Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.924030

55 (2015) 1333–1341
July

Taylor & Francis
Taylor & Francis Group

Litchi pericarps used as adsorbents for methylene blue removal from solution

Xinge Pan, Xiaochen Li*, Jili Yang, Shujuan Sun, Jiyu Tian, Zhenglei Kong

Water Conservancy and Civil Engineering College, Shandong Agricultural University, Tai'an 271018, Shandong, P.R. China,
Tel. 15053843403; email: xingepan@126.com (X. Pan), Tel. 15866021886; email: lixiaochen02@163.com (X. Li),
Tel. 13562802593; email: 857747251@qq.com (J. Yang), Tel. 13854867706; email: 250650674@qq.com (S. Sun),
Tel. 15163802757; email: 805844994@qq.com (J. Tian), Tel. 15153884772; email: kongzhenglei@163.com (Z. Kong)

Received 1 October 2013; Accepted 8 May 2014

ABSTRACT

The adsorption capacity of methylene blue (MB) on raw or chemically modified litchi pericarp (LP or MLP, respectively) was investigated as a function of contact time, pH, and adsorbent dose. The adsorption isotherms, kinetics, and thermodynamic characteristics were also studied using batch assays. The optimum MB adsorption efficiency on LP and MLP occurred at a contact time of 180 min, pH of 6.0–9.0, and adsorbent dosage of 2 g/L. Langmuir, Freundlich and Dubinin–Radushkevich isotherms and a pseudo second-order kinetic model satisfactorily fit the equilibrium adsorption with high correlation coefficients ($R^2 >$ 0.97). Based on the Langmuir model, the maximum adsorption capacities of MB on LP and MLP were 100 and 139 mg/g, respectively. The results of thermodynamics studies indicated that MB adsorption on both LP and MLP was a spontaneous and exothermic process. The physical characteristics of LP and MLP were also studied using FTIR.

Keywords: Litchi pericarp; Methylene blue; Adsorption; Isotherms; Kinetics; Thermodynamics

1. Introduction

Dye-containing wastewater is discharged from many industries, such as those that manufacture textiles, foods, paper, plastics, and leather. The dye effluents contain complex compounds and toxic synthetic substances. Even very small amounts of dyes can be harmful to aquatic life in downstream environments [1–3]. Methylene blue (MB), one of the most widely applied dyes, is commonly used to color paper and dye cotton, wood, and silk [4]. Although MB is not a very strongly hazardous substance, its harmful effects include increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans suffering from acute exposure [5,6]. Therefore, wastewater containing MB must be properly treated before discharging into the environment.

Several conventional methods have been applied to remove dyes from wastewater, such as coagulation, chemical oxidation, membrane separation, electrochemical processing, and aerobic and anaerobic microbial degradation. However, these methods are not widely used because of inherent limitations [7]. The adsorption technique can effectively remove dyes from wastewater [8–10]. Currently, activated carbon is typically used as an absorbent to remove a wide variety of dyes because of its large surface area and high sorption capacity [11,12]. However, the relatively high cost of activated carbon combined with the need for a regeneration system inevitably restricts its widespread

---

*Corresponding author.

application [13]. Thus, it is necessary to identify alternative methods and low-cost adsorbents for removing dyes from solution. Recently, some nonconventional adsorbents based on agricultural wastes have been studied, such as peanut hulls [14], sugarcane bagasse [15], lemon peel [16], pomelo peel [17], jackfruit peel [18], papaya seeds [19], tea waste [20], walnut shells [21], cashew nut shells [22], pine cones [23], and banana peel [24].

Litchi (*Litchi chinensis* Sonn.), a subtropical fruit, is one of the most popular fruits in Southeast Asia, especially in China. The annual litchi production in China is approximately 1.5 million tons [25]. Litchi pericarp (LP) accounts for more than 15% of the fresh weight of litchi, thereby resulting in notable processing waste volumes [26]. Moreover, LP contains significant amounts of chemical components such as esters, fatty acids, heterocyclic compounds, cyclic ethers, cyclic olefins, and polysaccharides [27]. The abundant carboxyl, hydroxyl, and amide groups in these constituents could play critical roles in adsorption processes, suggesting that LP may also be suitable as a prospective adsorbent. Therefore, the recycling of LP can not only reduce disposable solid wastes, but also provide a new low-cost adsorbent for removing dyes from solution. However, to the best of our knowledge, the adsorption of dyes by LP has, so far, not been reported.

The main purpose of this study was to investigate the feasibility of LP as a new adsorbent for removing MB from aqueous solutions. Raw and chemically modified litchi pericarps (MLPs) were employed as adsorbents in this study. The optimal adsorption conditions were determined in terms of contact time, pH value, and sorbent dose by batch assays. The adsorption equilibrium isotherms, adsorption kinetics, and thermodynamics of MB adsorption onto LPs were also investigated. The adsorption mechanism was investigated using FTIR.

