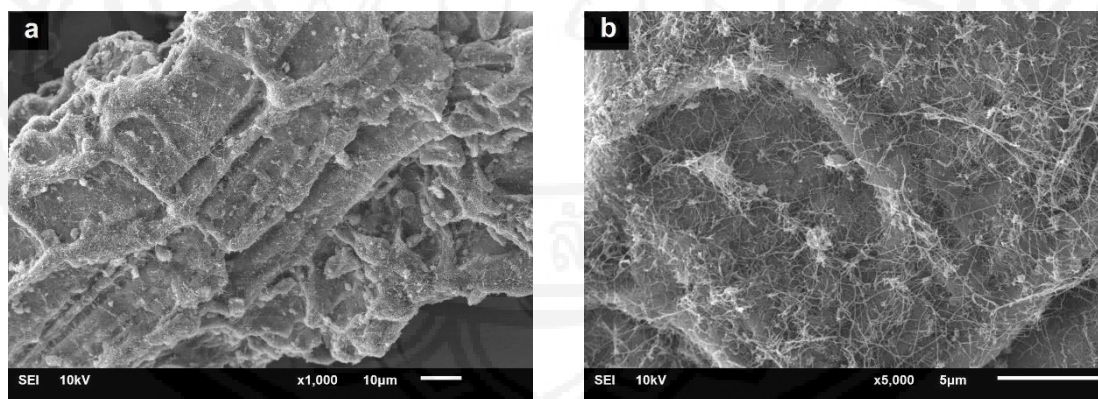

Figure 2 SEM images of cajeput tree bark at magnification (a) ×1,000 and (b) ×5,000

Table 2 Elemental compositions of cajeput tree bark

Elemental	Weight (%)	Atomic (%)
C	72.96	79.04
O	24.34	19.79
Na	0.41	0.23
Mg	0.54	0.29
Cl	1.75	0.64

FTIR spectra of cajeput tree bark were recorded in the range of 400-4000 cm^{-1}, as shown in Figure 3. It can be observed that the broadband at 3429 cm^{-1} was associated with O-H stretching of a hydroxyl group. The peaks at 2931 and 2870 cm^{-1} corresponded to C-H stretching. Peaks at 1738, 1638, 1506, 1456 and 1376 cm^{-1} were due to C=O stretching, C=C stretching of the aromatic group, N-H bending, C-H bending, and O-H bending, respectively. The absorption bands in the range of 1321-1048 cm^{-1} corresponded to C-O stretching of alcohols, carboxylic acids, esters, ethers and C-N stretching of amine. Also, the peaks between 920-562 cm^{-1} were characteristic of aromatic C-H out of plane bending (Talib, Zakaria, Hua, & Othman, 2014; Afroze et al., 2015; Paosen, Saising, Septama, & Voravuthikunchai, 2017; Veiga et al., 2017; Hanif et al., 2018).
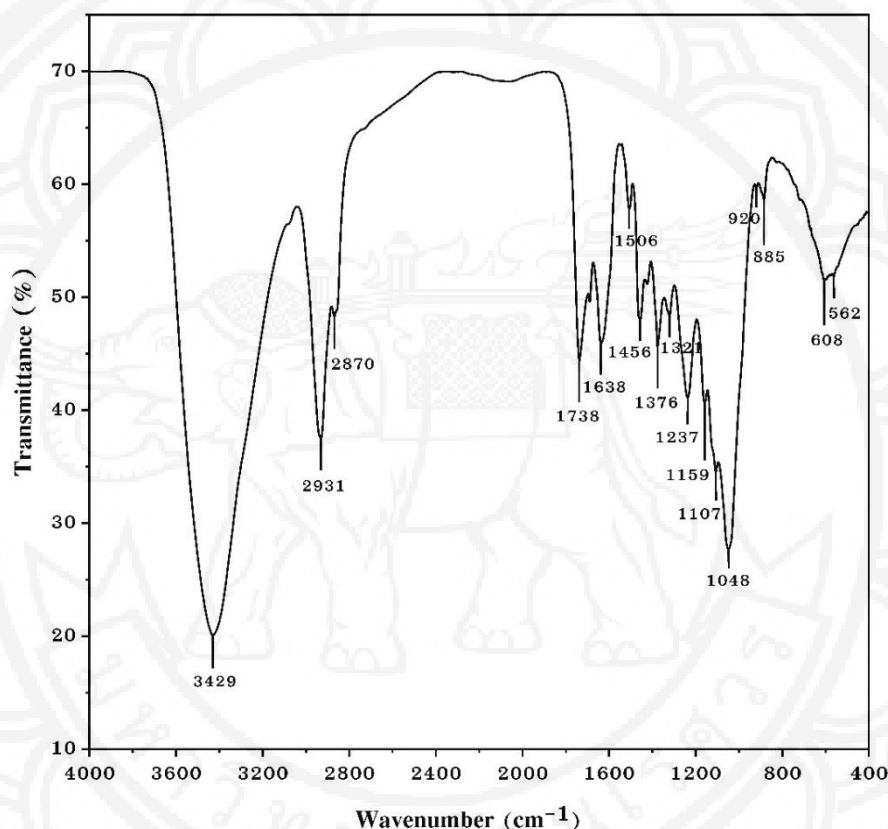

