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Removal of methylene blue from wastewater using fallen leaves as an adsorbent

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ABSTRACT

The potential of the fallen leaves of Platanus as a natural biosorbent was investigated for adsorptive removal of methylene blue (MB) from aqueous solutions. Variables, including solution pH, initial MB concentration, biosorbents dose and ionic strength, were investigate to determine their effects on biosorption. The removal rate at pH = 7 is the maximum value (95.23%). The extent of the MB removal increased with initial MB concentration, biosorbent dose and ionic strength. Furthermore, the fallen leaves could be regenerated through the desorption of MB in deionized water and reused to adsorb the dye again. The equilibrium data could be well interpreted by Temkin isotherm followed by Langmuir and Freundlich isotherms. Lagergren first-order, Ho second-order, and Weber and Morris intraparticle model were used to explain the behavior of the adsorbent, and the kinetic data fitted well with Ho second-order model. The values of activation energy were 14.26 kJ/mol, which indicated that MB biosorption onto the leaves was mainly physical. The thermodynamics parameters: ΔG°, ΔH°, and ΔS° were evaluated, which indicated the biosorption was a spontaneous, endothermic process, meanwhile an increase in temperature was advantaged for leaves to adsorb MB. The results of Fourier transform infrared spectroscopy showed that the functional groups hydroxyl (–OH) and carboxyl (–COOH) may be potential biosorption sites for MB dye.

Keywords: Fallen leaves; Methylene blue; Isotherms; Kinetics; Thermodynamics

1. Introduction

The textile industry plays an important part in the economy of several countries around the world. Dyeing is an essential operation during textile fiber processing, and this operation produces more and more dyeing wastewater with the development of textile industry. The colored water can affect plant life and aquatic animals, and thus, an entire ecosystem may be destroyed by various dyes in water.

Color can cause hazard to the environment due to the presence of a large number of contaminants like toxic organic residues, acids, bases, and inorganic contaminants [1]. In addition, most of the dyes are hard to remove by biological treatment processes. Conventionally, the dyes can be treated by physical and chemical methods. Various physicochemical

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techniques, such as chemical coagulation, adsorption on active carbon, reverse osmosis, and ultrafiltration [2], are usually used to treat dyeing wastewater. However, these methods are only available for the wastewater with lower dye concentrations. In recent years, some highly effective techniques such as ozonation and Fenton's reagent has been reported, but the high cost of these methods leads us to further consideration.

Currently, the sorption technique for the treatment of wastewater containing dye is proved to be effective and attractive. In addition, this method will become inexpensive if the material used as sorbent is cheap and does not require any expensive additional pretreatment step [3]. Natural adsorbents can recycle the waste that is usually abandoned and pollutes the environment.

An extensive number of sorption studies is found in the literature, and biosorption is proved to be low-cost and effective. Rastogi et al. [1] used fly ash as an adsorbent by hydrocyclone to remove methylene blue (MB) from wastewater. Prahas et al. [4] tried to prepare activated carbon with jackfruit peel waste, and the activated carbons had well-developed pore sizes and big surface areas. Ma et al. [2] reported that Fe_2O_3-modified kaolin had higher catalytic activity in the electrochemical degradation of MB wastewater. Study of various parameters by Uddin et al. [3] revealed that adsorption equilibrium of tea waste reached within 5 h for MB concentrations of 20–50 mg/L, and the mechanism of adsorption was reversible and ion-exchange. Khan et al. [5] studied the interaction of Acid Yellow 99 (AY 99) with coir pith, and the results established that one gram of coir pith could adsorb 442.13 mg of AY 99. Chowdhury et al. [6] investigated the adsorption of malachite green using chemically modified rice husk; adsorption thermodynamics, kinetics, and isosteric heat were studied. Kumar and Ahmad [7] examined the biosorption characteristics of crystal violet from the aqueous solution onto treated ginger waste. Deniz and Saygideger [8] removed a hazardous azo dye (Basic Red 46) from aqueous solution by princess tree leaf. Thus, the leaf as a low-cost and abundant biosorbent could be an alternative for the removal of dyes from wastewater.

In this experiment, fallen leaves of Platanus were used to adsorb MB from aqueous solution. Variables of the system, including solution pH, initial MB concentration, biosorbents dose, and ionic strength, were investigate to determine their effects on biosorption. The isotherm constants for the Langmuir, Freundlich and Temkin isotherm model have been obtained using linear regressive analysis. Lagergren first-order, Ho-second order, and Weber and Morris intraparticle model were used to explain the behavior of the adsorbent. The thermodynamics parameters: ΔG°, ΔH°, and ΔS° have been calculated. The characterization of leaves before and after biosorption was analyzed by Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM) method.

2. Materials and methods

2.1. Materials

The fallen leaves used as an adsorbent in the present investigation were collected from Qingdao University of Science and Technology campus. The leaves were washed with hot distilled water for several times to clean the dust and dissolvable substance. Then, the leaves were dried at 343 K for 24 h and cut into appropriate sizes (0.9–0.45 mm). At last, the adsorbent was stored in desiccators for use.