2. Methods and materials

2.1. Adsorbent preparation

Litchis (*L. chinensis* Sonn.) were purchased from a local market in Tai’an City, Shandong, People’s Republic of China. Pericarps were gently separated from the fruit, washed with tap water, and then rinsed thrice with deionized water. Subsequently, they were cut into small pieces and dried at 70℃ in a convection oven until a constant weight was achieved. The dry LPs were ground and sieved to obtain 60 mesh particles.

To chemically modify the substrate, dried LPs (5.0 g) were mixed with 0.1 M NaOH (50 mL) for 24 h [28]. After decanting and filtering three times, the MLPs were rinsed several times with deionized water. The products were then ground and sieved to separate 60 mesh particles for experimental use.

2.2. Adsorbate preparation

MB was purchased in Tianjin, People’s Republic of China. The MB (C.I. Basic Blue 9, Da Mao Chemical Reagent Factory) used in this study had a molecular weight of 373.90 g/mol and the molecular formula, $C_{16}H_{18}ClN_3S{\cdot}3H_2O$. The maximum absorption wavelength was 668 nm. A stock MB solution with a concentration of 0.5 g/L was prepared using powdered MB and water.

2.3. Operating parameters

Batch experiments were carried out using a series of polyethylene centrifuge tubes (100 mL) covered with Teflon sheets. The effects of contact time, pH, and adsorbent dose were studied initially at an MB concentration of 50 mg/L. One parameter was progressively changed while keeping the other two parameters constant. The experiments were carried out in triplicate and the negative controls (with no sorbent), and were simultaneously carried out to ensure that adsorption was by LP and MLP biomass, and not by the container. The initial and equilibrium dye concentrations were determined by absorbance measurements using a double beam UV–vis spectrophotometer (Model UV-2450, Shimadzu Corp., People’s Republic of China) at a detection wavelength of 668 nm.

The MB adsorption efficiency, $A\%$, was calculated from Eq. (1):

$$A\% = (C_0 - C_e)/C_0 \times 100 \tag{1}$$

where C_0 and C_e are the initial and equilibrium MB concentrations (mg/L), respectively.

2.4. Adsorption isotherm measurements

Solutions with MB concentrations of 50, 100, 150, 200, and 250 mg/L were prepared by serially diluting the MB stock solution. For the absorption experiments, prepared LP or MLP powder (60 mesh, 0.1 g) was added to the serially diluted MB solutions (50 mL) without changing the pH, and each mixture was agitated in a shaking water bath for 3 h at 25℃. Subsequently, the reaction mixture was centrifuged, and the absorbance of the residual dye in the supernatant was measured at 668 nm. Langmuir [29], Freundlich [30], and Dubinin–Radushkevich (D-R) [31] isotherms were plotted using standard linear equations, and the two corresponding parameters were calculated from the respective graphs.

2.5. Kinetics studies

For the kinetics studies, a batch technique was used because of its simplicity. A series of polyethylene centrifuge tubes (100 mL) containing 50 mL MB solution (50 mg/L) was kept in a thermostatically controlled shaking water bath (25℃). As described above, the prepared LP or MLP powder (60 mesh, 0.1 g) was added to each tube, and the tubes were mechanically agitated at 220 rpm. At 3 h intervals, a mixture was centrifuged, and the absorbance of the supernatant was measured at 668 nm. Pseudo-first-order [32], Pseudo-second-order [33] and Weber–Morris [34] models were employed to discuss the rate and kinetics of the adsorption of MB on the prepared adsorbents.

2.6. Thermodynamics studies

For the thermodynamics studies, a series of polyethylene centrifuge tubes (100 mL) containing 50 mL MB solution (50 mg/L) was kept in a thermostatically controlled shaking water bath. The temperatures were set at 25, 35, 45, and 55℃. At given time intervals, the solutions were centrifuged and the absorbance of the supernatant was measured at 668 nm. The standard free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated to assess the feasibility of the adsorption process.

2.7. Adsorption/desorption of MLP

Batch process was used for desorption studies in which a known amount of adsorbent and 50 mL of MB solution (100 mg/L) are present. After adsorption, the solution was filtered and the adsorbent was washed several times with distilled water to remove any excess of MB solution. It was then treated with 50 mL of 0.05 M HCl. The amount of MB desorbed was then determined as usual.

3. Results and discussion

3.1. Effect of contact time

The effect of the contact time with LP and MLP on the MB adsorption was investigated to determine the time required to reach equilibrium for the maximum adsorption. As can be observed from Fig. 1, treatment of MB by LP led to rapid adsorption during the initial 30 min, followed by a period of slower adsorption, and finally, saturation at 120 min. This progression resulted in the initial vacancy of the sorbent sites during the first rapid adsorption phase, and the decrease in the number of active sites as the contact time increased, which slowed the adsorption process [17]. In contrast to LP, the MB adsorption efficiency on MLP reached ~100% within 30 min, indicating that MB adsorption on MLP would reach equilibrium much faster than on LP. Moreover, it was clear that the final adsorption efficiency of MB was also much higher for MLP than for LP.