Figure 3 FTIR spectra of cajeput tree bark

Effect of pH

The pH of solution is one of the most significant parameters affecting adsorption process. The variation of pH value impacts on the surface charge of adsorbent and the degree of ionization of adsorbate. Figure 4 shows the effect of pH on the methylene blue adsorption in the pH range of 2-10. The result revealed that the percentage removal of methylene blue increased from 83.12% to 98.35% with an increase in a pH of solution from 2 to 7. After pH 7 until pH 10, the percentage removal of methylene blue was constant. It indicated that the methylene blue removal efficiency was high at alkaline condition of solution. Consequently, pH 7 was selected as an optimum pH for further adsorption experiments since it was approximate to a natural pH of the methylene blue solution.

At low pH values, the adsorption of methylene blue decreased due to the presence of excess H^+ ions in solution competing with the cation groups of methylene blue for the adsorption sites. Moreover, an increase in positively charged surface sites on the adsorbent did not favor the adsorption of cationic dye due to electrostatic repulsion. In contrast at high pH values, the surface of adsorbent became more negatively charged, thereby increasing the electrostatic attraction between negatively charged surface sites and cationic dye, resulting in an increase in the adsorption (Senthilkumaar, Varadarajan, Porkodi, & Subbhuraam, 2005; Baek, Ijagbemi, O, & Kim, 2010; Tichaona et al., 2013; Amrhar, Nassali, & Elyoubi, 2015).
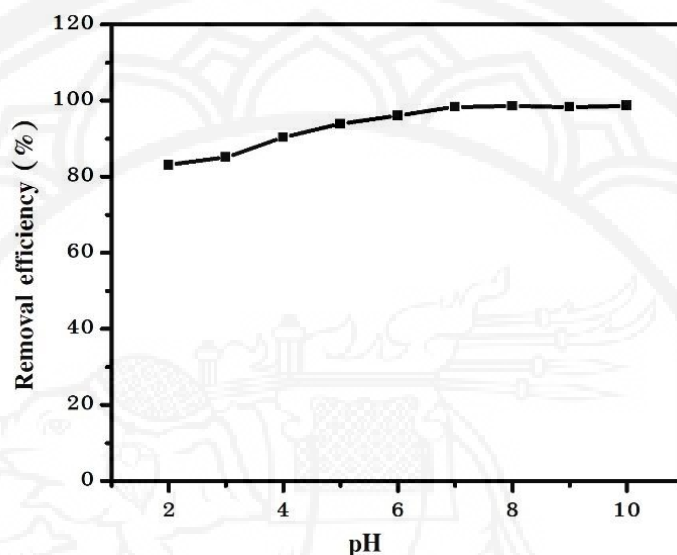

