

## Kinetics of methylene blue biosorption by phoenix tree's leaves powder

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### Abstract

The effect of contact time and the determination of the kinetic parameters of biosorption of methylene blue (MB) from aqueous solution onto phoenix tree's leaves powder are important in understanding the biosorption mechanism. The effect of contact time on biosorption quantity was studied at different initial concentration of 30, 70 and 130 mg/l (295 K), and at different temperatures of 295, 309 and 333 K (initial concentration of 130 mg/l), respectively. The pseudo-first-order model and pseudo-second-order model were adopted to fit the experimental data using non-linear regressive analysis and both can describe the adsorptive process. But the pseudo-second-order model was the better choice to express the biosorption behavior according to higher determined coefficient ( $R^2 > 0.99$ ) and the small difference (less than 1 mg/l) between the calculated equilibrium quantity and the experimental equilibrium quantity, suggesting that the biosorption mechanism be a chemisorption process. The intraparticle diffusion model was also used to express the adsorption process at three steps. The activation energy of biosorption ( $E_a$ ) was determined 15.5 kJ/mol based on the pseudo-second-order rate constants. The lower value of  $E_a$  shows that MB biosorption process by leaves powder may be an activated chemical adsorption. The results show that the process of biosorption MB is endothermic process and rise in temperature favors the biosorption. [Life Science Journal. 2007;4(1):89-93] (ISSN: 1097-8135).

**Keywords:** phoenix tree's leaves powder; biosorption; methylene blue; kinetic; non-linear regressive analysis

### 1 Introduction

Many industries use dyes to color their products and also consume substantial volumes of water. The presence of small amounts of dyes in water is highly visible and undesirable<sup>[1]</sup>. Due to increasingly stringent restrictions on pollutant content of industrial effluents, it is necessary to remove dyes from wastewater before it is discharged into environment.

Adsorption techniques are proved to be an effective and attractive process for removal of non-biodegradable pollutants (including dyes) from wastewater<sup>[2,3]</sup>. Activated carbon is commonly used as adsorbent to remove dyes from wastewater due to its excellent adsorption ability. But the high cost limited its widespread use. Many low-cost adsorbents, including natural materials, biosorbents, and waste materials from industry and agriculture, have been proposed by some workers<sup>[4-7]</sup>.

In China many cities have planted phoenix tree's in main roads, parks and schools. So a lot of phoenix tree's leaves fallen in autumn and often are collected as

waste by cleaners. Like other plant materials, the phoenix tree's leaves contain abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl and amidogen etc, which make biosorption processes possible<sup>[8]</sup>. Thus the research is needed to develop an alternative technology for utilizing these leaves. Several researchers reported plant-leaf used to adsorb heavy metals from solution<sup>[9-11]</sup>, but no research was reported about the kinetic of dye biosorption onto fallen leaves.

Methylene blue (MB) is selected as a model compound in order to evaluate the capacity of adsorbents for the removal of MB from aqueous solutions. The researchers had proved several low-cost biomaterials such as giant duckweed, sawdust, and rice husk and cereal chaff could be used for the removal of MB from solutions<sup>[12-15]</sup>. The equilibrium and isotherms of MB adsorption by phoenix tree's leaves has been studied, but the kinetic behavior has not been studied<sup>[16]</sup>. The aim of this work was to study the kinetic of the utilization of phoenix tree's leaves powder to adsorb MB from aqueous solutions. The kinetic parameters, such as the rate constant of pseudo-first-order adsorption ( $k_1$ ), the rate constant of pseudo-second-order adsorption ( $k_2$ ), the

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constants of intraparticle diffusion model and the apparent activation energy ( $E_a$ ), were calculated to determine rate constants and adsorption mechanism.

### 1.1 Kinetic models of adsorption

The models of adsorption kinetics are correlated with the solution uptake rate, hence these models are important in water treatment process design. In order to elucidate the adsorption mechanism and potential rate controlling step, three kinetic models including the pseudo-first-order, the pseudo-second-order and intraparticle diffusion models are tested to fit experimental data obtained from batch MB adsorption experiments<sup>[17-18]</sup>.

#### 1.1.1 Pseudo-first-order rate equation of Lagergren

The pseudo-first-order equation of Lagergren is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where  $q_e$  and  $q_t$  are the amount of MB adsorbed per unit weight of biosorbent at equilibrium and at any time  $t$ , respectively (mg/g) and  $k_1$  is the rate constant of pseudo-first-order adsorption (g/mg·min). After integration and applying boundary conditions, for  $t=0$ ,  $q=0$ , the form of Eq. (1) becomes Eq. (2):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

#### 1.1.2 Pseudo-second-order rate equation

The pseudo-second-order equation based on adsorption equilibrium capacity can be expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where  $k_2$  is the rate constant of pseudo-second-order adsorption (g/mg·min)

Integrating this equation for boundary conditions for  $t=0$ ,  $q=0$  gives

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

#### 1.1.3 Intraparticle diffusion model

The intraparticle diffusion model is

$$q_t = k_i t^{1/2} + C \quad (5)$$

where  $k_i$  is the intraparticle diffusion rate constant (g/mg· $1/2$ min),  $C$  is the intercept.