As is well known, the time required to reach equilibrium will increase with an increased initial concentration of the adsorbate. Therefore, we also investigated the adsorption by LP and MLP of MB at a concentration of 250 mg/L; the time to equilibrium was determined to be 180 min by batch experiments. Kinetics data for the adsorption of MB by various adsorbents have revealed widely different adsorption rates. For example, the equilibrium times reported for the adsorption of 50 mg/L MB were 30 and 207 min on papaya seeds [19] and pomelo (*Citrus grandis*) peel [17], respectively.

3.2. Effect of pH

The pH of the solution controls the magnitude of electrostatic charges that bind the ionized dye molecules [35]. In this study, the effect of the initial pH of the solution was determined by agitating LP or MLP powder (0.1 g) in MB solution (50 mL, 50 mg/L) while varying the solution pH from 2.0 to 10.0. Fig. 2 clearly shows that the adsorption of MB on both LP and MLP was at a minimum at pH 2.0, and an increase in MB adsorption efficiency was exhibited upon a solution pH increase to 6.0. However, no significant changes in

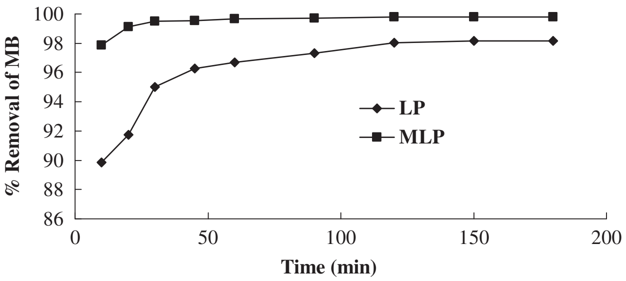

Fig. 1. Effect of contact time on the adsorption of MB by LP and MLP (MB concentration: 50 mg/L; adsorbent concentration: 2 g/L; agitation speed: 220 rpm; temperature: 25℃).

the adsorption efficiency could be identified within the pH range 6.0–10.0. Similar results were reported for the adsorption of MB on banana peel [24] and papaya seeds [19]. The observed influence of pH may be attributed to the fact that, at lower pH values, the surface charge becomes positive, and the higher H^+ concentration strongly competes with the dye cations for the active sites on the LP and MLP surfaces, and results in a reduction in MB binding on the adsorbent surface. Increasing the pH results in a higher number of functional groups available for the binding of MB because of the decreased H^+ concentration, and consequently, the MB adsorption is enhanced. This demonstrates that electrostatic attraction may be considered as one of the important mechanisms responsible for the adsorption of MB on LP and MLP [20]. Additionally, the maximum MB adsorption efficiencies on LP and MLP were 98.17 and 99.72%, respectively, suggesting the higher adsorption capacity of MLP compared to raw LP.

3.3. Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of MB was carried out at LP or MLP loadings of 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, and 5.0 g/L, keeping the initial MB concentration at 50 mg/L, and the temperature at 25℃. Fig. 3 shows the effects of adsorbent dose on the MB adsorption efficiency. The minimum MB adsorption efficiencies of 65.19 and 91.47% were observed at doses of 0.5 g/L for LP and MLP, and were followed by noticeable increases in the MB adsorption upon increasing the dose from 0.5 to 2.0 g/L and 1.0 g/L, respectively. However, no noticeable increases in the MB adsorption could be detected with further increases in the LP and MLP doses. Similar results were also found for the adsorption of MB with walnut shells [21] and papaya seeds [19]. This effect may be attributed to the fact that, at a lower adsorbent dosage, an increase in the available surface area and the number of adsorption sites upon additional dosing results in higher MB adsorption efficiency. However, at higher adsorbent doses, clustering and/or aggregation of adsorbents may occur, resulting in a decrease in the total surface area and the number of binding sites of the adsorbent [21]. Thus, an optimum adsorbent dose of 2 g/L was required for MB removal from solution.

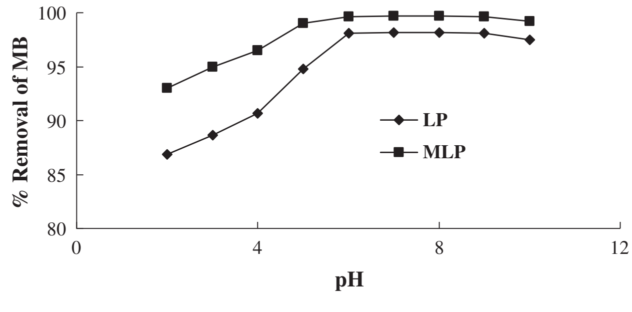

Fig. 2. Effect of pH on the adsorption of MB by LP and MLP (MB concentration: 50 mg/L; adsorbent concentration: 2 g/L; agitation speed: 220 rpm; contact time: 180 min; temperature: 25℃).

