Research Article

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Removal of Methylene Blue Dye in Water Using Longkong Fruit Peels

Vanida Chairgulprasert* and Hongnapa Waehayee
Department of Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, Pattani, Thailand

* Corresponding author. E-mail: vanida.c@psu.ac.th DOI: 10.14416/j.ijast.2018.07.002
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Abstract
The adsorption of methylene blue dye from water onto longkong waste peel has been investigated under various experiment conditions. Batch experiments were conducted to determine the effect of pH, initial dye concentration, contact time, adsorbent dose and temperature. The equilibrium time was found to be 205 min at the optimum pH of 7. The capacity of adsorption was improved with increasing of initial dye concentration and temperature. In contrast, as the mass of adsorbent increased, a decrease in the adsorption capacity was obtained. For isotherm study, the adsorption data of longkong peel was best fitted to Freundlich model. The kinetics of adsorption followed the pseudo second order model. Thermodynamic parameters such as, enthalpy, entropy and free energy changes were evaluated. The adsorption process was exothermic and spontaneous.

Keywords: Adsorption isotherm, Adsorption kinetics, Methylene blue, Longkong, *Aglaia dookkoo* Griff

1 Introduction

Many industries such as textile, leather, rubber and cosmetic consume various synthetic dyes. Therefore, their effluents could harm the environment. Dyes affect the aquatic plants and also cause allergy, dermatitis, skin irritation, cancer and mutations in humans [1]. There are many processes used to remove dyes from solutions including precipitation, flocculation, electro-kinetic coagulation, electro-flotation, ion exchange, membrane filtration, electro-chemical destruction, irradiation and ozonation [2]–[4]. Adsorption is one of the versatile techniques to remove dyes from the waste water. A wide variety of adsorbents have been applied including clay, silica beads, zeolite, activated carbons, ash and agricultural wastes [5]–[11].

Longkong, *Aglaia dookkoo* Griff, belongs to the Maliaceae family and originates in western South-East Asia, from Peninsular Thailand in the west to Borneo in the east (Indonesia) [12], [13]. It is a well-liked fruit from South of Thailand due to its juicy, sweet and slightly sour taste with sweet aroma smell. Longkong fruit contains various nutrients [13], essential oils, and organic acids [14], and its extract has been applied in cosmetics [15]. The fresh and dried fruit peel contains volatile oil, brown resin and reducing acids [16], [17]. Longkong peel also had high total phenolic content [18]. The fruit peels have also been used in traditional Thai's medicine [19], yet, the peel were usually discarded as waste after consuming the fruits edible flesh.

The aim of this research is to study the removal of Methylene Blue (MB) dye using longkong fruit peels. Each of these parameters including pH, exposure time, initial dye concentration, dose of adsorbent and solution temperature was optimised in order to maximise the adsorption efficiency.

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2 Materials and Methods

2.1 *Preparation of longkong peels*

Longkongs were obtained from Pattani province, Thailand. The peels were washed and dried in the shade for 24 h before being dried in the oven at 70°C for 72 h. The dried peels were milled and sieved through a 20 mesh screen. The resulting powders were stored in air tight polyethylene bags and used for the different experiments in this study.

2.2 *Characterization of adsorbent*

The FTIR spectroscopy (Bruker, Tensor 27) technique was applied to detect the chemical structure of longkong fruit peels before and after MB adsorption using a KBr window.

2.3 *Preparation of adsorbate*

The 1000 mg/L stock solution of Methylene Blue (MB) was prepared in distilled water and further diluted to the desired concentration. The acidity and basicity of MB was adjusted to pH 2 to 12 using either 0.1 M hydrochloric acid or 0.1 M sodium hydroxide.

2.4 *Determination of pH_{pzc}*

The pH_{pzc} was determined according to the following procedure [20]. Each 100 mL of sodium chloride solution was adjusted by varying the pH to 2–12. The 0.3 g longkong peels were then added and the mixture was shaken at 180 rpm, 30°C. After 24 h, the supernatant liquid was collected, and the pH measured. The relations between the initial and the change pH values ($\Delta pH = pH_{final} - pH_{initial}$) were plotted and the corresponding pH_{pzc} was evaluated.

