



## Study of equilibrium, kinetic and thermodynamic parameters about methylene blue adsorption onto natural zeolite

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### ABSTRACT

Adsorption equilibrium and kinetic of methylene blue (MB) onto natural zeolite was studied in a batch system. Variables of the system include contact time, pH, salt concentration, temperature, and initial MB concentration. The increase in temperature resulted in a higher MB loading per unit weight of the zeolite. Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan and Temkin isotherm models were applied to experimental equilibrium data of MB adsorption depending on temperature. The effect of contact time at different temperatures and initial concentration were fitted to pseudo-second-order kinetic model. Linear regressive method and nonlinear regressive method were used to obtain the relative parameters. The error analysis was conducted to find whether linear method or nonlinear method was better to predict the experimental results and which model was better to fit the experimental data. Both methods were suitable to obtain the parameters. The Redlich–Peterson equation was best to fit the equilibrium data. The pseudo-second-order kinetic model can be used to describe the adsorption behavior. The nonlinear method may be better with the absolute error as limited condition. The adsorption process was spontaneous and endothermic.

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### 1. Introduction

Adsorption has been an effective separation process for a wide variety of applications, especially for removal of non-biodegradable pollutants (including dyes) from wastewater [1,2]. Adsorption capacity and characteristic of adsorbents were always examined using adsorption isotherm [3]. The linear least-squares method to the linearly transformed adsorptive equations was widely applied to confirm the experimental data and models using coefficient of determination [3–5]. However, depending on the way adsorptive equation linearized, the error distribution changes worse [6–9]. So it will be an inappropriate technique to use the linearization method for estimating the adsorptive model parameters.

Adsorption isotherms of Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan and Temkin equations and pseudo-second-order model are often adopted to predict the adsorptive process in batch mode. Although linear least-square regressive analysis is often used to calculate the relative parameters [10–12], nonlinear regressive analysis is also adopted to obtain the param-

eters [13–16]. The comparison of linear and nonlinear regressive method about these models had been analyzed [5,6,8].

Natural zeolite is easily obtained in many places and has been used as an adsorbent to remove dyes, ammonia ions and heavy metals [17–19]. Methylene blue (MB) is selected as a model compound in order to evaluate the capacity of natural zeolite for the removal of MB from its aqueous solutions in batch mode.

Thus, in the present study, linear and nonlinear method was used to estimate the isotherms parameters, kinetic model parameters. A comparative analysis was made between the linear and nonlinear method in estimating the relative parameters for the adsorption of MB onto zeolite. The error of prediction from two methods was analyzed.

#### 1.1. Adsorption isotherms

##### 1.1.1. Langmuir isotherm

The Langmuir adsorption isotherm has been successfully applied to many pollutants adsorption processes and has been the most widely used sorption isotherm for the sorption of a solute from a liquid solution [20]. The saturated monolayer isotherm can be represented as

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

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The above equation can be rearranged to the common linear form:

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \times \frac{1}{c_e} + \frac{1}{q_m} \quad (2)$$

where  $c_e$  is the equilibrium concentration ( $\text{mg l}^{-1}$ );  $q_e$  is the amount of MB adsorbed onto per unit mass of zeolite ( $\text{mg g}^{-1}$ );  $q_m$  is  $q_e$  for a complete monolayer ( $\text{mg g}^{-1}$ ), a constant related to sorption capacity; and  $K_L$  is a constant related to the affinity of the binding sites and energy of adsorption ( $\text{l mg}^{-1}$ ).

### 1.1.2. Freundlich isotherm

Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface. The Freundlich isotherm is commonly presented as [21]:

$$q_e = K_F c_e^{1/n} \quad (3)$$

where  $K_F$  and  $n$  are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively. Eq. (3) can be linearized by taking logarithms:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (4)$$

### 1.1.3. Redlich–Peterson isotherm

The three-parameter Redlich–Peterson equation which has a linear dependence on concentration in the numerator and an exponential function in the denominator has been proposed to improve the fit by the Langmuir or Freundlich equation and is given by Eq. (5) [22]:

$$q_e = \frac{A c_e}{1 + B c_e^g} \quad (5)$$

where  $A$ ,  $B$  and  $g$  are the Redlich–Peterson parameters,  $g$  lies between 0 and 1. For  $g = 1$ , Eq. (5) converts to the Langmuir form.

Three isotherm constants,  $A$ ,  $B$  and  $g$  can be evaluated from the linear plot represented by Eq. (6) using a trial and error optimization method:

$$\ln \left( \frac{A c_e}{q_e - 1} \right) = g \ln c_e + \ln B \quad (6)$$

### 1.1.4. Koble–Corrigan isotherm

Koble–Corrigan model is also three-parameter equation for the representing equilibrium adsorption data. It is a combination of the Langmuir and Freundlich isotherm type models and is given by Eq. (7) [23]:

$$q_e = \frac{A c_e^n}{1 + B c_e^n} \quad (7)$$

where  $A$ ,  $B$  and  $n$  are the Koble–Corrigan parameters.