Solid morphology was determined by scanning electron microscopy (SEM, JSM6700F, JEOL, Japan).

2.2. Adsorbate/methylene blue

MB is a basic dye, with the molecular formula $C_{16}H_{18}C1N_3S{\cdot}3H_2O$ and molecular weight 373.90, and was chosen as adsorbate. The chemical structure is shown in Fig. 1. The stock solution of MB was prepared (1,000 mg/L), and the desired concentration can be obtained by diluting stock solution with distilled water. The concentration of MB in aqueous solution was measured by a double-beam UV–VIS spectrophotometer (TU-1901, Beijing Pgeneral, China) at λ_{max} of 665 nm. A calibration plot was made in the concentration range of 1–10 mg/L for determination of the dye concentration.

2.3. pH at point zero charge (pH_{PZC}) determination

The pH_{PZC} (point of zero charge) is pH when the charge on the leaves surface is zero. The procedure of pH drift method [4] could be described as follows:

To a series of 250-mL conical flasks, 50 mL of 0.01 N NaCl was added. Then, the initial solution pH

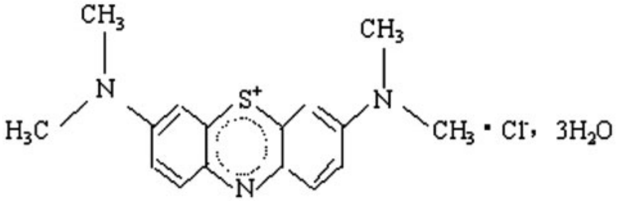

Fig. 1. Chemical structure of MB dye.

values ($pH_{initial}$) were adjusted in range between 2 and 12 with interval 2 using 0.01 N HCl solutions and 0.01 N NaOH. After constant value of pH initial had been reached, 0.15 g of leaves sample was added into each conical flask and caped them immediately. Then, shook them for 48 h to reach equilibrium. After 48 h, pH of solution was measured noted as pH_{final}. The pH_{PZC} of leaves sample is the point when $pH_{initial} = pH_{final}$.

2.4. Sorption experiments

Biosorption experiments were carried out with 200 mL MB solutions of desired concentration mixing 0.5 g adsorbent in a 250-mL Erlenmeyer flask. The mixture was agitated (400 rpm) at 25℃ for 7 h unless otherwise stated. The influence of hydrogen ion concentration on the biosorption process was studied over a pH range of 3–11, with adjustments being made using 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. The effect of initial MB concentration was studied in the range from 50 to 500 mol L^{-1} at pH 7. The effect of biosorbents dose on the biosorption capacity of each adsorbent was investigated in the biosorbents dose ranged from 0.5 to 2 g at pH 7. And the ionic strength was adjusted with NaCl solution (0.0–0.1 mol L^{-1}).

The removal rate of dye was calculated as follows:

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

where C_0 is the initial dye concentration in the solution (mg/L); C is the liquid phase dye concentration at certain adsorption time (mg/L).

The adsorption capacity q (mg/g), defined as follows:

$$q = \frac{V(C_0 - C)}{M} \tag{2}$$

where V is the volume of solution (L); and M is the weight of biosorbent used (g).

The amount of dye adsorbed at equilibrium, q_e (mg/g), was calculated as follows:

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{3}$$

where C_e is the liquid-phase dye concentration at equilibrium (mg/L).

2.5. Desorption and reuse experimental

For desorption experiments, MB-loaded leaves (obtained from previous adsorption process with 0.5 g adsorbent and 1.0 g adsorbent, at a fixed pH of 7 and initial MB concentration of 100 mg/L) were all placed in 250-mL Erlenmeyer flask and contacted with 50 mL of deionized water. The mixtures were agitated on a rotary shaker for 2 h at room temperature. The remaining procedure was the same as that employed in the biosorption equilibrium experiments. After desorption, the regenerated biosorbent was reused in adsorption experiments.

2.6. Recycling experiment

MB-loaded leaves (obtained from previous adsorption process with 0.5 g adsorbent, at a fixed pH of 7 and initial MB concentration of 100 mg/L) were centrifuged and directly added to the same with the previous wastewater, and the process was repeated for three times.

2.7. Equilibrium, kinetic, and thermodynamic studies

2.7.1. Biosorption isotherm

Isotherm studies were performed by mixing 0.25 g leaves with 100 mL of MB solution in 250-mL conical flask for 400 min to equilibrium, the concentration ranging from 100 to 500 mg/L, and the temperature ranging from 293 to 323 K.

Sorption equilibrium provides fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation [3]. In present investigation, the equilibrium data were attempted using the nonlinear forms of the Langmuir, Freundlich and Temkin models isotherm, which are shown as below:

Langmuir model [9]:

$$q_e = \frac{K_L C_e}{1 + K_L C_e} q_m \tag{4}$$

where q_e is the dye uptake capacity calculated according to Eq. (3) (mg/g), C_e is the concentration of dye in the solution (mg/L) when equilibrium is reached, q_m is the uptake capacity when the surface is completely covered with dye (maximum uptake capacity), and K_L is a constant that represents the affinity between the biosorbent and dye.

