



Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder

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ARTICLE INFO

Article history:

Received 5 August 2008

Received in revised form 20 April 2009

Accepted 21 April 2009

Available online 3 May 2009

Keywords:

Adsorption

Dye

Methylene blue

Pineapple leaf

ABSTRACT

The ability of an unconventional bio-adsorbent, pineapple leaf powder (PLP) for the adsorption of methylene blue (MB) from aqueous solution was studied. It was observed that intra-particle diffusion was involved in the adsorption process and that the kinetic data fitted well with a pseudo-second-order equation. Fitting parameters revealed that the rate of adsorption increased with decrease in dye concentration and decrease in ionic strength while the mixing speed did not have a significant effect on adsorption. The adsorption was favorable at higher pH and lower temperature, and the equilibrium data were well fitted by the Langmuir isotherm. The maximum adsorption capacity varied from 4.68×10^{-4} to 9.28×10^{-4} mol/g when pH increases from 3.5 to 9.5. Thermodynamic parameters suggest that the adsorption is a typical physical process, spontaneous, and exothermic in nature. The results revealed that this agricultural waste has potential to be used as an economical adsorbent for the removal of methylene blue from aqueous solution.

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1. Introduction

Dyes are widely used as coloring agents in a variety of industries, such as textiles, cosmetics, pulp mills, leather, dye synthesis, printing, foods, and plastics. Because many organic dyestuffs are harmful to human beings and hazardous to aquatic organisms, removal of dyestuffs from wastewater has received considerable attention over the past decades. Among the numerous dye removal techniques, adsorption is the preferred method and gives the best results as it can be used to remove various types of coloring materials [1]. Activated carbon is the most widely employed adsorbent for the removal of color from textiles due to its effectiveness and high adsorption capacity; however, its use is still limited because of high operating costs. The need for regeneration and difficulty of separation from the wastewater after use are also major concerns associated with activated carbon. To lower the cost of wastewater treatment, many researchers have focused on finding non-conventional alternative adsorbents. Non-conventional adsorbents or so-called low-cost adsorbents are generally referred to non-hazardous waste produced from industry, agriculture, and biosorbents. Extensive lists and reviews of these types of adsorbent for contaminant removal have been made [1–10]. In particular, the use of agricultural waste in adsorption system has been drawn

attention from a large number of researchers because: (1) it is abundantly available; (2) most of the types of agriculture waste are readily to be used and do not require a complex pretreatment step or activation process before applications; (3) regeneration of these adsorbents may not be necessary (unlike activated carbon, where regeneration is essential); and (4) less maintenance and supervision are required for the operation of the adsorption process. Nevertheless, use of these cheap alternatives for wastewater treatment remains limited due to both insufficient documentation in real wastewater systems and the necessity of post-usage disposal.

Pineapple is largely cultivated in tropical countries, such as China, India, Thailand, Indonesia, and Taiwan. In Taiwan, the total area of cultivated pineapple plants is 12,225 acres and 439,872 tons of pineapple are harvested annually, according to a 2006 report from the Taiwan Council of Agriculture. Normally leaves on farmland are used as a natural compost material or burned on site after the harvest, creating a point source of air pollution. The major constituents of pineapple leaf are cellulose (70–80%), lignin (5–12%), and hemicellulose [11]. Some studies have focused on improving the use of this natural bio-adsorbent in short and fiber-reinforced rubber composites [12,13] because the leaves of the pineapple plant yield strong, fine silky fibers. Such uses of pineapple leaves are doubly beneficial, providing a natural adsorbent and decreasing the amount of agricultural waste.

Despite that many low-cost adsorbents have been studied for decontamination purposes, studies of the pineapple leaf as an economical adsorbent for dye removal have not yet entered the

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scientific literature. Utilization of this waste for the treatment of wastewater is a win–win strategy because it not only converts the waste into a useful material but it also prevents on-site burning of the waste and saves on disposal costs. The aim of this work was to evaluate the potential of pineapple leaf as a low-cost adsorbent in the removal of a basic dye, methylene blue (MB), from aqueous solution. Methylene blue was chosen as a target contaminant to characterize the adsorptive properties of pineapple leaf as it is a common cationic dye used in the medical, textile and printing industries. We investigated parameters that may affect the adsorption, including initial dye concentration, agitation speed, ionic strength, pH, and temperature. Models to fit the adsorption equilibrium and kinetic data were also formulated. Thermodynamic parameters for the present system were determined based on isotherm data. Results of this study will be useful for using this natural waste as an economic bio-adsorbent in the removal of methylene blue from wastewater.

2. Materials and methods

2.1. Materials

All reagents were of analytical grade chemicals. All solutions were prepared with double distilled water. The cationic dye used in this study, MB or basic blue 9, was purchased from Riedel-de Haën Co., Germany. MB has a molecular weight of 373.9 g/mol and its chemical formula is $C_{16}H_{18}ClN_3S$. The cationic MB dye produces an intense molecular cation (C^+) and reduced ions (CH^+) in the aqueous solution. MB concentration in the sample solution was determined using a spectrophotometer (HACH DR-2010, USA) at a wavelength of 665 nm.