2.5 *Batch adsorption*

The batch system was employed for all studies. The typical experiment was conducted in 250 mL conical flask using 100 mL MB solution and the pH was adjusted as required. Powders of longkong peels were added and the mixture was shaken at 180 rpm by a mechanical shaker at controlled temperature. After a period of desired time, the suspension was filtered and

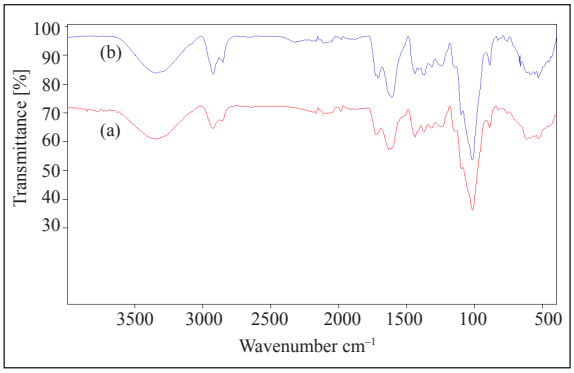

Figure 1: FTIR spectrum of longkong peel (a) before adsorption and (b) after MB dye adsorption.

the residual MB concentrations were measured using a UV-Vis spectrophotometer (Biochrome, Libra S11) at a wavelength of 665 nm. Experimental parameters of pH (2–12), contact time (10–300 min), initial metal ion concentration (10–50 mg/L), dose of adsorbent powder (0.1–1.0 g) and temperature (30–50°C) were varied in order to establish optimum conditions for MB adsorption.

For experiments regarding to contact time and concentrations, 3 mL of the solution was withdrawn after 5 min and at every 10 min for 50 min, then at every 30 min for 150 min. For the rest of the experiments, the sampling was taken every 50 min. All experiments were completed in triplicate.

The MB dye uptake capacity (q_t, mg/g) of longkong peels was calculated from the Equation (1).

$$q_t = (C_i - C_t)V/W \quad (1)$$

3 Results and Discussions

3.1 *FTIR Characterization*

The FTIR spectra of longkong peel before and after MB adsorption showed some distinct changed as seen in Figure 1. The broad band at 3351 cm^{-1} representing OH and/or NH stretching vibrates was a little shifted to 3348 cm^{-1} indicating the binding of MB with –OH and –NH groups. The peak at 1710 cm^{-1} assigned to C=O of carbonyl group and a strong absorption at 1613 cm^{-1} assigned to C=O stretching of carboxylic group. There were the significant shifted in C=O of carbonyl and carboxylic groups to 1729 and 1631 cm^{-1}

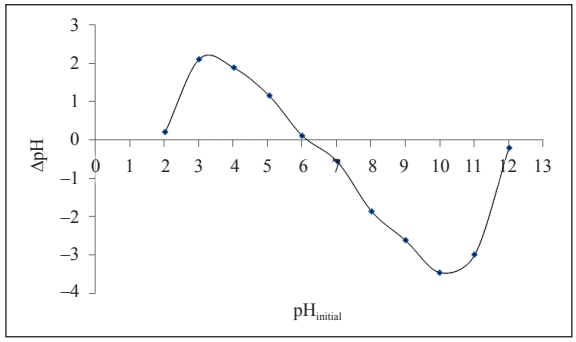

Figure 2: Determination of pH_{pzc} of longkong peel.

respectively, suggesting that both groups could be the main groups involving in binding to MB dyes. The fingerprint peaks at 1031 and 1371 cm^{-1} corresponding to C-O and C-N bonds were also moved to 1018 and 1441 cm^{-1} for loading longkong peels.

3.2 *Point of Zero charge*

The pH_{pzc} is a crucial characteristic for adsorbent to indicate its net surface charge. At the beginning, the ΔpH increased and then dropped to a minimum value at pH 10 and then raised again (Figure 2). The curve intersected the axis at pH = 6.2, thus the pH_{pzc} of longkong peel was 6.2 which indicated that the net surface adsorbent charge was zero. Additionally, when the medium pH is above 6.2, the surface become negatively charges whereas it is lower the surface become positively charges [21].