The value of  $q_e$ ,  $k_1$ ,  $k_2$ ,  $k_i$  and  $C$ , can be determined using non-linear regressive analysis by least square sum of difference between calculated values and experimental values through the relation of  $q_t \sim t$  shown in Eq. (2), (4), (5), respectively.

### 1.2 Determination of activation energy

The activation energy for MB adsorption was calculated by the Arrhenius equation<sup>[18,19,20]</sup>:

$$k = k_0 e^{-\frac{E_a}{RT}} \quad (6)$$

where  $k_0$  is the temperature independent factor in g/mg·min,  $E_a$  is the apparent activation energy of the reaction of adsorption in J/mol,  $R$  is the gas constant,

8.314 J/mol·K and  $T$  is the adsorption absolute temperature, K. The linear form is:

$$\ln k = -\frac{E_a}{RT} + \ln k_0 \quad (7)$$

When  $\ln k$  is plotted versus  $1/T$ , a straight line with slope  $-E_a/R$  is obtained.

## 2 Materials and Methods

### 2.1 Materials

The phoenix tree's leaves powder was obtained from Zhengzhou city in autumn. The collected materials were washed with distilled water for several times to remove the dirt particles. The washed leaf was dried in an oven at 373 K for 24 hours, then ground and screened through a set of sieves to get different geometrical sizes 40-60 mesh. This produced a uniform material for the complete set of biosorption tests which was stored in an air-tight plastic container for all investigations. The results of element analysis about leaf are 45.8% for carbon, 5.4% for hydrogen, 36.4% for oxygen, 1.0% for nitrogen, 0.1% for sulfur.

The stock solutions of MB were prepared in distilled water. All working solutions were prepared by diluting the stock solution with distilled water to the needed concentration. Both leaf and MB solution were placed in a 50 ml conical flask for adsorptive experiment. Fresh dilutions were used for each biosorption study.

### 2.2 Methods

The phoenix tree's leaves of 0.02 g were added to each 10 ml volume of MB solution (the pH of initial solution is near 7.5). The initial concentrations of MB solution tested were 30, 70 and 130 mg/l, and the experiments were carried out at 295 K in a constant temperature shaker bath (100 rpm). The samples were then collected at different time intervals and were centrifuged. Then the samples were analyzed using a UV spectrophotometer (Shimadzu Brand UV-3000) to monitor the absorbance changes at a wavelength of maximum absorbance (668 nm).

Batch biosorption tests were also done at different contacting time at the initial concentration of MB 130 mg/l and the temperatures were controlled with a water bath at 309 K and 323 K, respectively.

The data obtained in batch mode studies was used to calculate the MB biosorption quantity at given time. It was calculated by using the following expression:

$$q_t = \frac{V(c_0 - c_t)}{m} \quad (8)$$

Where  $q_t$  is the MB biosorption quantity at the given time in mg/g,  $V$  is the sample volume,  $c_0$  is the initial MB concentration,  $c_t$  is the MB concentration at related given time, and  $m$  is the dry weight of the biomass.

### 3 Results and Discussion

#### 3.1 Effect of contact time on biosorption quantity

Figure 1 showed the effect of contact time on biosorption quantity per gram leaves powder ( $q_t$ ) at different conditions.

As shown in Figure 1, a third-stage kinetic behavior is evident: a rapid initial biosorption followed by a slower biosorption rate, then the biosorption is near equilibrium with longer period of much slower uptake. The values of  $q_t$  increased quickly at initial stage of biosorption. The time to reach step of slower biosorption is significantly different at various initial concentration. The time is long with initial concentration increasing.

Also from Figure 1, the bigger capacity of MB biosorption was observed in the higher temperature. It was due to the increasing tendency of MB ions to adsorb from the solution to the interface with increasing temperature. The increase of the values of  $q_t$  at the same given time with increased temperature indicated that the biosorption of MB ions onto leaf was endothermic in nature.

#### 3.2 Analysis kinetic constants

Linear regressive analysis method is simple and convenient, so it is often used to obtain the isotherm and kinetic constants according to the experimental data<sup>[21-25]</sup>. But different forms of the equation affected  $R^2$  values more significantly during the linear analysis. The non-linear analysis may be a method of avoiding such errors<sup>[26]</sup>. In this paper, a non-linear Chi-square of determination test was used. According to Eq. (2), (4) and (5), the constant of pseudo-first-order and pseudo-second-order models were listed in Table 1 using non-linear regressive analysis. The fitted curves of first and second kinetic model were shown in Figure 1 and Figure 2, respectively.