Mature pineapple leaves were collected from a tract of farmland near the campus of I-Shou University. The fresh leaves are sword-shaped and measure about 75–90 cm in length and 5–7 cm in width. Upon collection, each leaf was first washed with tap water two or three times to remove dust and impurities. The leaves were air dried and subsequently oven dried at 80 °C for 2 days. Prior to use, the dried leaves were powdered using a grinder. The pineapple leaf powder (PLP) was passed through an ASTM 200 mesh screen. Particles with diameter less than 75 μm were used for adsorption studies. To characterize the PLP samples, a number of basic properties were determined. The specific surface area and average pore volume of each PLP sample were determined using a BET- N_2 (Brunauer, Emmett, Teller) surface area analyzer (Beckman Coulter SA3100). The pH_{zpc} (pH at zero point of charge) of the PLP particles was determined with a zeta meter (Lazer Zee[®] model 500, Pen Kem Inc.). The gravimetric density of the PLP particles was determined following the methods described in ASTM (American Society for Testing and Materials) D854-92. The pH of each PLP sample was measured in water suspension at a 1:1 weight ratio of PLP to distilled water using a pH meter. A scanning electron micrograph (SEM) (Philips 501 scanning electron micrograph) was used to characterize the morphology of the adsorbent. An FTIR (Fourier transform infrared spectroscopy) spectrophotometer Bruker Vector 22 covering a wave number range of 400–4000 cm^{-1} was used to identify the chemical components of the PLP.

2.2. Kinetic adsorption experiments

Kinetic studies were carried out to establish the effect of time on the adsorption process and to quantify the adsorption rate. The effects of mixing speed, initial MB concentration, and ionic strength on the adsorption kinetics were investigated. The general experimental procedures were as follows: (1) 1 L of solution containing a fixed MB concentration with a constant ionic strength of NaNO_3

was prepared. (2) Solution pH was adjusted to 6.5 using either with 0.1 M HNO_3 or 0.1 M NaOH . (3) A concentration of 0.5 g/L PLP was added to the solution. (4) The resultant solution was agitated on a magnetic stirrer at a constant speed and room temperature (27 °C) for 2 h. (5) A 5 mL liquor was removed at given time intervals and immediately filtered through the 0.45 μm membrane filter (supor-450, Gelman Sci.) to collect the supernatant. (6) The residual MB concentration in the supernatant was determined. Each run of the experiment was replicated and the average values were used in the data analysis. Blank tests without adsorbent (PLP) were run in parallel to avoid possible adsorption on the reactor and the filter apparatus.

Experiments to investigate the effect of mixing speed on adsorption rate were carried out using the procedure described above except that the mixing speed was maintained at 200, 400, and 500 rpm. Various initial MB concentrations (5×10^{-6} – 4×10^{-5} M) were prepared for gauging the effect of initial MB concentration on adsorption rate. The effect of ionic strength on adsorption rate was investigated using the procedures described above except that different ionic strengths (5×10^{-3} – 7×10^{-2} M) were used.

The amount of MB adsorbed at contact time t (min), q_t (mol/g), was calculated using Eq. (1):

$$q_t = \frac{C_0 - C_t}{W} \quad (1)$$

where C_0 and C_t (mol/L) represent the concentrations of MB in the solution at time $t=0$ and $t=t$, respectively, and W (g/L) was the dose of PLP.

2.3. Equilibrium adsorption experiments

Isotherm experiments were carried out to obtain the maximum adsorption capacity and thermodynamic parameters as affected by solution's pH and temperature. The experimental procedures were as follows: (1) A series of 100 mL solution containing different MB concentrations with a constant ionic strength of 1×10^{-2} M (NaNO_3). (2) Solution pH was adjusted to cover a range from 3.5 to 9.5 using either HNO_3 or NaOH . (3) A concentration of 0.3 g/L of PLP was added to the solution. (4) The bottles were shaken on a reciprocal shaker at 150 excursions/min and at room temperature (27 °C) for 80 min. This contact time was found to be adequate for reaching equilibrium adsorption based on the results of a separate kinetic study. (5) At the end of shaking, the final pH of the mixed liquor was recorded. (6) The liquor was filtered through the 0.45 μm filter paper to collect the supernatant. (7) The residual MB concentration in the supernatant was analyzed. The experimental procedure employed for studying the effect of temperature on the dye adsorption isotherm was the same as that described above except that the pH of the mixed solution was adjusted to 5.5 and the temperature was controlled under isothermal conditions at 4, 14, 24, 34, 44, and 54 °C by placing the mixtures in a water circulation bath with temperature that remained constant within ± 0.2 °C. In order to assure thermal equilibrium, the bottles were first put into the bath for about 30 min prior to the experiment. Control samples without present MB in the mixed suspension were also used.