3.3 *Effect of pH*

The effect of pH was investigated using 0.3 g longkong peels in 10 mg/L MB dye 100 mL with in a pH range of 2–12 for 90 min. As shown in Figure 2, MB adsorption increased as the pH was increased from 2 to 3, and a little change was observed at above pH 3. However, the appropriate pH was recorded at 7 (Figure 3). At low pH, active sites could be highly protonated by hydronium ions leading to repulsive force between active sites and MB cations. When the solution pH increased, less hydronium ions were presented thus promoted the attraction between active sites and MB dyes. This result also agreed with the pH_{pzc} value. The effective pH of solution was above pH_{pzc} value. It could be explained that longkong peels contained various

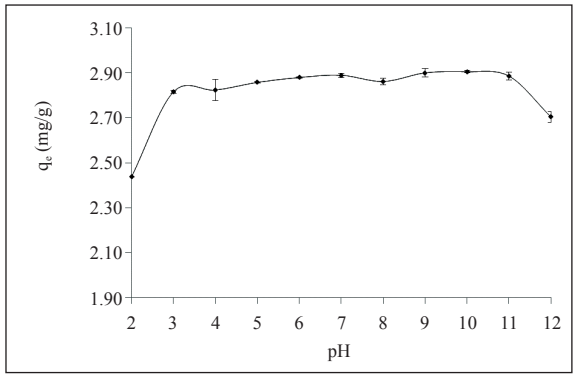

Figure 3: Effect of variation in pH (2–12) on MB removal by longkongs [dose 0.3 g, MB conc. 10 mg/L contact time 90 min, T 30°C].

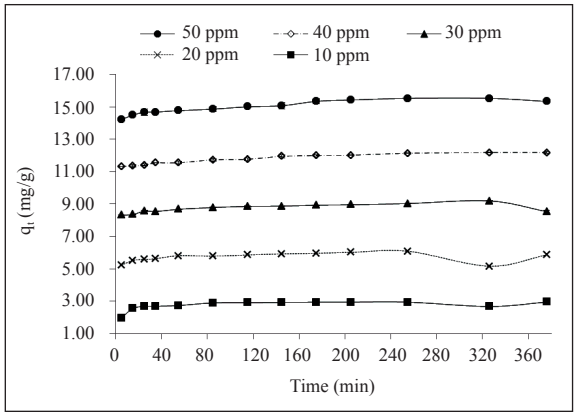

Figure 4: Effect of contact time (10–300 min) and concentration (10–50 mg/L) on MB removal by longkong peels [Dose 0.3 g, pH = 7, T 30°C].

acidic function groups that dissociated to give much negative charges leading to electrostatic interaction between adsorbent and MB cations which may play an important role in MB uptake [22], [23]. Similar adsorption activities have been recorded by various reports [24]–[26].

3.4 *Effect of contact time and initial concentration*

The effect of time on adsorption of MB was studied using 0.3 g longkong peels in five different initial concentrations of MB (10, 20, 30, 40 and 50 mg/L) at pH 7. The results were shown in Figure 4. It was found that the MB uptake increased with increasing of contact time. At the initial stage, the rate of MB

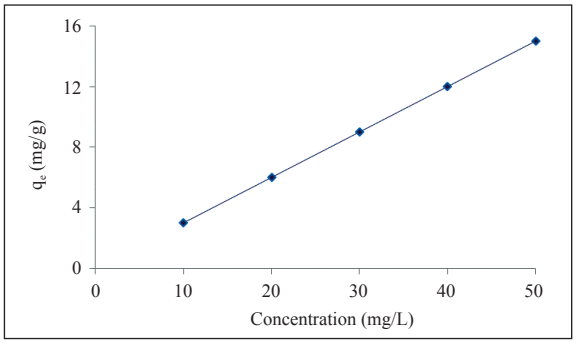

Figure 5: Effect of initial concentration on MB (10–50 mg/L) removal by longkong peels [contact time 205 min, dose 0.3 g, pH = 7, T 30°C].