One of the essential characteristics of this model can be expressed in terms of the dimensionless separation factor for equilibrium parameter, R_L [8], defined as follows:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

The value of R_L indicates the type of isotherm to be irreversible (R_L = 0), favorable ($0 < R_L < 1$), linear (R_L = 1) or unfavorable ($R_L > 1$).

Freundlich model [10]:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{6}$$

where K_F is the biosorption equilibrium constant, and n is a constant indicative of biosorption intensity. In general, $0.1 < \frac{1}{n} < 0.5$, it is easy to adsorb; $\frac{1}{n} > 2$, the material is difficult to adsorb.

Temkin model [11]:

$$q_e = \left(\frac{RT}{b}\right) \ln\,(AC_e) \tag{7}$$

where b and A are the Temkin constants. R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K).

The linearized forms of the Langmuir, Freundlich and Temkin equations can be written as follows:

Langmuir model:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \tag{8}$$

Freundlich model:

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

Temkin model:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \tag{10}$$

2.7.2. Reaction kinetics

For the kinetics of adsorption process, three theoretical models have been considered: Lagergren first-order; Ho-second order, and Weber and Morris intraparticle model.

First order [12]:

$$\frac{\mathrm{dq}}{\mathrm{d}t} = k_1(q_e - q) \tag{11}$$

where q is the adsorption capacity defined according to Eq. (2) (mg/g), q_e is the equilibrium capacity calculated according to Eq. (3) (mg/g), k_1 is the Lagergren constant (1/min) and t is the contact time (h).

Second order [13]:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_2(q_e - q)^2 \tag{12}$$

where k_2 is the second-order constant (mg/g min), which can be used to estimate the activation energy (E_a) of the adsorption using S. Arrhenius equation:

$$k_2 = A_0 \exp\left(-\frac{E_a}{RT}\right) \tag{13}$$

where A_0 is the temperature-independent factor (g/mg min), R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature(K).

Weber and Morris intraparticle model [14]:

$$q = K_i t^{\frac{1}{2}} + C \tag{14}$$

where K_i is the intraparticle diffusion rate constant (mg/g min$^{1/2}$), and C is a constant bound up with the thickness of the boundary layer.

The linearized forms of the first-order and second-order can be written as follows:

First order:

$$\ln\left(\frac{q_e - q}{q_e}\right) = -k_1 t \tag{15}$$

Second order:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{16}$$

2.7.3. Thermodynamics

Thermodynamic considerations of a biosorption are necessary to define the feasibility, spontaneity, and heat change for the biosorption process. The Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) investigated in this study can be estimated by the following equations:

$$\Delta G^\circ = -RT \ln K_C \tag{17}$$

$$\ln K_C = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{18}$$

where K_C is the equilibrium constant (q_e/C_e). By plotting lnK_C vs. $1/T$, the values of ΔH° and ΔS° can be determined from the slope and intercept.

2.8. FT-IR measurements

Before and after biosorption, the leaves were characterized by FT-IR spectrums (FT-IR-8400S, SHIMADZU, Japan). Samples were freeze-dried and stored in the desiccator. They were mixed with KBr in the ratio of 1:100 and were pressed to pellet. The pellet was immediately analyzed in the range of 4,000–400 cm^{-1} with an interval of 1.93 cm^{-1}.

3. Results and discussion

3.1. Compare of MB adsorption capacity among different adsorbents

Table 1 summaries the maximum MB adsorption capacity (q_0) of the leaves with different adsorbents materials as reported in previous studies. The results show that the adsorption capacity of the leaves is lower than that of *Posidonia oceanica* (*L.*) dead leaves, Wheat straw, *Corynebacterium glutamicum*, *Scolymus hispanicus* Banana stalk, and Peanut hull. Nevertheless, the adsorption capacity of the leaves is comparable with other bio-adsorbents and natural minerals, and as waste, it is so cheap. Hence, the leaf can be used as effective low-cost adsorbents to remove MB from aqueous solution.

Table 1
Adsorption capacity of different adsorbents for MB adsorption

Adsorbents	Sorption capacity q_0 (mg/g)	References
Posidonia oceanica (*L.*) dead leaves	482.6	[15]
Wheat straw	396.9	[16]
Corynebacterium glutamicum	337.5	[17]
Scolymus hispanicus	263.92	[18]
Banana stalk	243.90	[19]
Peanut hull	158.1	[20]
Platanus leaf	145.62	This work
Kenaf core fibres	131.6	[21]
Saccharomyces cerevisiae	117.4	[22]
Sugarcane bagasse	115.3	[23]
Wheat bran	99.84	[24]
Tea waste	85.16	[3]
Date stones	43.47	[25]
Fly ash	42.06	[1]
Palm-trees waste	39.47	[25]
Paspalum notatum	31	[26]
Kaolin	25	[2]
Mansonia sawdust	16.11	[27]
Cotton dust	15.78	[28]
Beer brewery waste	4.92	[29]
Rice husk	4.41	[30]

3.2. pH_{PZC}

It can be seen from Fig. 2 that pH = 7 is the point where $pH_{initial} = pH_{final}$, so pH = 7 is the pH_{PZC} of leaves sample. The net charge in the leaves surface is zero on condition that the solution approaches pH = 7. The pH_{PZC} is bound up with the effect of pH on dye adsorption, which is discussed below.