2.4. Mathematical models

The kinetic data was analyzed using pseudo-second-order (PSO) intra-particle diffusion (IPD) models. The PSO model is a well-known kinetic model proposed by Ho and McKay [14] based on the adsorption capacity, and is expressed as follows:

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

where q_t represents the amount of adsorbed MB on the PLP sample (mol/g) at time t (min), q_e is the amount adsorbed at equilibrium (mol/g), and k is the PSO rate constant (g/(mol min)). After integrating the equation and applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (2) becomes

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \quad (3)$$

In a rapidly stirred batch reactor, the IPD is likely a slow process and is therefore rate-determining [15]. The IPD equation originally proposed by Weber and Morris [16] was used to identify the diffusion mechanism:

$$q_e = k_p t^{1/2} + C \quad (4)$$

where k_p is the IPD rate constant (mol/(min^{1/2} g)) and C is the intercept, which gives an indication of the thickness of the boundary layer (i.e., the larger the intercept, the greater the boundary layer effect [17]).

The Langmuir adsorption isotherm [18] was used to describe the MB adsorption:

$$q_e = \frac{K_L C_e Q_m}{1 + K_L C_e} \quad (5)$$

where q_e is the amount of MB adsorbed at equilibrium (mol/g), K_L is the Langmuir adsorption constant (L/mol), C_e is the equilibrium MB concentration (mol/L), and Q_m is the maximum adsorption capacity (mol/g).

The graphical computer software, KaleidaGraph™ [19], was used to perform a non-linear fit of the experimental data. In applying the above models to describe the kinetic data, the least-squares correlation coefficient (r^2) and normalized standard deviation (s , %) were calculated for each experiment. The value of s was calculated using:

$$s = 100 \times \sqrt{\frac{\sum [(q_{t,\text{exp}} - q_{t,\text{cal}})/q_{t,\text{exp}}]^2}{n - 1}} \quad (6)$$

where $q_{t,\text{exp}}$ and $q_{t,\text{cal}}$ are, respectively, the measured and calculated MB adsorbed at time t , respectively, and n is the number of data points.

3. Results and discussion

3.1. Adsorbent characteristics

The SEM micrograph of a typical PLP sample at 1000× magnification depicted in Fig. 1 shows that the surface of PLP is porous. A pore volume of 0.021 mL/g and a specific surface area of 5.24 m²/g were measured. The density of PLP is 1.53 g/cm³, which shows that the gravitation method can be used to separate the adsorbent. The pH value of PLP is 6.42, indicating that this natural material can be considered a neutral adsorbent. The result of zeta potential measurements shows that the pH_{zpc} of PLP sample is 2.3. Therefore, at a solution pH greater than the pH_{zpc} , the PLP possesses a negatively charged surface, which is favorable for adsorbing cationic MB. The main ingredients of PLP are cellulose, hemicellulose, and lignin. The FTIR spectra of PLP show an intense and broad band ranging from 3050 to 3750 cm⁻¹ due to the hydrogen-bonded OH vibration of the cellulosic structure of PLP [12]. A strong and sharp band at 2910 cm⁻¹ is attributed to the C–H stretching vibration from CH₂ group of cellulose and hemicellulose. The peak at 1735 cm⁻¹ is due to C=O stretching of carbonyl groups (>C=O) in hemicellulose. The peaks at 1435 and 1255 cm⁻¹ indicate the existence of lignin and hemicellulose structures, respectively [20]. Bands at 1400 and 1060 cm⁻¹ reflect the C–N and C–O stretches [11]. From the FTIR spectra, it is clear that some surface functional groups are present on the PLP, but the specific surface functional groups are unclear.

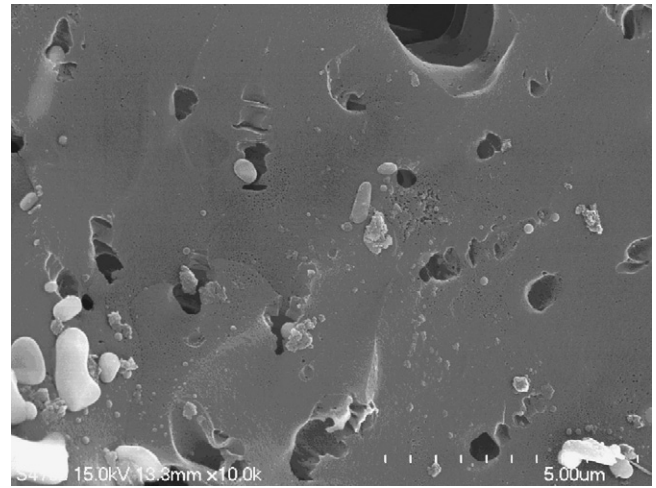


Fig. 1. SEM image of PLP (1000×).