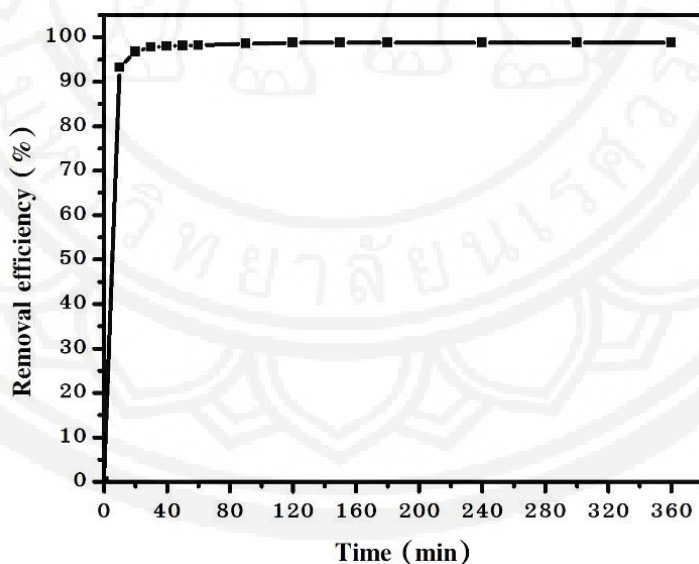Figure 4 Effect of pH on the adsorption of methylene blue onto cajeput tree bark

Figure 5 Effect of contact time on the adsorption of methylene blue onto cajeput tree bark

Effect of contact time

The effect of contact time on the adsorption of methylene blue onto cajeput tree bark is presented in Figure 5. According to the results, the adsorption rate increased rapidly at initial stages of contact time within the first

10 min and then the adsorption rate became constant at a contact time of 90 min. The percentage removal of methylene blue was 98.57% at 90 min. It can be explained that a large number of adsorption sites on the adsorbent surface were available as a result the adsorption rate was very fast at the initial stages. As the surface of adsorbent had been fully covered by the dye molecules, the rate of adsorption slowed down and finally reached equilibrium. For the next adsorption studies, the optimum contact time of 90 min was used to ensure that the equilibrium condition was attained.

Effect of initial concentration

The adsorption of methylene blue onto cajeput tree bark was investigated at various initial concentrations ranging from 50 to 150 mg/L. Figure 6 shows the effect of initial methylene blue concentration on the adsorption. The amount of methylene blue adsorbed at equilibrium (q_e) increased from 24.67 mg/g to 61.15 mg/g with increasing initial concentration. This can be explained that the high initial concentration of dye gave a high driving force to overcome the mass transfer resistance of the dye between aqueous solution and solid phase. However, the percentage removal of methylene blue decreased from 98.02% to 81.50% as the initial concentration increased. This may be due to the saturation of available active sites on the adsorbent surface. At the higher initial dye concentration, the active sites for dye molecule adsorption were scarce (Bharathi & Ramesh, 2013; Afroze et al., 2015).
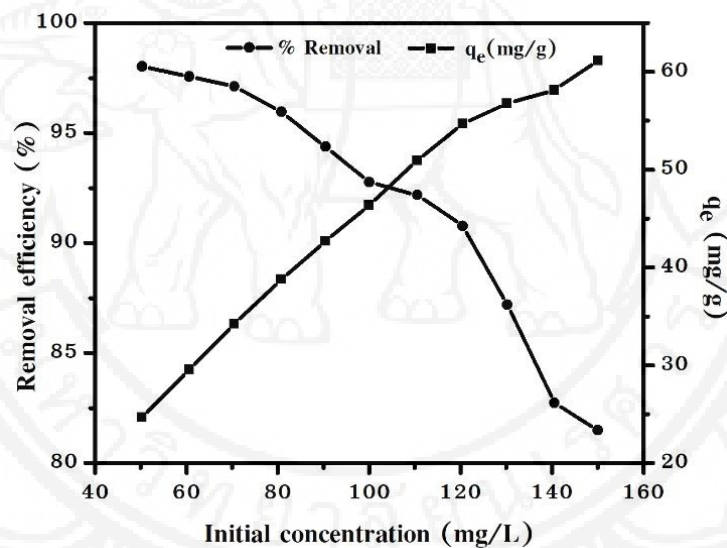