The equilibrium adsorption quantity became larger with an increase of initial MB concentration. However, both values of  $k_1$  and  $k_2$  decreased for the increase of the initial concentration. And all values of  $k_1$  and  $q_{e(\text{theo-1})}$ ,  $k_2$  and  $q_{e(\text{theo-2})}$  increased with the temperature increasing.

From Table 1, the theoretical  $q_{e(\text{theo-2})}$  obtained from pseudo-second-order model agreed more perfectly with the experimental  $q_{e(\text{exp})}$  values than those from pseudo-first-order model. Furthermore, the determined coefficients ( $R^2$ ) of second order model were larger than those of first order model, respectively. These showed that the pseudo-second-order biosorption mechanism appear to produce a better model for adsorption in MB/leaf systems at the experimental conditions. So the process could be best described by the second-order equation. The overall rate of MB biosorption process appeared to

be controlled by the chemical process. This suggested that the rate-limiting step may be the chemical adsorption<sup>[23]</sup> and the pseudo-second-order kinetic model can be applied to predict the amount of dye uptake at different contact time intervals and at equilibrium.

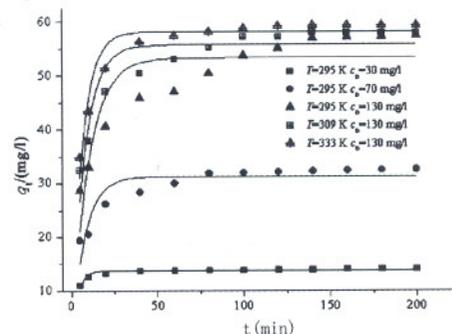


Figure 1. The fitted curves of pseudo-first-order kinetic model and the experimental points at different conditions.

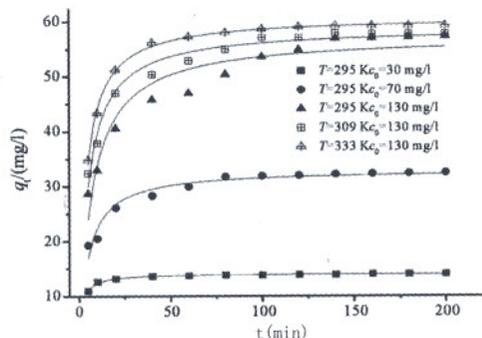


Figure 2. The fitted curves of pseudo-second-order kinetic model and the experimental points at different conditions.

The pseudo-second (or first)-order kinetic model cannot give a definite mechanism of biosorption. So the intraparticle diffusion model is considered as a rate-limiting step<sup>[18,27]</sup>. The dye was adsorbed by the exterior surface of the leaf particle at the beginning of biosorption, and the biosorption rate was very fast. As the biosorption of the exterior surface was near saturation, the MB molecular entered into the leaf particle by the pore within the particle and was adsorbed by the interior surface. When the molecular dye diffused in the pore of the particle, the diffusion resistance increased and the diffusion rate decreased<sup>[28,29]</sup>. As MB concentration in the solution decreased, the diffusion rate became lower and lower and the diffusion processes reached the final equilibrium stage. Figure 3 was the plot of  $q_t \sim 1/2t$  with three-stage stage at different experimental conditions.

Table 2 listed the parameters of non-linear regressive analysis according to three adsorptive steps. The values of  $k_{i1}$ ,  $k_{i2}$  and  $k_{i3}$  increased with initial MB con-

centration rise. The driving force of diffusion was important during biosorption processes. The increases of MB concentration results in increase of the driving force, which will increase the diffusion rate of the molecular dye in pore<sup>[28,29]</sup>. The values of  $k_{i1}$  increased with temperature rise, but the values of  $k_{i2}$  and  $k_{i3}$  are

opposite with temperature rise.

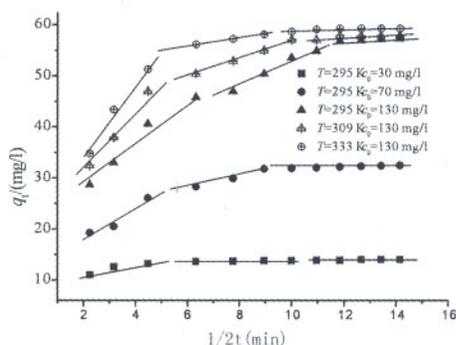
As the constants of  $C$  in Table 2 is not zero, the fitted curves of three steps according to non-linear regressive analysis did not pass through the origin, so the biosorption process may be of a complex nature consisting of both surface adsorption and intraparticle diffusion<sup>[14,28,29]</sup>.