3.3. Influencing factors

3.3.1. Effect of pH

The pH value of the solution is an important control parameter in the adsorption process. Fig. 3(a) shows the effect of initial solution pH on the removal rate of dye from the beginning to equilibrium within 400 min. It is observed that the removal rate of dye increases in the initial and later stage at the pH range 3–7; however, the removal rate increases slightly in the initial stage but decreases a little in the later stage at the pH range 7–11. The lower removal rate at equilibrium is because of the active sites were covered by adsorbate. A similar result [31] was reported for the adsorption of MB previously.

The result can be explained on the basis of the zero point charge of the biosorbent: The pH affects surface-binding sites of biomaterials and the ionization process of dye molecule [32]. The zero point charge of the leaves is found to be 7. When the pH is higher than pH_{PZC}, there is a net negative charge on the surface of the biosorbent and the ionic state of ligands such as carboxyl, phosphoryl, sulfhydryl, hydroxyl, and amino groups [18] will promote the reaction with MB as a cationic dye through electrostatic forces of attraction. The lower removal rate at equilibrium is because of the active sites were covered by adsorbate.

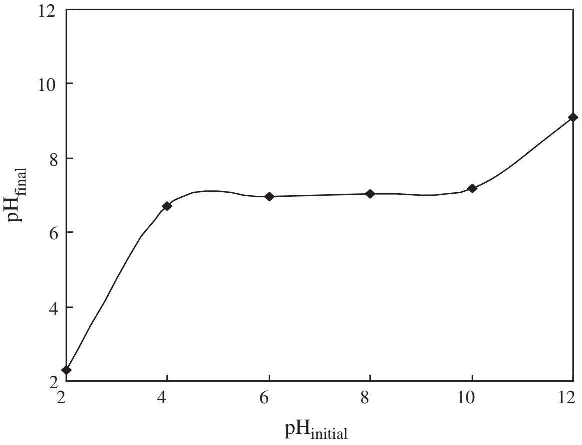

Fig. 2. Determination of point of zero charge of the sorbents.