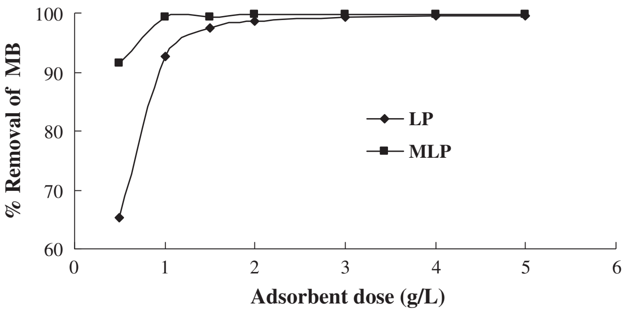

Fig. 3. Effect of adsorbent dose on the adsorption of MB by LP and MLP (MB concentration: 50 mg/L; agitation speed: 220 rpm; contact time: 180 min; temperature: 25℃).

3.4. Isotherm analysis

Adsorption isotherms are important for describing the interaction of the adsorbate with the adsorbent, and they also enable assessment of the adsorption capacity of the adsorbent [35]. In this study, the equilibrium data for LP and MLP were modeled with Langmuir, Freundlich, and D-R isotherm models.

The Langmuir adsorption model is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The expression of the Langmuir model is given by the following linear equation (Eq. (2)):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K} + \frac{C_e}{q_{\max}} \tag{2}$$

where q_e is the amount of adsorbed MB (mg/g), C_e is the concentration at equilibrium (mg/L), $q_{\max}$ is the monolayer capacity of the adsorbent (mg/g), and K is the adsorption constant (L/mg). According to Eq. (2), a plot of C_e/q_e vs. C_e yields a straight line with a slope of $1/q_{\max}$ and an intercept of $1/q_{\max}K$.

The Freundlich equation can be expressed as follows (Eq. (3)):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

where K_F and $1/n$ are Freundlich isotherm constants. According to Eq. (3), the values of K_F and n are calculated from the intercept (log K_F) and slope ($1/n$) of the plot of log q_e vs. log C_e.

The D-R equation can be expressed (Eq. (4)):

$$\ln C_{\text{ads}} = \ln X_m - \beta\varepsilon^2 \tag{4}$$

where C_{ads} is the number of metal ions adsorbed per unit weight of adsorbent (mol/g), X_m is the maximum adsorption capacity (mol/g), β is the activity coefficient related to the mean adsorption energy, and ε is the Polanyi potential. The Polanyi potential is given by (Eq. (5)):

$$\varepsilon = RT \ln\,(1 + 1/C_e) \tag{5}$$

where R is the gas constant (8.314 J/(mol K)), and T is the temperature (K). The saturation limit X_m may represent the total specific micropore volume of the adsorbent. The slope of the plot of ln C_{ads} (mol/g) vs. ε^2 gives β (mol^2/J^2), and the intercept represents the adsorption capacity, X_m (mol/g). The adsorption space in the vicinity of a solid surface is characterized by a series of equi-potential surfaces which possess an equal adsorption potential. This adsorption potential is independent of temperature, but varies from the nature of adsorbent and adsorbate. The adsorption energy can be determined from (Eq. (6)):

$$E = 1/\sqrt{-2\beta} \tag{6}$$

The corresponding isotherm parameters obtained from this study are listed in Table 1. It is evident from the table that the relatively high correlation coefficients R^2, 0.9975, 0.9794 and 0.9871, and 0.9731, and 0.9823 and 0.9874, for the Langmuir, Freundlich, and D-R isotherms of LP and MLP, respectively, suggested that three models could be used to satisfactorily explain the equilibrium adsorption of MB by LP and MLP. Based on the values of the correlation coefficients, it can be concluded that the adsorption process of MB on LP better fits the Langmuir model, while MB adsorption on MLP better follows the isotherm of the D-R model. Additionally, the maximum adsorption capacities obtained from the Langmuir model were 100 and 138.89 mg/g for LP and MLP, respectively, indicating the higher adsorption capacity of MLP compared to LP.