Figure 6 Effect of initial concentration on the adsorption of methylene blue onto cajeput tree bark

Isotherm studies

The linear form of the Langmuir and Freundlich isotherms are shown in Figure 7 and Figure 8, respectively. The isotherm constants and correlation coefficient (R^2) are given in Table 3. It was found that the Langmuir isotherm was best fitted to the equilibrium data of methylene blue adsorption based on R^2 value of 0.9959 compared to 0.9590 for Freundlich isotherm. This suggested that the adsorption occurred on the homogeneous surface of the cajeput tree bark. Moreover, the methylene blue was adsorbed in the form of monolayer coverage on the surface of the cajeput tree bark. The maximum adsorption capacity (q_m) and the Langmuir constant (K_L) were found to be 64.43 mg/g and 0.4792 L/mg, respectively. Table 4 presents the comparison of maximum adsorption capacity of various adsorbents for the removal of methylene blue.

Obviously, the maximum adsorption capacity of cajeput tree bark was higher in comparison with the other adsorbents. Therefore, the cajeput tree bark is suitable as adsorbent for adsorption of methylene blue.
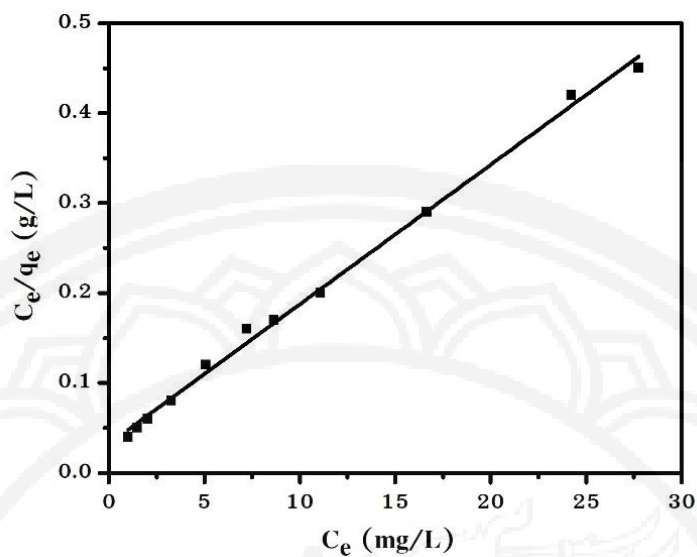

Figure 7 Langmuir isotherm for the adsorption of methylene blue onto cajeput tree bark
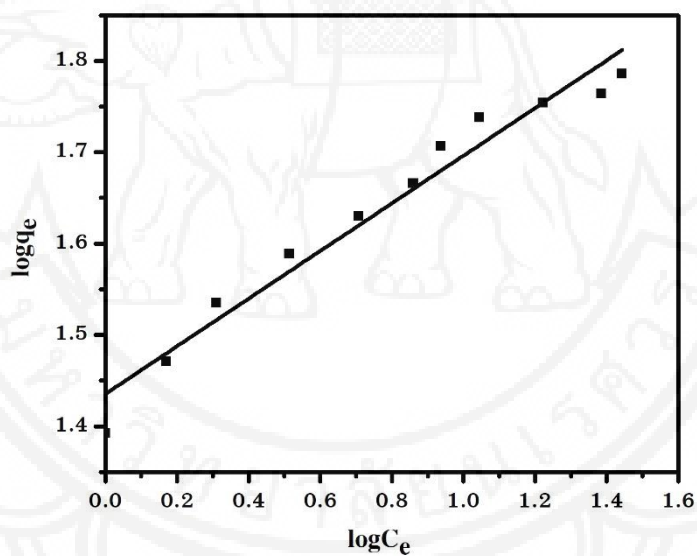