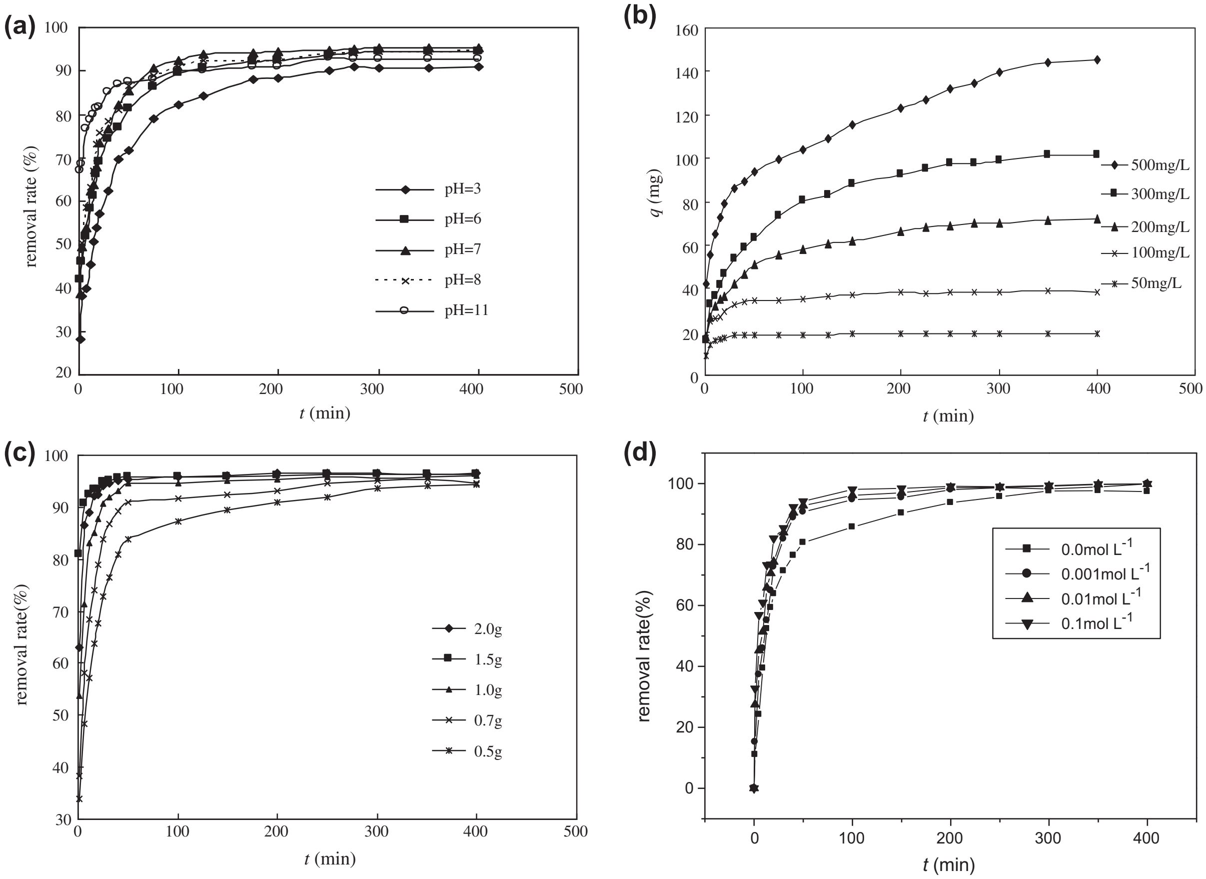

Fig. 3. Influence of different single element: (a) effect of pH, (b) effect of initial MB concentration, (c) effect of biosorbent dose, and (d) effect of ionic strength on the adsorption of MB.

At lower pH (pH< pH_{PZC}), the overall surface charge will become positive on the cells, and the H^+ ions compete effectively with dye cations [26] causing a decrease in removal rate. So the removal rate at pH = 7 is the maximum value (95.23%).

3.3.2. Effect of initial methylene blue concentration

The results are shown in Fig. 3(b). As seen from this figure, the amount of MB adsorbed increases from 19.44 to 145.62 mg/g with an increase in initial MB concentration from 50 to 500 mg/L. Initial concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases [33]. So the increasing adsorption capacity with increasing initial MB concentrations can be attributed to the driving force from the concentration gradient between bulk and sorbent surface. A higher initial dye concentration enhances the adsorption process and increases the sorption capacity. Doğara et al. [31], Asgher and Bhatti [34] observed a similar trend.

It also can been seen from Fig. 3(b) that the equilibration time necessary for adsorption increases from 50 to 300 min with the increasing of initial MB concentration from 50 to 500 mg/L. During the adsorption rapid adsorption occurred in the initial stage, and the sorption is controlled by film diffusion from bulk to the surface [31] due to the time to reach equilibrium related to initial dye concentration.

3.3.3. Effect of biosorbents dose

Fig. 3(c) shows the effect of biosorbents dose on the removal rate of dye. From Fig. 3(c), it is observed that removal rate increases from 94.34 to 96.47% for an increase in adsorbent dosage from 0.5 to 2.0 g. A similar result was previously reported for MB by some researchers [18,26]. In the initial stage, faster adsorption occurs with the increase in dose, which is due to increase surface area and more vacant adsorption sites. But at equilibrium, the further increase in biomass (0.5–2.0 g) does not lead to a significant improvement in biosorption yield (93.34–96.47%). It could be explained that the very fast superficial adsorption onto the leaf surface produces a lower solute concentration than when leaf dose is lower, so the concentration gradient decreases and the amount of MB onto unit weight of adsorbent is reduced, thus causes that adsorption sites remain unsaturated during the adsorption reaction. As the value of the removal rate is 94.34% when leaf dose is 0.5 g, this dose is more economical.

3.3.4. Effect of ionic strength

The dye wastewater has commonly higher salt concentration, and effects of salt concentration or ionic strength are important in the study of dye adsorption. Fig. 3(d) shows the effect of various NaCl concentrations on the removal rate of dye. Increasing the ionic strength of the medium exhibited a positive effect on the adsorbed amounts of MB. Fig. 3(d) suggests that increased ionic strength favors the approximation association process of the fallen leaves, giving rise to new sites where dye molecules can be trapped. The adsorbed amount increases as the dissociated dye ions free for binding electrostatically onto the solid surface of oppositely changed increase [35]. The latter effect seems to be dominant on the adsorption capacity of the surface. From this point of view, this result indicates that the fallen leaves can be used for the removal of MB dye from salty waters.

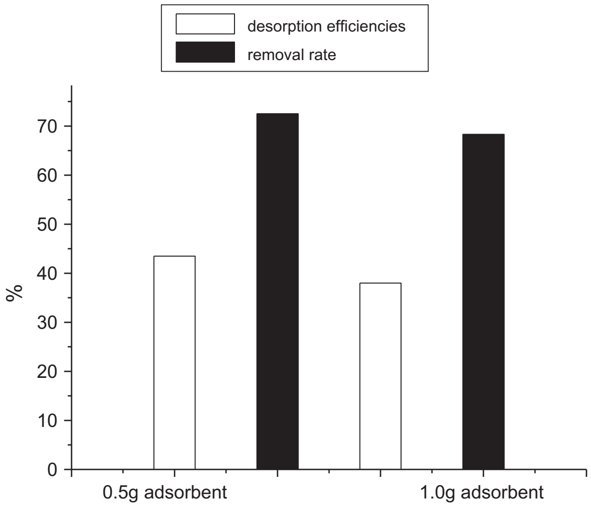

Fig. 4. Desorption and reuse of fallen leaves.