The values of $1/n$ in the Freundlich isotherm can give an indication of the favorability of adsorption [19]. The results in Table 1 show that the value of $1/n$ obtained in the present assay, varying between 0 and 1, indicates favorable adsorption of MB onto LP and MLP. Moreover, the magnitude of the Freundlich constant K_F indicates an easy uptake of MB from aqueous solution. The E value calculated was 14.624 and 13.531 kJ/mol ($16.0 > E > 8.0$) for LP and MLP, which was consistent with an ion exchange adsorption mechanism [31]. Additionally, the maximum sorption capacity of MB has been reported to be 53.1 mg/g for perlite [36], 5.57 mg/g for fly ash [5], 68.03 mg/g for peanut hulls [37], and 85.16 mg/g for tea waste [20]. When compared to these reported adsorbents, the much higher maximum sorption capacity of MB on MLP obtained in this study suggests the higher potential of MLP as a new adsorbent for removing dyes from solutions.

3.5. Adsorption kinetics

Pseudo-first-order, pseudo-second-order and Weber–Morris kinetic models were employed to determine the MB adsorption kinetics by LP and MLP. Lagergren proposed a method for adsorption analysis using a pseudo-first-order kinetics equation in the form of Eq. (7):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

where q_e (mg/g) is the adsorption capacity at equilibrium, q_t (mg/g) is the adsorption capacity at time t, and k_1 is the pseudo-first-order rate constant. At the initial condition $q_t = 0$ at $t = 0$, Eq. (7) can be expressed as (Eq. (8)):

Table 1
Isotherm parameters for the adsorption of MB by LP and MLP

	Langmuir			Freundlich			D-R	
Adsorbents	$q_{\max}$ (mg/g)	K (L/mg)	R^2	K_F	n	R^2	E (kJ/mol)	R^2
LP	100	0.244	0.9975	29.08	0.3096	0.9731	14.624	0.9871
MLP	138.89	1.180	0.9794	65.01	0.4405	0.9823	13.531	0.9887

$$\log\ (q_e - q_t) = \log\ q_e - \frac{k_1}{2.303} t \tag{8}$$

According to Eq. (8), the values of k_1 and q_e can be obtained from a linear plot of log $(q_e - q_t)$ against time t.

The pseudo-second-order kinetic equation based on the equilibrium adsorption can be described as follows (Eq. (9)):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\ t \tag{9}$$

where k_2 (g/(mg min)) is the pseudo-second-order rate constant, q_e (mg/g) is the adsorption capacity at equilibrium, and q_t (mg/g) is the adsorption capacity at time t. The equilibrium adsorption capacity q_e, and the pseudo-second-order rate constant, k_2, can be calculated from the slope ($1/q_e$) and the intercept ($1/(k_2 q_e{}^2)$) of the plot of t/q_t against time t.

The Weber–Morris can be expressed as follows (Eq. (10)):

$$q_t = k_{\mathrm{id}} t^{1/2} \tag{10}$$

where k_{id} is the intra-particle diffusion rate constant.

Table 2 shows the adsorption rate constants for MB adsorption on LP and MLP determined by pseudo-first-order and pseudo-second-order models. As observed from Table 2, the correlation coefficients (R^2) for the pseudo-first-order model were very low, and the theoretical $q_{e(\mathrm{cal.})}$ values obtained by the pseudo-first-order model were distant to the experimental $q_{e(\mathrm{exp.})}$ values, suggesting that the adsorption of MB on LP and MLP was not likely to follow such a model. However, the correlation coefficients were very high ($R^2 = 1$) for the pseudo-second-order model for both LP and MLP. Moreover, the theoretical $q_{e(\mathrm{cal.})}$ values obtained by the pseudo-second-order model were much closer to the experimental $q_{e(\mathrm{exp.})}$ values than those obtained by the pseudo-first-order model. Therefore, it can be concluded that the pseudo-second-order model provides a better estimation for MB adsorption on LP and MLP. Similar kinetics results were also observed for the adsorption of MB on other bio-adsorbents, such as jackfruit peel [18], papaya seeds [19], and guava (*Psidium guajava*) leaf powder [38]. Additionally, the higher k_2 value for MLP than for LP indicated that the MB adsorption was faster on MLP.

In order to understand the rate-controlling steps affecting the adsorption process, the experimental data was fit to the Weber–Morris model. For this model, if the intraparticle diffusion is the sole rate-limiting step, a plot of q_t vs. $t^{1/2}$ will pass through the origin [34]. However, it was not observed in Fig. 4, indicating that the surface adsorption and intraparticle diffusion occurred concurrently during the adsorption process.

3.6. Thermodynamics studies

Thermodynamics parameters—standard free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°)—were calculated from the experimental data acquired upon changing the temperature (298–328 K) using the Van't Hoff equation (Eq. (11)) [39]:

$$\ln K_d = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{11}$$

where T is the temperature (K), R is the ideal gas constant (8.314 J/(mol K)), and K_d is the thermodynamic equilibrium constant, which is defined as follows (Eq. (12)) [40]:

$$K_d = \frac{q_e}{C_e} \tag{12}$$

where q_e is the equilibrium adsorption capacity of MB on the adsorbent (mg/g), and C_e is the equilibrium concentration of MB in aqueous solution (mg/L).