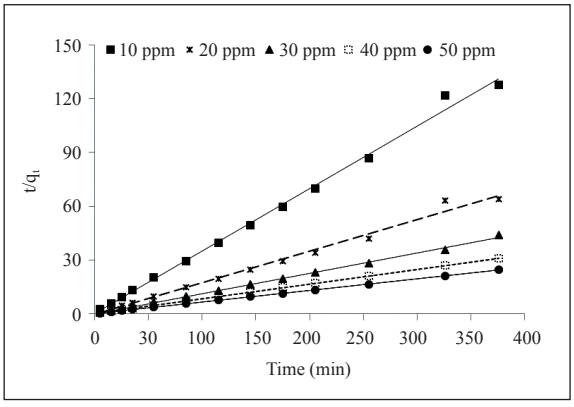

Figure 6: Pseudo second order kinetic plots of MB dye removal by longkong peels.

uptake occurred rapidly and gradually decreased then constant after the equilibrium was obtained. This might be attributed to the high availability of active sites on adsorbents and MB cationic dyes at the beginning stage. Later, a decrease in actives sites and dye ions resulting in lower adsorption rate and finally, lack of available active sites for further MB uptake [27], [28]. The optimum time for each concentration is slightly different. However, at highest concentration of MB, the maximum uptake occurred within 205 min.

The MB adsorption also depended on the initial concentration of adsorbate. The adsorption capacity at equilibrium increased from 2.94 to 15.42 mg/g as the initial MB concentration increased from 10 to 50 mg/g as shown in Figure 5. This result was explained that at higher concentration, the mass transfer driving force increased, thus raised the interaction between MB and longkong peels [29], [30].

3.5 *Adsorption kinetics*

The kinetics of adsorption for MB removal by longkong peels was examined using the two most common models for pseudo-first-order [31] and pseudo-second-order kinetics [32]. The first-order and linearised models were first investigated, using Equations (2) and (3), respectively to fit the data.

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (2)$$

$$\log(q_e - q_t) = \log q_e - K_1.t/2.303 \quad (3)$$

Where q_t and q_e correspond to the mass of MB ions adsorbed onto the powders at time t (min) and at equilibrium respectively, while K_1 is the first-order rate constant. However, the plot of log $(q_e - q_t)$ versus t displayed low regression coefficients, (R^2) indicating that the data could not be acceptably modelled by this equation.

Alternatively, the pseudo-second-order indicated in Equations (4) and (5) was employed to fit the data, where K_2 is the second-order rate constant.

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (4)$$

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (5)$$

The MB adsorption followed the pseudo-second-order as the plot of t/q_t with t gave high regression coefficients (R^2 = 0.9957–0.9999) as illustrated in Figure 6. Moreover, the derived q_e value is close to experimental q_e data (Table 1).

Table 1: Pseudo second order model parameters, calculated mass adsorbed, q_e (cal) and experimental mass adsorbed, q_e (exp) for removal of MB dye by longkong peels

[Dyes] (mg/L)	q_e (exp) (mg/g)	Pseudo-second-order		
		q_e (cal) (mg/g)	K_2	R^2
10	2.94	2.87	0.71	0.9957
20	6.01	5.67	–0.08	0.9906
30	8.98	8.87	2.54	0.9978
40	12.01	12.21	0.03	0.9999
50	15.42	15.50	0.03	0.9998

3.6 *Adsorption isotherm*

The MB adsorption data were fitted to three isotherm models including Langmuir, Freundlich and Temkin isotherms.

On the basic of Langmuir isotherm, adsorbates are adsorbed onto specific sites of adsorbents. All active sites on the homogeneous surface are identical. The energy of adsorption is constant and no movement of adsorbate over the surface [33]. The Langmuir equation and its linear form were expressed by the Equations (6) and (7).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{7}$$

Where q_e (mg/g) is the mass of MB adsorbed per unit mass of adsorbent, C_e (mg/L) is the equilibrium concentration in solution, q_m (mg/g) is the monolayer adsorption capacity and K_L is the Langmuir equilibrium constant. The plot of specific sorption (C_e/q_e) against equilibrium concentration (C_e) for MB adsorption gave the linear regression (R^2) and other parameters in Table 2.