3.4. Desorption and reuse

Desorption is for the utmost importance for inexpensive biomass generation. It may decrease the process cost and also the dependency of the process on a continuous biosorbent supply. MB-loaded leaves were reused after desorption, and the results are shown in Fig. 4. The desorption efficiencies of deionized water was found to be 43.5% (0.5 g adsorbent) and 38% (1.0 g adsorbent). After desorption, the removal rate of MB was 72.5% (0.5 g adsorbent) and 68.3% (1.0 g adsorbent). We can see that the fallen leaves as an adsorbent can be desorbed easily for MB solutions. The leaves have good secondary adsorption ability after desorption. Therefore, the fallen leaves can be reused for further dye adsorption.

3.5. Recycling

The MB-loaded leaves were reused without any treatment (Fig. 5). The results show that removal rate of MB decreased with the increase in number of fallen leaves utilization. This is because that the leaves had a large number of dye when it was used to adsorb again. Removal rate of MB were 83.5 and 68% at secondary adsorption and third adsorption, respectively. The effect is still considerable, and the leaves as an adsorbent can be recycled.

3.6. Equilibrium, kinetic and thermodynamic studies

3.6.1. Biosorption isotherm

The relationship between the amount of dye at constant temperature and its concentration in the

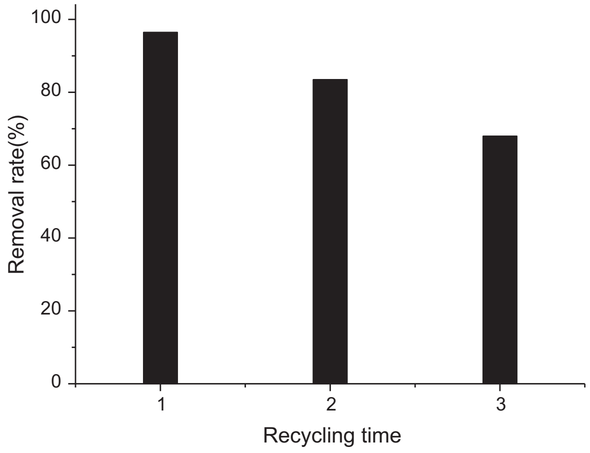

Fig. 5. Multiple recycling of fallen leaves.

Table 2
Calculated equilibrium constants for the sorption of MB onto leaves

	Langmuir isotherm				Freundlich isotherm			Temkin isotherm		
Temperature (K)	K_L	q_m (mg/g)	R_L	r^2	K_F	n	r^2	A	b	r^2
293	0.154	96.15	0.0128	0.990	21.34	3.478	0.941	2.212	151.3	0.991
303	0.176	99.01	0.0112	0.990	24.33	3.716	0.882	3.865	164.1	0.952
313	0.745	95.24	0.0027	0.934	31.28	3.971	0.947	9.264	164.3	0.984
323	0.692	101.01	0.0029	0.945	34.66	4.085	0.906	11.91	168.8	0.971

equilibrium solution is called the adsorption isotherm [33]. Adsorption isotherm study is essential to understand the adsorbate/adsorbent interaction and optimizate of the use of the adsorbent. In addition, it is important to analyze the equilibrium data, which accurately represents the results and can be used for designing the biosorption system. In order to understand the adsorption isotherm process, it is necessary to correlate the equilibrium adsorption data to different isotherm models. The Langmuir isotherm assumes monolayer coverage of sorbate on homogeneous site of the adsorbent, uniform energy of sorption, and no interaction between molecules adsorbed on neighboring sites. Freundlich isotherm is an empirical equation and assumes a heterogeneous surface with a nonuniform distribution of biosorption heat over the surface. Temkin isotherm considers the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and assumes that the fall in the heat of adsorption is linear rather than logarithmic.

The relevant constants are presented in Table 2. Analysis of the experimental data shows that the values of q_m, K_L and K_F increase with temperature rise, so an increase in temperature is advantage to adsorb MB

Table 3
Kinetics data for the sorption of MB onto leaves

	Lagergren first order		Ho second order		Weber and Morris intraparticle model		
	k_1 (1/min)	r^2	k_2 (mg/g min)	r^2	K_i (mg/g min$^{1/2}$)	C	r^2
Dose (g)							
0.5	0.0132	0.961	0.0038	0.9998	0.861	22.29	0.716
0.7	0.0099	0.853	0.0089	0.9999	0.469	19.11	0.561
1.0	0.0084	0.700	0.0302	1	0.205	15.74	0.444
1.5	0.0064	0.527	0.1003	1	0.044	12.12	0.402
2.0	0.0108	0.683	0.1426	1	0.063	8.611	0.322
Concentration (mg/L)							
50	0.0180	0.150	1.6 × 10–2	0.9999	0.310	14.50	0.546
100	0.0177	0.700	4.1 × 10–3	0.9997	0.859	24.68	0.768
200	0.0128	0.887	7.5 × 10–4	0.9970	2.642	26.65	0.900
300	0.0136	0.909	3.5 × 10–4	0.9954	4.368	26.39	0.936
500	0.0108	0.856	2.8 × 10–4	0.9888	5.065	51.30	0.970
pH							
3	0.0163	0.977	0.0235	0.9993	1.259	16.12	0.856
6	0.0172	0.969	0.0037	0.9997	1.042	21.32	0.812
7	0.0197	0.958	0.0046	0.9999	1.006	22.55	0.747
8	0.0153	0.955	0.0510	0.9999	0.890	23.94	0.756
11	0.0168	0.941	0.0100	0.9999	0.449	29.98	0.760
Temperature (K)							
293	0.0204	0.931	0.0041	0.9992	1.678	17.17	0.809
303	0.0227	0.896	0.0056	0.9992	1.539	19.18	0.710
313	0.0220	0.893	0.0061	0.9994	1.476	19.64	0.724
323	0.0227	0.925	0.0065	0.9991	1.502	19.96	0.747