According to Eqs. (11) and (12), ΔH° and ΔS° were calculated from the slope and the intercept of the plot of ln K_d vs. $1/T$. Then, the values of ΔG° at different temperatures were calculated using Eq. (11).

Table 3 shows the thermodynamics parameters for the adsorption of MB by LP and MLP. The negative values of ΔH° show that the adsorption process was

Table 2
Kinetics parameters studied for MB adsorption on LP and MLP

	Pseudo-first-order				Pseudo-second-order		
Adsorbents	$q_{e(\mathrm{exp.})}$ (mg/g)	$q_{e(\mathrm{cal.})}$ (mg/g)	k_1 (g/mg min)	R^2	$q_{e(\mathrm{cal.})}$ (mg/g)	k_2 (g/mg min)	R^2
LP	49.50	2.48	0.0309	0.703	49.75	0.032	1
MLP	49.95	0.35	0.0353	0.835	50.00	0.24	1

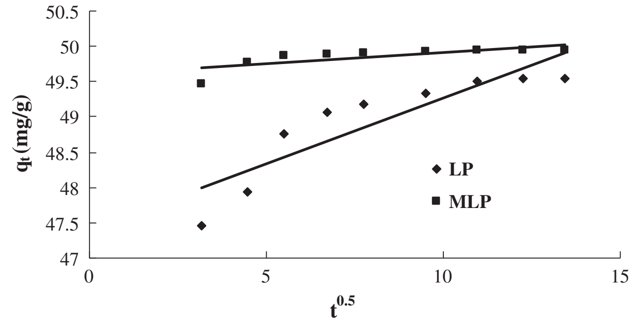

Fig. 4. Weber–Morris model plots of MB adsorption onto LP and MLP.

exothermic, and the positive values of ΔS° suggest increased randomness at the solid/solution interface during the adsorption of MB on LP and MLP. The negative values of ΔG° indicate the spontaneous nature of the adsorption for MB over the temperature range 298–328 K.

3.7. FTIR spectra of LP and MLP

The origin and nature of the biosorbent, such as its physical structure, chemical nature and functional groups may control the biosorption performance. The FTIR spectra of raw litchi peel, before and after chemical treatment in the range of 4,000–400 cm^{-1} were taken to identify the functional groups in the biosorption. The FTIR spectra of LP (a) and MLP (b) are shown in Fig. 5.

The examination of the obtained spectra has the typical peaks for –OH groups at 3,338–335 cm^{-1}, alkyl CH at 2,924–2,926 cm^{-1}, the C=O bond of non-ionic carboxylic acids at 1,740–1,741 cm^{-1}, asymmetric/antisymmetrical C=O vibration of ionic carboxylate groups at 1,622–1,624 cm^{-1}, and –OH groups at 1,028–1,032 cm^{-1} are assigned to C–OH stretching vibrations of alcoholic [41]. The comparisons of LP and MLP, the stretching peak intensity of OH and –COO^{-}, indicated the OH and –COO^{-} were exposed on the surface of litchi peels.

Table 3
Thermodynamics parameters for the adsorption of MB by LP and MLP

Adsorbents	T (K)	K_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
LP	298	29.74	−8.42	−8.04	1.26
	308	26.81	−8.43		
	318	24.82	−8.44		
	328	21.93	−8.45		
MLP	298	399.06	−14.86	−14.71	0.50
	308	338.97	−14.86		
	318	276.49	−14.87		
	328	233.44	−14.87		

Gong et al. [14] have showed the OH and COO^{-} were major functional groups in the adsorption of cationic dyes. The adsorption reaction mechanism between OH and COO^{-} and MB^{+} may be written as following.

$$\mathrm{R-OH} \xrightarrow{\mathrm{NaOH}} \mathrm{R-ONa} \xrightarrow{\mathrm{MB^+}} [\mathrm{R-O}]^{-}\ \mathrm{MB^+}$$

$$\mathrm{R-COO^-} + \mathrm{MB^+} \longrightarrow [\mathrm{R-COO}]^{-}\ \mathrm{MB^+}$$

3.8. Desorption studies

As was known, the reusability was a very important factor for developing a novel adsorbent in practice applications. Therefore, the adsorption–desorption cycle was repeated four times using the same biomass of MLP with 0.05 M HCl. The adsorption removal (%) was calculated, whose initial concentration was 100 mg/L. The results showed that, in the first cycle, the removal efficiency by adsorption was more than 99.58% for MB. From the second to fourth cycle, the MLP biomass had slightly changed adsorption removal ranged from 90.74 to 81.05%. The results showed that the MLP can be repeatedly used in biosorption process without detectable losses in their adsorption capacities.