Figure 8 Freundlich isotherm for the adsorption of methylene blue onto cajeput tree bark

Table 3 Isotherm constants and correlation coefficient of methylene blue adsorption onto cajeput tree bark

| Isotherm	Parameters	Value
Langmuir	q_m (mg/g)	64.43
	K_L (L/mg)	0.4792
	R^2	0.9959
Freundlich	n	3.83
	K_F	27.25
	R^2	0.9590

Table 4 Maximum adsorption capacity of various adsorbents for methylene blue

Adsorbent	Maximum adsorption capacity, q_m (mg/g)	Reference
Cajeput tree bark	64.43	This study
Orange peel	18.60	Annadurai, Juang, & Lee, 2002
Banana peel	20.80	Annadurai et al., 2002
Rice husk	40.59	Vadivelan & Kumar, 2005
Wheat shells	16.56	Bulut & Aydln, 2006
Cereal chaff	20.30	Han et al., 2006
Oak sawdust	29.94	Ferrero, 2007
Granular activated carbon	21.50	Yener, Kopac, Dogu, & Dogu, 2008
Spent coffee grounds	18.73	Franca, Oliveira, & Ferreira, 2009
Natural zeolite	19.94	Han et al., 2009

Kinetic studies

The adsorption kinetics of methylene blue onto cajeput tree bark were analyzed by the pseudo-first-order and pseudo-second-order kinetic models. Figure 9 and Figure 10 display the linear plot of $\log(q_e-q_t)$ versus t for the pseudo-first-order kinetic model and t/q_t versus t for the pseudo-second-order kinetic model, respectively. The calculated constants and correlation coefficient (R^2) of each kinetic model are listed in Table 5.