3.2. Kinetic studies

3.2.1. Effect of agitation speed

In the batch adsorption systems, agitation speed plays a significant role in affecting the external boundary film and the distribution of the solute in the bulk solution [21]. The results showed that the adsorption equilibrium of MB almost remained unchanged as agitation speed was increased. A similar trend was observed for varying agitation speeds at different times. These observations can be explained by the fact that the boundary layer resistance was very small and the mobility of the system was high under the experimental conditions. In other words, the diffusion of the MB ion from the solution to the surface of the PLP and into the pores occurred quickly and easily. Since the uptake of MB was not significantly influenced by the degree of agitation, an agitation speed of 200 rpm was therefore used for all further experiments.

3.2.2. Effect of ionic strength

Fig. 2 shows the amount adsorbed as a function of contact time at various initial concentrations. The amount adsorbed increased

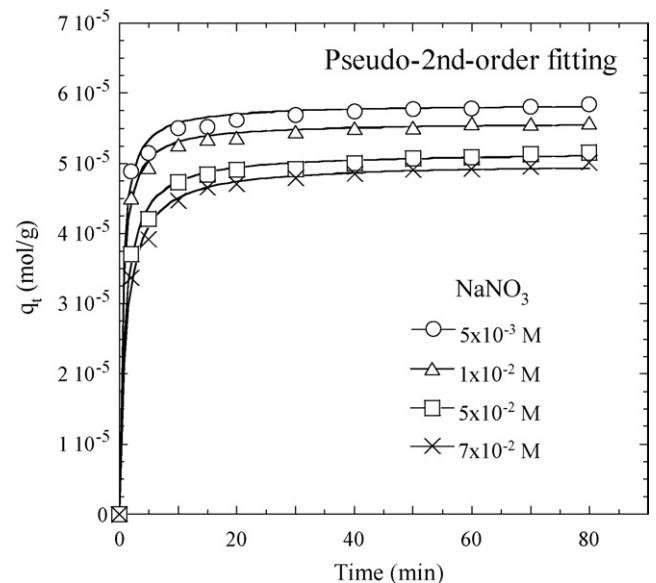


Fig. 2. Effects of ionic strength on the adsorption kinetics. Solid lines represent the best fit of PSO equation. Conditions: initial MB 2×10^{-5} M, PLP 0.3 g/L, 27 °C, final pH 6.5 ± 0.1 .

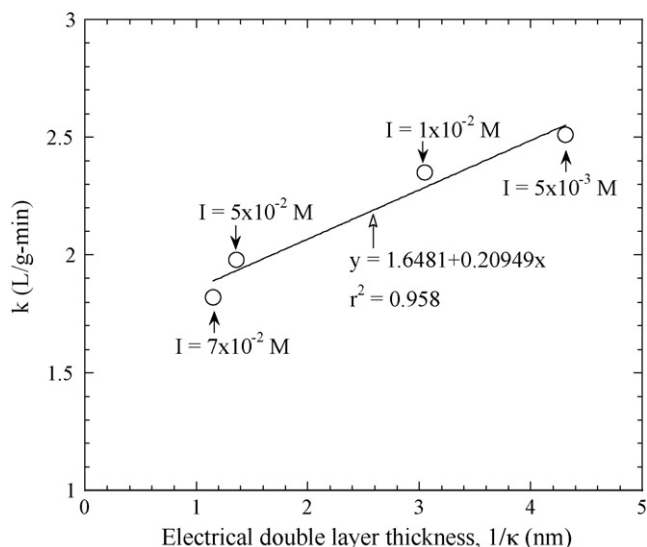


Fig. 3. A linear relationship between rate constant and EDL thickness ($1/\kappa$).

with time and reached a plateau when dynamic equilibrium was attained. The time required to reach the adsorption equilibrium was 60 min for this concentration range. As shown, the adsorption process was divided into three stages: (1) an initial stage with adsorption occurring instantly, (2) subsequently slow adsorption, and (3) a final stage with adsorption reaching equilibrium and remaining constant. The first stage can be attributed to the rapid attachment of MB to the surface of the PLP by surface mass transfer. At this stage, more than 80% of PLP adsorption was found in all cases. The second stage was slower, possibly because many of the available external sites was already occupied and because of the slow diffusion of MB molecules into the pore spaces of the PLP. An asymptotic trend was found after approximately 20 min regardless of the initial MB concentration applied to the adsorption system. The amount adsorbed did not vary significantly at contact times longer than the equilibrium time (60 min). The kinetics of the adsorption process indicates that the adsorption of MB onto PLP can be considered as a fast adsorption process because more than 95% of MB was adsorbed within 20 min. Such finding reveals the benefits of using this low-cost adsorbent, or so-called eco-adsorbent, for the treatment of wastewaters rich in dyes in general and MB in particular.