onto leaves. The R_L and n value in the study are found 0.029–0.0128, and 3.478–4.085, respectively, which illustrate that MB is favorably adsorbed on the leaves. Based on the linear regression correlation coefficient, r^2, the adsorption can be well interpreted by Temkin isotherm followed by Langmuir and Freundlich isotherms. A similar result was reported for the adsorption of Acid Orange 52 on *Paulownia tomentosa* Steud. leaf [33]. This behavior suggests the interactions between adsorbate and adsorbate, and the fallen leaves of the heat of adsorption is linear.

3.6.2. Reaction kinetics

In order to examine the controlling mechanism and the rate of adsorption process, several kinetic models are available to understand the behavior of the adsorbent. Table 3 shows the estimated kinetic parameters for the sorption. The rate constant of the first order changes more largely with variation in dose of adsorbent and concentrations of MB than pH and temperature. The rate constant for second-order model changes regularly with varying dose of adsorbent, concentrations of MB, pH, and temperature. For intraparticle model, the constants of C were not zero, which figures that the straight line does not pass through the origin, and this indicates that the intraparticle diffusion is not the only rate-controlling step. If the plot of q vs. $t^{1/2}$ gives a straight line, the sorption process is controlled by intraparticle diffusion only; however, if the data exhibit multi-linear plots, two or more steps influence the sorption process [16]. The low linear regression correlation coefficient r^2 of intraparticle model shows that the adsorption process is complex and involved more than one mechanism [33]. The compare of r^2 for the sorption of all the test metals, the result suggests that adsorption fits well with Ho-second order model. This means that rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites on the biosorbent [36].

The value of k_2 can be used to calculate activation energy (E_a) in the Arrhenius equation. Low activation energies (5–50 kJ/mol) are characteristics of physical adsorption [33]. The E_a of MB adsorption is 14.26 kJ/mol, indicating that the adsorption is mainly physical process.

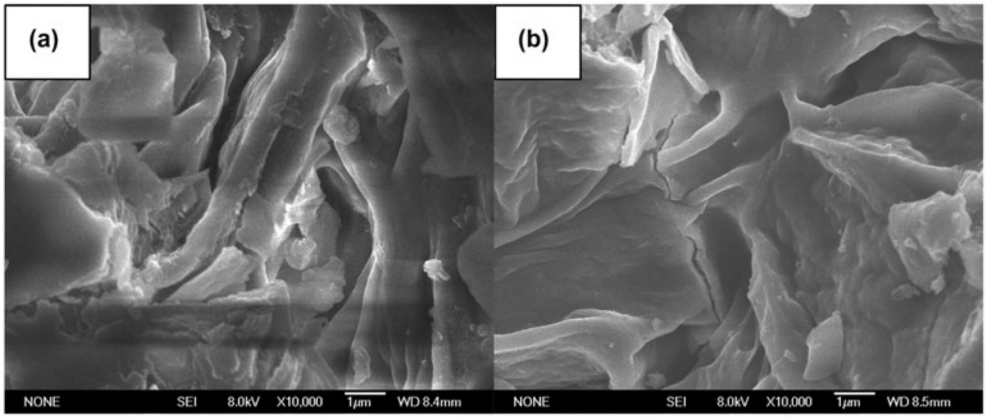

Fig. 6. Scanning electron micrograph of leaves before (a) and after adsorption (b).

Table 4
Thermodynamic parameter for the sorption of MB onto leaves

Concentration (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol) 293 K	303 K	313 K	323 K
100	28.32	112.9	−4.931	−5.380	−7.445	−7.763
200	41.71	149.3	−2.183	−3.528	−4.443	−6.687
300	17.36	60.68	−0.184	−1.135	−1.832	−1.871
400	17.33	53.91	1.471	1.225	0.171	−0.028
500	13.77	38.88	2.342	2.154	1.398	1.26