**Table 1.** Kinetic parameters for the biosorption of MB onto fallen phoenix leaves powder at various initial MB concentration and temperature using non-linear regressive analysis

Kinetic model	295 K 30 mg/l	295 K 70 mg/l	295 K 130 mg/l	309 K 130 mg/l	323 K 130 mg/l
Pseudo-first-order equation					
$k_1$ (g/mg·min)	0.304 ± 0.019	0.131 ± 0.019	0.101 ± 0.018	0.130 ± 0.016	0.153 ± 0.02
$q_{e(theo-1)}$ (mg/g)	13.76 ± 0.09	31.24 ± 0.72	53.23 ± 1.65	55.64 ± 1.12	58.13 ± 0.70
$q_{e(exp)}$ (mg/g)	14.0	33.2	57.8	58.5	60.0
$R^2$	0.900	0.806	0.776	0.856	0.932
Pseudo-second-order equation					
$k_2$ (g/mg·min)	0.0534 ± 0.00185	0.00643 ± 0.00077	0.00250 ± 0.00040	0.00360 ± 0.00030	0.00432 ± 0.00009
$q_{e(theo-2)}$ (mg/g)	14.06 ± 0.029	32.98 ± 0.47	57.35 ± 1.28	58.85 ± 0.59	60.84 ± 0.14
$q_{e(exp)}$ (mg/g)	14.0	33.2	57.8	58.5	60.0
$R^2$	0.992	0.950	0.927	0.976	0.998

**Table 2.** Estimated parameters of intraparticle diffusion model at various stages using non-linear regressive analysis

	295 K, 30 mg/l	295 K, 70 mg/l	295 K, 130 mg/l	309 K, 130 mg/l	323 K, 130 mg/l
Step-1					
$k_{i1}$ /(g/mg·1/2min)	0.949 ± 0.352	3.12 ± 0.82	4.26 ± 0.48	6.56 ± 0.28	7.29 ± 0.90
$C_1$	9.14 ± 1.20	11.70 ± 2.82	19.79 ± 2.09	17.52 ± 0.96	19.18 ± 3.08
$R^2$	0.879	0.934	0.975	0.998	0.985
Step-2					
$k_{i2}$ /(g/mg·1/2min)	0.0582 ± 0.0118	1.33 ± 0.13	2.40 ± 0.17	1.81 ± 0.04	0.682 ± 0.033
$C_2$	13.24 ± 0.10	19.80 ± 1.02	28.79 ± 1.73	38.89 ± 0.1	51.95 ± 0.27
$R^2$	0.924	0.990	0.985	0.999	0.995
Step-3					
$k_{i3}$ /(g/mg·1/2min)	0.0380 ± 0.0122	0.151 ± 0.012	0.202 ± 0.035	0.180 ± 0.059	0.0518 ± 0.0280
$C_3$	13.48 ± 0.15	30.37 ± 0.15	54.47 ± 0.48	55.37 ± 0.35	58.61 ± 0.35
$R^2$	0.764	0.982	0.970	0.753	0.632



**Figure 3.** Plots of  $q_t$  and  $1/2t$  with three-step stage at different conditions.

### 3.3 The apparent activation energy of the biosorption of MB on leaf

The magnitude of activation energy may give an idea about the type of adsorption. There are two main

types of adsorption: physical and chemical. Chemical adsorption is specific and involves forces much stronger than physical adsorption. There are two kinds of chemical adsorption including activated and nonactivated ones. Activated chemical adsorption means that the rate varies with temperature according to finite activation energy (8.4 – 83.7 kJ/mol) in the Arrhenius equation. In nonactivated chemical adsorption, the activation energy is near zero<sup>[22]</sup>. The values of rate constant from the pseudo-second-order can be used to calculate the activation energy of adsorptive process. The energy of activation ( $E_a$ ) was determined from the slope of the Arrhenius plot of  $\ln k_2$  versus  $1/T$  (figure not shown) according to Eq. (7) and was found to be 15.5 kJ/mol. These values are of the same magnitude as the activation energy of activated chemical adsorption. The positive values of  $E_a$  suggest that rise in temperature favors the biosorption and the process is an endothermic in nature.

#### 4 Conclusion

The following conclusions can be drawn:

(1) The phoenix tree's leaves powder was found to have a much higher biosorption capacity for removing MB.

(2) The capacity of MB biosorption on leaf powder increased with an increasing of temperature.

(3) The biosorption kinetics study of MB are good in accordance with the pseudo-first-order model and pseudo-second-order model using non-linear analysis and later is better to express the biosorption process. The intraparticle diffusion model also can express the adsorption at different stage. The biosorption process may be of a complex nature.

(4) The process of MB adsorbed onto leaf may be controlled by chemical adsorption. But they have the lower activated energy, the adsorption may be controlled by an activated chemical adsorption.

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