The influence of ionic strength on the MB adsorption kinetic was studied with a series of experiments at different NaNO_3 concentrations (5×10^{-3} – 7×10^{-2} M). The results show that the amount of MB adsorbed decreased in the presence of NaNO_3 . The PSO model fit parameters (given in Table 1) show that an increase in ionic strength led to a decrease in the adsorption rate constant. Ionic strength is one of the key factors affecting the electrical double layer (EDL) structure of a hydrated particulate. The thickness of EDL (m), $1/\kappa$, can be determined from the relationship:

$$\frac{1}{\kappa} = \left(\frac{2F^2 I \times 1000}{\epsilon \epsilon_0 RT} \right)^{-0.5} \quad (7)$$

where F is the Faraday constant (96,500 C/mol), I is the ionic strength (M), R is the molar gas constant (8.314 J/mol K), T is the absolute temperature (K), ϵ is the dielectric constant of water (78.5), and ϵ_0 is the vacuum permittivity (8.854×10^{12} C/V m). Fig. 3 depicts the linear relationship between rate constant k_2 and the thickness of the EDL. When ionic strength was increased from 5×10^{-3} to 7×10^{-2} M, the value of k decreased from 3.63×10^4 to 1.82×10^4 (g/(mol min)) (Table 1). As indicated by Eq. (7), an

Table 1
Pseudo-second-order adsorption rate constants and q_e values obtained at different initial MB concentrations and ionic strengths.

	Initial MB concentration (M)							
	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	2×10^{-5}	2×10^{-5}	2×10^{-5}	2×10^{-5}
Ionic strength (M)	1×10^{-2}	1×10^{-2}	1×10^{-2}	1×10^{-2}	5×10^{-3}	1×10^{-2}	5×10^{-2}	7×10^{-2}
PLP (g/L)	0.5	0.5	0.5	0.5	0.3	0.3	0.3	0.3
q_e (mol/g)	8.25×10^{-6}	1.73×10^{-5}	3.18×10^{-5}	6.13×10^{-5}	5.84×10^{-5}	5.58×10^{-5}	5.16×10^{-5}	5.00×10^{-5}
k_2 (g/(mol min))	9.09×10^5	1.93×10^5	7.22×10^4	3.33×10^4	3.63×10^4	3.44×10^4	2.18×10^4	1.82×10^4
r^2	0.999	0.999	0.999	0.999	0.998	0.999	0.999	0.999
s (%)	0.7	1.2	1.6	1.5	1.7	1.7	1.7	1.9

Table 2

Comparison of adsorption capacity of methylene blue on various adsorbents.

Adsorbents	SSA (m ² /g)	pH	Temp. (°C)	Q _m (mol/g)	K (L/mol)	Refs.
Natural-based						
Pineapple leaf powder	5.236	7.5	24	8.88×10^{-4}	4.80×10^4	This study
Rice husk	NA	NA	20	8.36×10^{-4}	2.00×10^6	[24]
Cotton waste	NA ^a	NA ^a	20	7.44×10^{-4}	9.67×10^5	[24]
Peanut hull	72.35	5.0	20	1.82×10^{-4}	5.87×10^4	[25]
Orange peel	22.1	7.2	30	5.51×10^{-5}	6.72×10^6	[26]
Neem leaf powder	NA ^a	NA ^a	27	2.35×10^{-5}	1.31×10^5	[22]
Carbon/polymer						
Commercial powder AC ^b	NA ^a	7.4	30	2.62×10^{-3}	1.79×10^5	[16]
Rice husk ash	101.3	6.4	30	2.16×10^{-3}	1.60×10^4	[27]
Rice husk carbon	NA	7.4	30	9.18×10^{-4}	1.34×10^5	[16]
H ₃ PO ₄ activated carbon	1184	NA	Room	8.45×10^{-4}	NA	[28]
Coconut shell carbon	NA ^a	7.4	30	7.43×10^{-4}	3.40×10^4	[16]
Polymer, Jalshakti [®]	NA ^a	5.5	NA ^a	4.61×10^{-4}	1.96×10^5	[29]
Groundnut shell carbon	NA ^a	7.4	30	4.41×10^{-4}	4.79×10^4	[16]
Bamboo dust carbon	NA ^a	7.4	30	3.82×10^{-4}	4.49×10^4	[16]
Granular AC ^b (Nuchar C-190)	NA ^a	5.5	NA ^a	2.79×10^{-4}	1.20×10^4	[29]
Coconut shell fibers carbon	978	6.0	30	5.24×10^{-5}	2.57×10^4	[30]
Coir pith carbon	167	6.9	20	1.57×10^{-5}	3.48×10^5	[4]
Biosorbent						
<i>Sargassm muticum</i>	NA ^a	5.5	25	7.46×10^{-4}	9.35×10^3	[31]
<i>Diamionethane sporopollenin</i>	NA ^a	NA ^a	NA ^a	4.8×10^{-5}	1.12×10^5	[32]
Sewage sludges	NA ^a	NA ^a	25	3.08×10^{-4}	1.12×10^4	[33]
Ash/clay						
Spent activated clay	171	6	28	4.93×10^{-4}	6.47×10^4	[34]
Clay	30	NA ^a	20	1.56×10^{-4}	NA ^a	[35]
Kaolinite	27.49	NA ^a	27	3.75×10^{-5}	NA ^a	[36]
Sono-chemical treated fly ash	35.4	9.7	30	1.2×10^{-5}	NA ^a	[37]
Fly ash	NA ^a	7.5	30	8.23×10^{-6}	2.86×10^5	[38]
Petrified sediment	28.1	7.0	30	6.4×10^{-6}	1.42×10^5	[7]
Sludge ash	3.7	9.8	24	5.00×10^{-6}	4.29×10^5	[1]