The Freundlich isotherm is based on the assumption that the adsorption is a multilayer process on heterogeneous surface [34]. The Freundlich equations are represented by Equations (8) and (9).

$$q_e = K_F C_e^{1/n} \tag{8}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{9}$$

Where K_F (L/g) is the Freundlich constant associated with the adsorption capacity and n is an empirical parameter related to the adsorption intensity and/or surface heterogeneity. The plot of log q_e against log C_e gave a straight line as shown in Figure 7 with R^2. The parameters of K_F and n calculated from the slope and the intercept are listed in Table 2.

The Temkin isotherm is based on the assumption that the adsorbent-adsorbate interactions that occur during surface coverage result in a linear decrease in the heat of adsorption [35]. This model is defined by Equations (10) and (11).

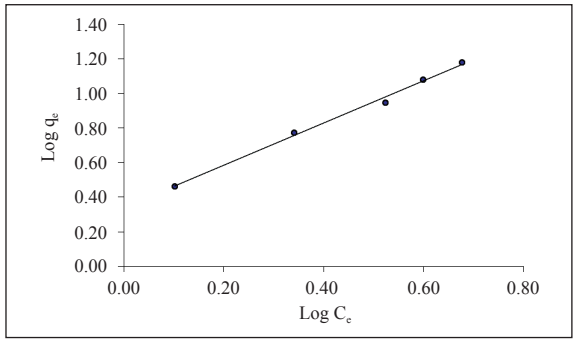

Figure 7: Freundlich isotherm plot for MB removal by longkong fruit peels.

Table 2: Langmuir, Freundlich and Temkin isotherm parameters for MB by longkong peels

Isotherm Parameters		Values
Langmuir:	R^2	0.8721
	K_L	0.0678
	q_m (mg/g)	–31.84
Freundlich:	R^2	0.9953
	K_F	2.19
	$1/n$	1.22
Temkin:	R^2	0.9293
	K_T (L/mg)	5.78
	B_T (kJ/mol)	0.05

$$q_e = \frac{RT}{b} \ln(K_T C_e) \tag{10}$$

$$q_e = B_T \ln K_T + B_T \ln C_e \tag{11}$$

T (K) is the absolute temperature, R (J/mol.K) is the ideal gas constant, K_T (L/mg) is the equilibrium binding constant (at maximum binding energy), b (kJ/mol) is the variation of adsorption energy, and B_T (kJ/mol) is the Temkin constant, corresponding to the heat of adsorption. The plot of q_e and ln C_e was presented in Figure 8.

Regarding to linear regressions (R^2) in Table 2, the Freundlich plot gave the best fitting to the experimental data, followed by Temkin and Langmuir models respectively. The value of slope 1/n is found to be more than 1 indicating that the adsorption is cooperative process. At low concentration, insignificant MB adsorption was obtained but at high concentration, the adsorption became noteworthy [36], [37]. This attributed that longkong peel surfaces are heterogeneous

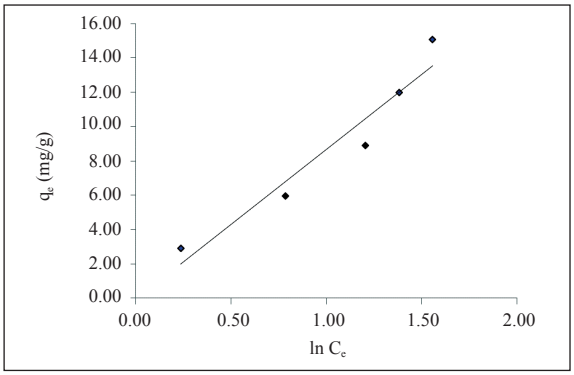

Figure 8: Temkin isotherm plot for MB removal by longkong fruit peels.