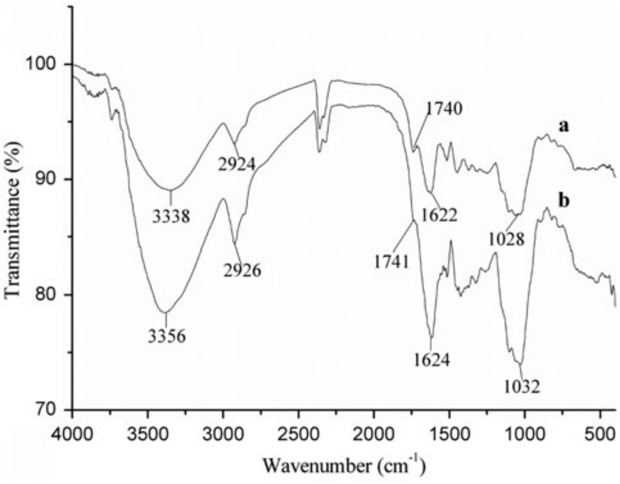

Fig. 5. FTIR spectra of LP (a) and MLP (b).

4. Conclusion

LP and MLP showed high MB adsorption capacities in aqueous solution, with maximum capacities of 100 and 139 mg/g, respectively, demonstrating their promising potentials as bio-adsorbents for the removal of MB from aqueous systems. The adsorption equilibrium of MB on LP and MLP could be described satisfactorily by the Langmuir, Freundlich, and D-R isotherms. The MB adsorption kinetics on LP and MLP could be estimated more suitably by a pseudo-second-order kinetic model than by a pseudo-first-order model, suggesting that MB adsorption was mainly controlled by a chemical process. Additionally, the results of thermodynamics studies indicated that MB adsorption on LP and MLP was a spontaneous and exothermic process. The FTIR analysis showed that OH and COOH were major functional groups in the adsorption of MB. The adsorption–desorption cycles suggested that MLP can be repeatedly used in adsorption process. Taking into consideration all the above obtained results, it can be suggested that LP should be a promising and favorable adsorbent for the removal of MB from aqueous solutions.

Acknowledgment

The present study was funded by the National Science Foundation for Young Scholars of China (No. 51208173).

References

[1] C.C. Wang, L.C. Juang, T.C. Hsu, C.K. Lee, J.F. Lee, F.C. Huang, Adsorption of basic dyes onto montmorillonite, J. Colloid Interface Sci. 273 (2004) 80–86.

[2] S. Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu, Removal of dyes from aqueous solution using fly ash and red mud, Water Res. 39 (2005) 129–138.

[3] K. Marungrueng, P. Pavasant, Removal of basic dye (Astrazon Blue FGRL) using macroalga *Caulerpa lentillifera*, J. Environ. Manage. 78 (2006) 268–274.

[4] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: A review, J. Hazard. Mater. 177 (2010) 70–80.

[5] K.V. Kumar, V. Ramamurthi, S. Sivanesan, Modeling the mechanism involved during the sorption of methylene blue onto fly ash, J. Colloid Interface Sci. 284 (2005) 14–21.

[6] V. Vadivelan, K.V. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, J. Colloid Interface Sci. 286 (2005) 90–100.

[7] M.T. Sulak, E. Demirbas, M. Kobya, Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran, Bioresour. Technol. 98 (2007) 2590–2598.

[8] G.M. Walker, L. Hansen, J.A. Hanna, S.J. Allen, Kinetics of a reactive dye adsorption onto dolomitic sorbents, Water Res. 37 (2003) 2081–2089.

[9] A.K. Jain, V.K. Gupta, A. Bhatnagar, A. Suhas, A comparative study of adsorbents prepared from industrial wastes for removal of dyes, Sep. Sci. Technol. 38(2) (2003) 463–481.

[10] J. Li, W. Zhang, Adsorptive removal of malachite green from aqueous solution using modified peanut shell, Desalin. Water Treat. 51 (2013) 5831–5839.

[11] A.L. Ahmad, M.M. Loh, J.A. Aziz, Preparation and characterization of activated carbon from oil palm wood and its evaluation on methylene blue adsorption, Dyes Pigm. 75 (2007) 263–272.

[12] H. Deng, L. Yang, G.H. Tao, J.L. Dai, Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation—Application in methylene blue adsorption from aqueous solution, J. Hazard. Mater. 166 (2009) 1514–1521.

[13] V.C. Srivastava, I.D. Mall, I.M. Mishra, Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA), Chem. Eng. J. 132 (2007) 267–278.

[14] R.M. Gong, M. Li, C. Yang, Y.Z. Sun, J. Chen, Removal of cationic dyes from aqueous solution by adsorption on peanut hull, J. Hazard. Mater. 121 (2005) 247–250.