^a NA: not available/not reported.^b AC: activated carbon.

increase in ionic strength leads to a decrease in EDL thickness and an increase in the amount of indifferent ions approaching the PLP surface. Thus, the results shown above can be attributed in part to increased competition between MB and Na⁺ ions for surface sites with increasing the ionic strength.

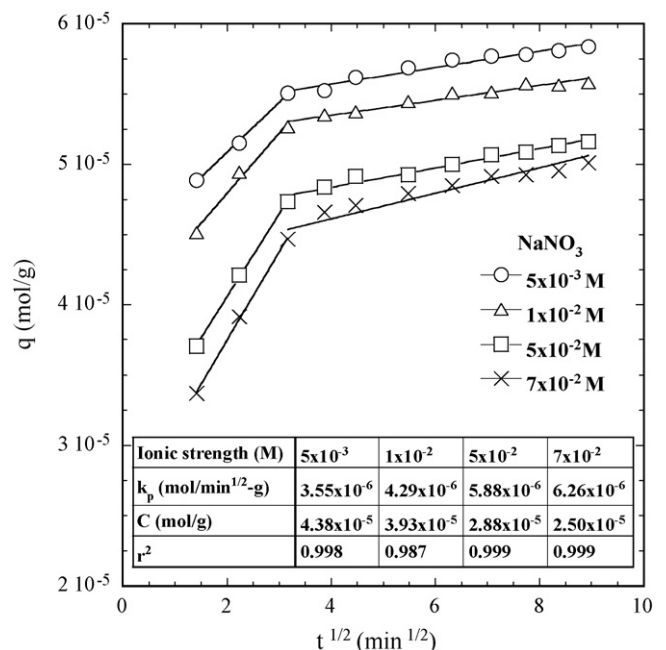
3.2.3. Effect of initial MB concentration

Results show that increased initial MB concentration led to increased MB adsorption. Apparently, the initial MB concentration plays an important role in affecting the capacity of MB to adsorb onto PLP. The higher the MB concentration is, the stronger the driving force of the concentration gradient, and therefore the higher the adsorption capacity. The corresponding PSO model fit parameters (given in Table 1) indicate that the data can be described by this model with relatively low standard deviation and high correlation coefficient. It was found that the adsorption rate was inversely proportional to the initial MB concentration. When initial MB concentration increased from 5×10^{-6} to 4×10^{-5} M, the PSO rate constant k_2 decreased from 9.09×10^5 to 3.33×10^4 g/(mol min). Higher initial MB concentration resulted in a lower diffusion efficiency and more competition of adsorbing ions for a fixed activated surface site; consequently, a lower k_2 value was observed. Similar results have also been reported by Crini et al. [21] for the adsorption of dyes onto cyclodextrin-based peat.

3.2.4. Intra-particle diffusion

Normally, if a plot of the amount of dye adsorbed versus $t^{1/2}$ shows two or more intercepting lines, the adsorption steps are independent of one another [22]. The IPD plots and the fit parameters of the effect of ionic strength are depicted in Fig. 4. These plots clearly exhibit two distinguishable intercepting lines, which indicate that the adsorption process was controlled by a multi-step

process, involving adsorption on the external surface and diffusion into the internal pores of the PLP. The first intercepting line represents IPD while the second indicates the solution was progressively reaching equilibrium adsorption. The slope of the first linear portion gives the intra-particle rate constant, k_p , and the intercept of this portion is proportional to the thickness of boundary

**Fig. 4.** IPD plots and fit parameters at different ionic strengths.

layer. As seen in Fig. 4, values of k_p increase slightly with increasing ionic strength. This may imply that the diffusion rate is not significantly affected by the changes in ionic strength. The boundary layer parameter, C , decreased with increasing ionic strength, indicating that the boundary layer effect becomes prominent at lower ionic strength.