Based on the comparison between the experimental q_e ($q_{e,exp}$) and calculated q_e ($q_{e,cal}$) values, it was observed that the calculated q_e value was very close to the experimental q_e value in the case of the pseudo-second-order kinetic model. Furthermore, the correlation coefficient value for the pseudo-second-order kinetic model ($R^2 = 0.9999$) was much closer to 1 than for the pseudo-first-order kinetic model ($R^2 = 0.8860$). These results indicated that the adsorption kinetics of methylene blue onto cajeput tree bark can be well described by the pseudo-second-order kinetic model. Thus, it can be concluded that the rate limiting step of the methylene blue adsorption was controlled by the chemisorption process, occurring through sharing or exchange of ions between adsorbate and adsorbent surface (Shih, 2012; Ertugay & Malkoc, 2014; Afroze et al., 2015). The methylene blue cation sticks to the cajeput tree bark surface by forming a chemical bond.
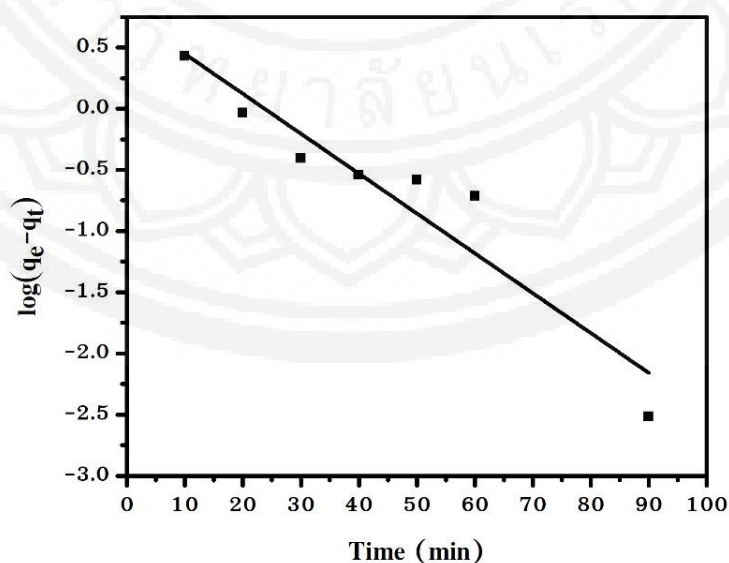
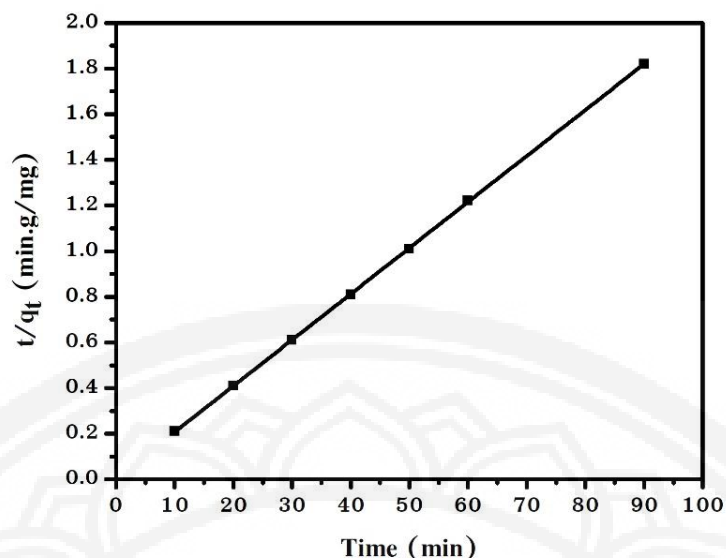**Figure 9** Pseudo-first-order kinetic model for the adsorption of methylene blue onto cajeput tree bark

Figure 10 Pseudo-second-order kinetic model for the adsorption of methylene blue onto cajeput tree bark

Table 5 Kinetic constants and correlation coefficient of methylene blue adsorption onto cajeput tree bark

Kinetic model	Parameters	Value
	$q_{e\ exp}$ (mg/g)	49.56
Pseudo-first-order	$q_{e,cal}$ (mg/g)	5.93
	k_1 (min^{-1})	0.0751
	R^2	0.8860
Pseudo-second-order	$q_{e,cal}$ (mg/g)	49.63
	k_2 (g/mg.min)	0.0624
	h (mg/g.min)	153.67
	R^2	0.9999

This present study recommends that a low-cost adsorbent prepared from cajeput tree bark can be used effectively for the removal of methylene blue from aqueous solutions. In the future, the researcher will consider the study of physical and chemical activation of cajeput tree bark to improve its effectiveness for adsorption. The researcher suggests further research focus on the adsorption process for dye removal from industrial wastewater. Moreover, the reuse of used cajeput tree bark adsorbent by desorption method will also be studied.

Conclusion

In this study, the adsorption capacity of methylene blue onto cajeput tree bark was influenced by pH, contact time and initial concentrations. The optimum condition for the adsorption of methylene blue was identified as pH 7 and contact time around 90 min. The adsorption capacity increased with an increase in initial methylene blue concentration. The equilibrium adsorption data fitted well with the Langmuir isotherm and the maximum monolayer adsorption capacity was 64.43 mg/g at 25°C. The adsorption kinetics of methylene blue were best fitted with the pseudo-second-order kinetic model. The results indicated that cajeput tree bark can be employed as a low-cost and effective adsorbent for the removal of methylene blue from aqueous solutions.

Acknowledgments

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