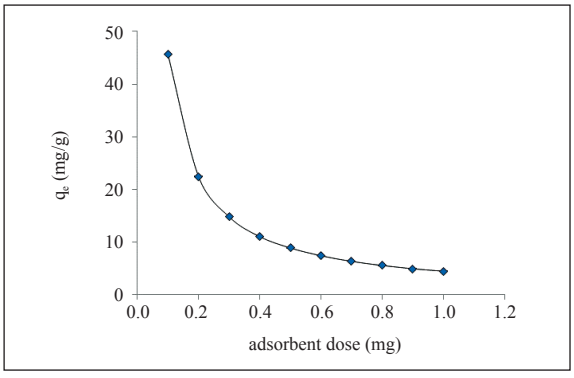

Figure 9: Effect of adsorbent dose on adsorption capacity of MB removal by longkong peel [MB conc. 50 mg/L, pH 7, contact time 205 min, T 30°C].

with plenty of different effective functional groups to adsorb MB cations. Hence, the MB uptake at high concentration became better. The Temkin model could also fit to the MB adsorption data. The calculated heat of adsorption was low implying a weak interaction between MB cations and adsorbents [38], [39].

3.7 *Effect of variation dose*

To evaluate the effective dose, the 50 mg/L MB was shaken with longkong peels which varying mass in the range of 0.1–1.0 g at 30°C for 205 min. The result was shown in the Figure 9. Apparently, the increase in the adsorbent dose led to the decrease of MB uptake which has also been found in previous publishes [40]. At low dosage of 0.1 g, the free actives still left unsaturated after adsorption. Therefore, more adsorbent

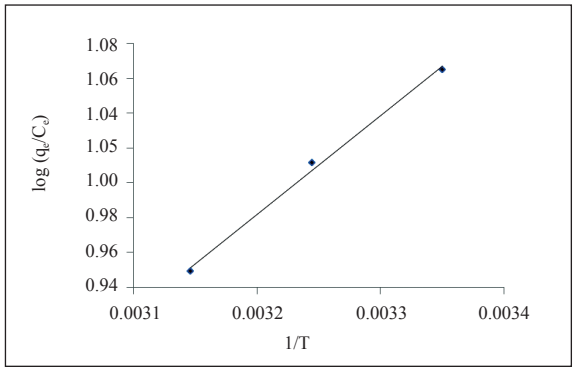

Figure 10: Thermodynamic plots of the adsorption of MB by longkong peels [MB conc. 50 mg/L, adsorbent dose 0.1 g, contact time 205 min, pH 7].

was not required but resulted in poor adsorption capacity [41]–[43].

3.8 *Effect of temperature and thermodynamics*

Longkong peels 0.1 g was mixed with MB 50 mg/L at 30, 40 and 50°C for 205 min to study the influence of temperature and thermodynamic parameters. It was discovered that increasing temperature caused to decreasing of adsorption capacity. At 30°C, the highest yield of adsorption was 45.85 mg/g, followed by 45.35 mg/g at 40°C and 44.71 mg/g at 50°C.

Thermodynamic parameters of changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined using the following Equations (12) and (13).

$$\text{Log } q_e/C_e = \Delta S/2.303R - \Delta H/2.303RT \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

Where R is the gas constant (8.314 J/mol.K) The plot between log (q_e/C_e) was illustrated in Figure 10. The values of ΔH and ΔS obtained from the slope and the intercept, and the calculated ΔG were presented in Table 3. A small negative value of enthalpy change indicated a physical adsorption, mostly, including weak exothermic attractive force, and that the process is energy-stable [44], [45]. Moreover, the negative ΔG reflected that the MB uptake onto longkong peels was favourable and spontaneous nature adsorption process. [46] The change in entropy was also negative value corresponding to the reduction of degrees of

independence of the adsorbed dyes proposing that disordered system is decreased at the interface adsorbate-solution during the adsorption [47].

Table 3: Thermodynamic parameters for the removal of MB dye onto longkong peels

(–) ΔG (kJ/mol), T (°C)			ΔH (kJ/mol)	ΔS (J/mol.K)
30	40	50		
–6.2	–6.06	–5.9	–10.85	–15.36

4 Conclusions

The longkong peels can be used as an economical adsorbent for removal of MB dye. The adsorption capacity was dependent on pH, contact time, initial dye concentration, adsorbent dose and temperature. The optimum removal capacity (45.85 mg/g) was occurred readily at a dosage of 0.1 g longkong peels in the dye concentration of 50 ppm, pH 7 and temperature 30°C over a period of time 205 min. The MB dye adsorption onto longkong peels was an exothermic, feasible and spontaneous process.

Acknowledgments

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