The driving force of diffusion is very important for the adsorption processes and is associated with the adsorbate concentration in the bulk solution. Therefore, the fit parameters of the IPD model for the effects of initial MB concentrations on adsorption were also made. The resulting values of k_p increase from 2.93×10^{-7} to 3.91×10^{-6} mol/(min^{1/2} g) when initial MB concentration increases from 5×10^{-6} to 4×10^{-5} M. It appears that an increase in adsorbate concentration results in an increase in the driving force, which leads to an increase in the MB diffusion rate. The results show that the values of intercept C increase from 7.32×10^{-6} to 4.54×10^{-5} mol/g as initial MB concentration increases from 5×10^{-6} to 4×10^{-5} M. This indicates that a higher initial MB concentration results in a stronger boundary layer effect in the adsorption process. The increase in the value of C also provides a measure of the abundance of solute adsorbed on the boundary layer. Similar boundary layer effects were served for the adsorption of malachite green on cyclodextrin-based adsorbent [21].

3.3. Equilibrium studies

3.3.1. Effect of pH

The effects of pH on the MB adsorption isotherms are shown in Fig. 5a. As shown, the amount of MB adsorbed increases with increasing pH. The maximum monolayer adsorption capacity (Q_m) and the corresponding Langmuir constants (K_L) are given in the figure. The high value of r^2 (>0.98) indicates that the experimental data were well correlated to the Langmuir model output. As shown, the values of K_L remain constant while the values of Q_m increase as the pH increases. The adsorption of MB onto PLP seems to be greatly affected much by the solution's pH. Such pH-dependence may be due in part to the fact that the surface charge of PLP is strongly related to the solution pH.

Results from the FTIR analysis indicate that PLP consists of various functional groups such as hydroxyl (–OH) and carbonyl (>C=O) that may be influenced by the pH. The pK_a of MB is 0.04 [23]; hence, MB is completely ionized at pH greater than 0.04 and serves as a cationic species. At alkaline pH, a significant strong electrostatic attraction exists between the positively charged cationic dye and the negatively charged PLP surface due to the ionization of PLP functional groups. As shown previously, the pH_{zpc} of PLP particles was 2.3. The PLP has a positively charged surface at pH less than the pH_{zpc} . On the contrary, when pH is greater than pH_{zpc} , the negatively charged PLP surface is favorable for the adsorption of cationic MB dye. Thus, less adsorption of basic MB dye occurs at lower pH. Additionally, less adsorption of MB at acidic conditions can be attributed in part to the presence of excess H^+ ions destabilizing the basic dye and competing with cationic dye ions for the adsorption sites. The effect of pH on the solid–liquid equilibrium can be described by the following possible mechanisms:

- (1) chemical interaction between the hydroxyl and carboxyl groups of the active component of PLP and the reactive group (Cl^-) of MB.



where S represents the active surface sites of PLP and $S-O^-$ represents the ionized surface functional groups of PLP; or

- (2) weak electrostatic interaction between the MB and the electron-rich sites of the PLP surface.

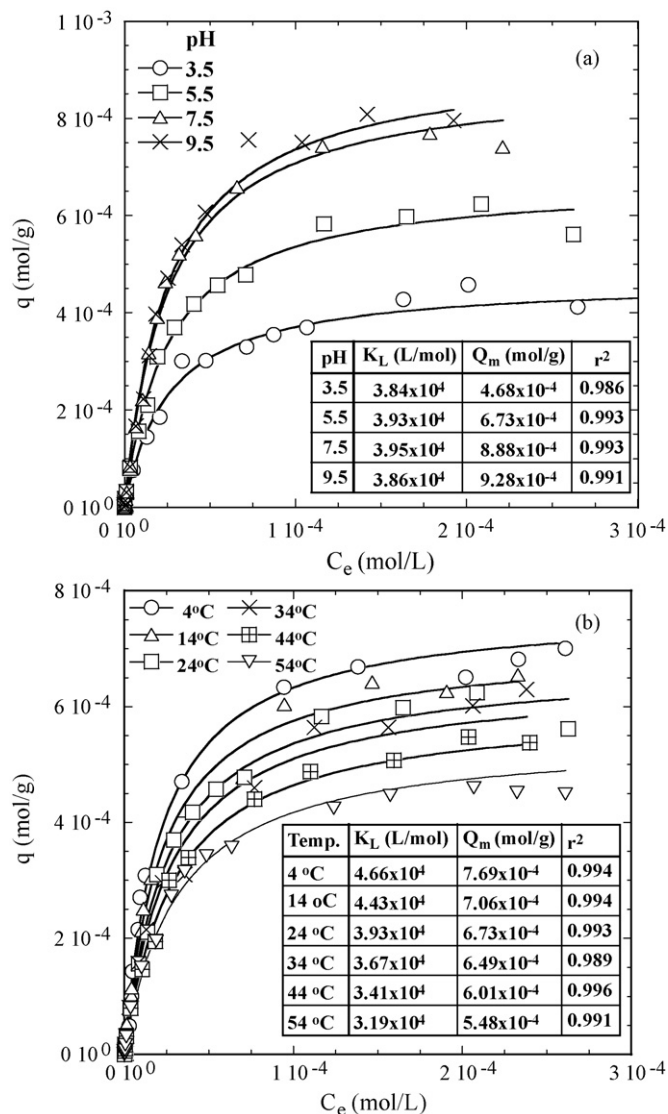


Fig. 5. Effect of (a) pH and (b) temperature on the isotherm for MB adsorption onto PLP. Solid lines are the best fit of Langmuir isotherm.