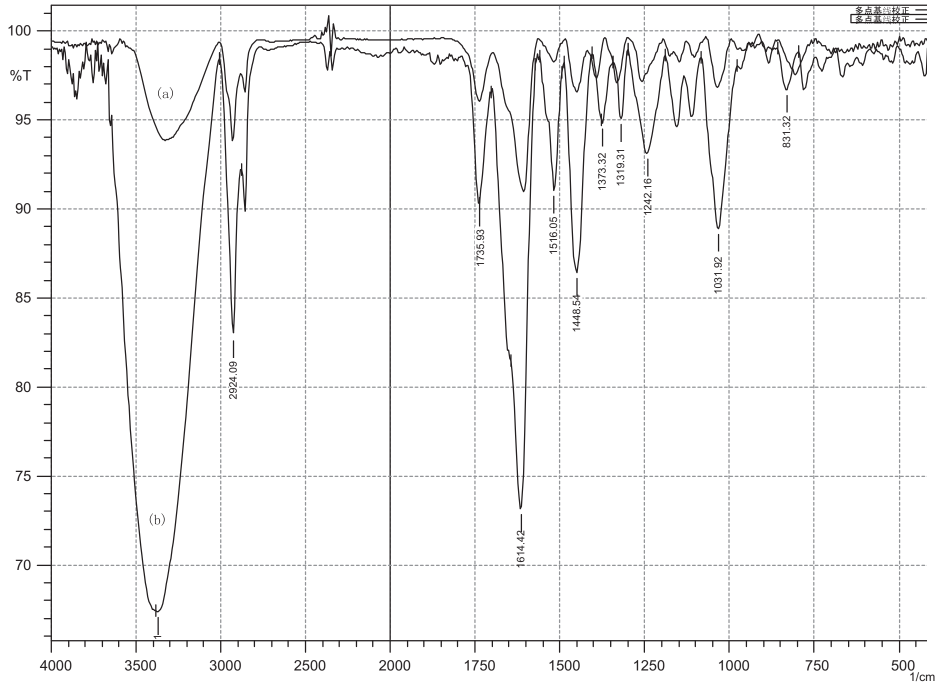

Fig. 7. FT-IR spectra of leaves before (a) and after adsorption (b).

3.6.3. Thermodynamics

The thermodynamic data reflect the feasibility and favorability of the biosorption. The calculated parameters such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) are showed in Table 4. The negative value of ΔG° indicates the spontaneous nature of MB adsorption onto leaves. The value of ΔG° decrease with an increase in temperature, indicating that a better adsorption is obtained at higher temperatures [16]. This conclusion is also confirmed with the analysis of adsorption isotherm data given in Table 2. The value of ΔG° increased with an increase in concentration of MB, suggesting that the adsorption reactions require more energy to convert reactants into products. The positive value of ΔH° shows that the adsorption is endothermic in nature. The positive value of ΔS° reflects the increased randomness at the solid/solute interface during the biosorption of dye.

3.7. SEM and FT-IR measurements

The morphology of leaves before and after adsorption examined by SEM and representative micrographs is shown in Fig. 6. It is observed that the layered crystallinity structure and pored structure of leaves existed before the reaction (Fig. 6(a)). After the adsorbing MB reaction, the porous structure of the leaves still existed, but a little more compacted and slippery (Fig. 6(b)) than before.

The FT-IR technique is an important tool to identify some characteristic functional groups [16] as each group possesses a unique energy absorption band. Fig. 7 shows the FT-IR of leaves before and after adsorption. Fig. 7, before and after adsorption shows show a similar pattern with a number of absorption peaks, suggesting complex properties of the biosorbents. The broad and strong absorption peak at 3,367.7 cm^{-1} is indicative of the existence of bonded hydroxyl groups. The peaks observed at 2,924.1 and 1,373.3 cm^{-1} are assigned to the stretch vibration and bending vibration of C–H bond, respectively. The peaks located at 1,735.9 and 1,614.4 cm^{-1} correspond to stretching of carboxyl groups from aldehydes and ketones. The band at 1,448.5 cm^{-1} is attributed to C–O stretching. The band at 1,319.3 cm^{-1} assigns to C–N groups on the biomass surface. The peak at 1,242.1 cm^{-1} may be from the stretch vibration of C–O in phenols, aldehydes, ketones, and lactones or carboxyl groups. The absorption at 831.3 cm^{-1} is related to C–H rocking vibrations of cellulose. The intensity is a function of the change in electric dipole moment and also the total number of such bonds in the sample [16]. The intensity decrease of –OH at 3,367.7 cm^{-1}

and –COOH at 1,735.9 and 1,614.4 cm^{-1} indicates chemical interactions involving –OH, –COOH on the leaf and the dye. Consequently, the results indicated that the biosorbents presented different functional groups such as hydroxyl (–OH) and carboxyl (–COOH), which may be potential biosorption sites for MB dye [25].

4. Conclusion

The fallen leaves of Platanus were used to remove MB from aqueous solution as a natural adsorbent. The removal rate at pH 7 is the maximum value (95.23%). The extent of the MB removal increased with initial MB concentration, biosorbent dose, and ionic strength. The maximum biosorption capacity of leaves in experiment was 145.62 mg/g. Furthermore, the fallen leaves could be regenerated through the desorption of MB in deionized water and reused to adsorb the dye again. The equilibrium data were described well by Temkin isotherm. The kinetic data were fitted well with Ho-second order model. Activation energy found as 14.26 kJ/mol indicated that MB biosorption onto the leaves was mainly physical process. The thermodynamics parameters indicated the spontaneous, endothermic, and feasibility nature of the biosorption process. The functional groups hydroxyl (–OH) and carboxyl (–COOH) may be potential biosorption sites for MB dye.

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