[15] D.M. Indra, C.S. Vimal, K.A. Nitin, Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash—Kinetic study and equilibrium isotherm analyses, Dyes Pigm. 69 (2006) 210–223.

[16] K.V. Kumar, Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel, Dyes Pigm. 74 (2007) 595–597.

[17] B.H. Hameed, D.K. Mahmoud, A.L. Ahmad, Sorption of basic dye from aqueous solution by pomelo (*Citrus grandis*) peel in a batch system, Colloids Surf., A 316 (2008) 78–84.

[18] B.H. Hameed, Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent, J. Hazard. Mater. 162 (2009) 344–350.

[19] B.H. Hameed, Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue, J. Hazard. Mater. 162 (2009) 939–944.

[20] Md.T. Uddin, Md.A. Islam, S. Mahmud, Md. Rukanuzzaman, Adsorptive removal of methylene blue by tea waste, J. Hazard. Mater. 164 (2009) 53–60.

[21] J. Yang, K.Q. Qiu, Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal, Chem. Eng. J. 165 (2010) 209–217.

[22] P. Senthil Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, S. Sivanesan, Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions, Desalination 261 (2010) 52–60.

[23] N.M. Mahmoodi, B. Hayati, M. Arami, C. Lan, Adsorption of textile dyes on pine cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies, Desalination 268 (2011) 117–125.

[24] K. Amela, M.A. Hassen, D. Kerroum, Isotherm and kinetics study of biosorption of cationic dye onto banana peel, Energy Procedia 19 (2012) 286–295.

[25] B. Yang, M.M. Zhao, Y. Liu, B.Z. Li, Characterization of litchi pericarp polysaccharide, Nat. Prod. Res. Dev. 17 (2005) 685–687.

[26] M. Nagle, K. Habasimbi, B. Mahayothee, M. Haewsungcharern, S. Janjai, J. Müller, Fruit processing residues as an alternative fuel for drying in northern Thailand, Fuel 90 (2011) 818–823.

[27] G.Q. Song, X.Z. Bu, L.Q. Gu, R. Chen, GC-MS analysis of components in litchi pericarp, Acta Sci. Nat. Univ. Sunyatseni 38(4) (1999) 48–51.

[28] X.M. Li, Y.R. Tang, X.J. Cao, D.D. Lu, F. Luo, W.J. Shao, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, Colloids Surf., A 317 (2008) 512–521.

[29] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[30] H.M.F. Freundlich, Uber die adsorption in losungen (Adsorption in solution), J. Phys. Chem. 57 (1906) 385–470.

[31] Z.L. Kong, X.C. Li, J.Y. Tian, J.L. Yang, S.J. Sun, Comparative study on the adsorption capacity of raw and modified litchi pericarp for removing Cu(II) from solutions, J. Environ. Manage. 134 (2014) 109–116.

[32] S. Lagergren, Zur theorie der sogenannten adsorption geloester stoffe (The theory about the adsorption of solute), K. Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.

[33] M.P. Tavlieva, S.D. Genieva, V.G. Georgieva, L.T. Vlaev, Kinetic study of brilliant green adsorption from aqueous solution onto white rice husk ash, J. Colloid Interface Sci. 409 (2013) 112–122.

[34] S. Karagöz, T. Tay, S. Ucar, M. Erdem, Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption, Bioresour. Technol. 99 (2008) 6214–6222.

[35] M.A.M. Salleh, D.K. Mahmoud, W.A.W.A. Karim, A. Idris, Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review, Desalination 280 (2011) 1–13.

[36] M. Doğan, M. Alkan, Y. Onganer, Adsorption of methylene blue from aqueous solution onto perlite, Water Air Soil Pollut. 120 (2000) 229–248.

[37] R.M. Gong, Y.Z. Sun, J. Chen, H.J. Liu, C. Yang, Effect of chemical modification on dye adsorption capacity of peanut hull, Dyes Pigm. 67 (2005) 175–181.

[38] V. Ponnusami, S. Vikram, S.N. Srivastava, Guava (*Psidium guajava*) leaf powder: Novel adsorbent for removal of methylene blue from aqueous solutions, J. Hazard. Mater. 152 (2008) 276–286.

[39] S. Liang, X.Y. Guo, N.C. Feng, Q.H. Tian, Isotherms, kinetics and thermodynamic studies of adsorption of Cu^{2+} from aqueous solutions by Mg^{2+}/K^{+} type orange peel adsorbents, J. Hazard. Mater. 174 (2010) 756–762.

[40] K. Saltalı, A. Sarı, M. Aydın, Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality, J. Hazard. Mater. 141 (2007) 258–263.

[41] M.R. Lasheen, N.S. Ammar, H.S. Ibrahim, Adsorption/desorption of Cd(II), Cu(II) and Pb(II) using chemically modified orange peel: Equilibrium and kinetic studies, Solid State Sci. 14 (2012) 202–210.