A comparison between MB adsorption capacities of various adsorbents is given in Table 2. Our results (8.88×10^{-4} mol/g) are quite similar to similar investigations for coal (8.67×10^{-4} mol/g), H_3PO_4 activated carbon (8.45×10^{-4} mol/g), and rice husk (8.36×10^{-4} mol/g). The MB adsorption capacity and the adsorption affinity constant of PLP are much higher than commercial granular activated carbon (Nuchar C-190) and other natural-based adsorbents such as rice husk, neem leaf powder, orange peel, and activated carbon derived from coconut shell fibers.

3.3.2. Effect of temperature

The effect of temperature on the adsorption isotherm was investigated under isothermal conditions in the temperature range of 4–54 °C. The temperature dependence of the MB adsorption isotherm is shown in Fig. 5b. The experimental results indicate that the magnitude of adsorption increases with decreasing temperature, suggesting that the adsorption reaction was exothermic in nature. The values of the adsorption constants obtained from the Langmuir model are in the figure.

To determine whether the process will occur spontaneously, a set of thermodynamic parameters for the MB–PLP adsorption system were calculated, including changes in the standard free energy

Table 3
Thermodynamic parameters for the adsorption of MB onto PLP.

ΔG° (kJ/mol)						ΔH° (kJ/mol)	ΔS° (J/(K mol))
4°C	14°C	24°C	34°C	44°C	54°C		
-24.76	-25.53	-26.12	-26.83	-27.51	-28.19	-5.93	76.4

(ΔG°), enthalpy (ΔH°), and entropy (ΔS°):

$$\Delta G^\circ = -RT \ln K_L \quad (9)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

The values of ΔH° and ΔS° were determined from the slopes and intercepts, respectively, of the van' Hoff plot ($\ln K_L$ versus $1/T$). The calculated thermodynamic parameters are given in Table 3. Because all ΔG° values are negative, the adsorption of MB onto PLP is a spontaneous process, confirming the affinity of PLP for the dye. Generally, a value of ΔG° in between 0 and -20 kJ/mol is consistent with electrostatic interaction between adsorption sites and the adsorbing ion (physical adsorption) while a more negative ΔG° value ranging from -80 to -400 kJ/mol indicates that the adsorption involves charge sharing or transferring from the adsorbent surface to the adsorbing ion to form a coordinate bond (chemisorption) [39–41]. As shown, the magnitude of ΔG° (-24.76 to -28.19 kJ/mol) for this adsorption system is a slightly above the physical adsorption range but significantly below the chemisorption range. These values suggest that the adsorption is a typical physical process enhanced by the chemical effect. The small negative value of ΔH° (-5.93 kJ/mol) indicates that the adsorption is physical in nature involving weak attractive forces and is exothermic. This implies that the adsorption process is energetically stable. The low value of ΔH° also implies loose bonding between the MB molecules and the PLP surface [41]. The positive value of ΔS° (76.4 J/(K mol)) indicates an increase in the degree of freedom (or disorder) of the adsorbed species. In general, the thermodynamic parameters indicate that the adsorption is spontaneous and exothermic.

4. Conclusions

Present studies showed that the adsorption of MB onto PLP is favored at high pH, lower temperature, and low ionic strength. The adsorption kinetics followed a pseudo-second-order kinetic model and intra-particle diffusion was involved in the adsorption process. Fitting of Langmuir isotherm data showed that the maximum adsorption capacity increases with increasing pH and decreasing temperature. PLP has a maximum adsorption capacity of 8.88×10^{-4} mol/g at pH 7.5 and 24°C , which is much higher than many low-cost adsorbents. Thermodynamic parameters suggest that the adsorption is a typical physical process, spontaneous, and exothermic in nature. This study revealed that the PLP can be used as an economical natural-based adsorbent to remove MB dye from aqueous solution. When the PLP used as adsorbent becomes saturated, it can be incinerated. Since the production of pineapple occurs year-round in most tropical countries, wasted pineapple leaves can easily be acquired and used for future commercial applications.

Acknowledgements

This work was supported by the National Science Council of R.O.C. (Grant No. NSC 96-2221-E-214-013-MY3). The authors express their thanks to the fellows of MANALAB, I-Shou University for supporting the SEM and EDS analyses.

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