Three isotherm constants,  $A$ ,  $B$  and  $n$  can also be evaluated from the linear plot represented by Eq. (8) using a trial and error optimization method:

$$\frac{1}{q_e} = \frac{1}{A c_e^n} + \frac{B}{A} \quad (8)$$

### 1.1.5. Temkin isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm [24]:

$$q_e = A + B \ln c_e \quad (9)$$

where  $A$  and  $B$  are isotherm constants.

## 1.2. Pseudo-second-order kinetic model

The pseudo-second-order equation based on adsorption equilibrium capacity can be expressed as [8,25]:

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \quad (10)$$

where  $k_2$  is the rate constant of pseudo-second-order adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

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

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (11)$$

The linear pseudo-second-order equation can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

The equilibrium sorption capacity,  $q_e$ , and the pseudo-second-order rate constant,  $k_2$ , can be determined using linear regressive analysis by Eq. (12) or nonlinear regressive analysis by Eq. (11), respectively.

## 1.3. The error analysis

In order to confirm the fit model for the adsorption system, it is necessary to analyze the data using error analysis, combined the values of determined coefficient ( $R^2$ ) from regressive analysis. The calculated expressions of some error functions are as follows [9,26,27]:

(1) The sum of the squares of the errors (SSE):

$$\text{SSE} = \sum (q_c - q_e)^2 \quad (13)$$

(2) The sum of the absolute errors (SAE):

$$\text{SAE} = \sum |(q_c - q_e)| \quad (14)$$

(3) The average relative error (ARE):

$$\text{ARE} = \frac{(\sum |(q_c - q_e)/q_e|)}{n} \quad (15)$$

(4) The average relative standard error (ARS):

$$\text{ARS} = \sqrt{\frac{\sum [(q_c - q_e)/q_e]^2}{n - 1}} \quad (16)$$

where  $n$  is the number of experimental data points,  $q_c$  is the predicted (calculated) quantity of MB adsorbed onto zeolite according to the isotherm equations and  $q_e$  is the experimental data.

## 2. Materials and methods

### 2.1. Materials

The dye used in batch experiments was methylene blue (C.I. no. 52015). MB has a molecular weight of  $373.9 \text{ g mol}^{-1}$ , which corresponds to methylene blue hydrochloride with three groups of water. The stock solutions of MB were prepared in distilled water ( $1 \text{ g l}^{-1}$ ). All working solutions were prepared by diluting the stock solution with distilled water to the desired concentration. The values of solution pH were near 7.5.

The natural zeolite used in the present study was obtained from Xinyang city in China. Before use, the zeolite was crushed and sieved through mesh screens, and a fraction of the particles of average size

(40–60 mesh) was soaked in tap water for 24 h, rinsed with distilled water. After drying at 373 K in an oven, the sample was stored. Some specifications of this natural zeolite are as follows [28]: the mineralogical composition was comprised primarily of clinoptilolite (~68.50%) and additionally of feldspar, montmorillonite and quartz by means of XRD. The surface of zeolite is rough and it is composed of some elements, such as silicon, oxygen, aluminium, potassium, etc. The FT-IR spectra of zeolite were composed of the peaks from adsorbed water, vibration of framework and Si–O and Al–O.

## 2.2. Methods

### 2.2.1. Effect of pH on adsorption

The effect of pH on the amount of MB removal was analyzed over the pH range from 2 to 10. The pH was adjusted using 0.1 mol l<sup>-1</sup> NaOH and 0.1 mol l<sup>-1</sup> HCl solutions. In this study 50 ml of dye solution of 30 mg l<sup>-1</sup> was agitated with 6 g l<sup>-1</sup> of zeolite. Agitation was made for 480 min at a constant agitation speed. The pH of original solution was near 7 and it was not adjusted. Flasks were agitated on a shaker for 480 min to ensure equilibrium was reached. The temperature was controlled with a water bath at the temperature of 298 K. Then the concentration of MB in the supernatant solution was analyzed using a UV spectrophotometer (Shimadzu Brand UV-3000) by monitoring the absorbance changes at a wavelength of maximum absorbance (668 nm).

### 2.2.2. Effect of salt concentration on adsorption

Batch adsorption tests were done at the initial concentration of MB 40 mg l<sup>-1</sup> (pH near 7.0) and zeolite (40–60 mesh) dose concentration is 6 g l<sup>-1</sup> in 50 ml solution. The effect of salt concentration (ionic strength) on the amount of MB adsorbed or removed by zeolite was analyzed over the NaCl or CaCl<sub>2</sub> concentration range from 0 to 0.20 mol l<sup>-1</sup>.

### 2.2.3. Equilibrium studies

Equilibrium experiments were carried out by contacting 0.3 g of natural zeolite with 50 ml of MB solution of different initial concentrations (16–230 mg l<sup>-1</sup>). A series of such conical flasks was then shaken at a constant speed of 100 rpm in a shaking water bath with temperatures 298, 318 and 333 K, respectively. After 14 h, the samples were then centrifuged and the left out concentration in the supernatant solution was analyzed for MB absorbance.

The data obtained in batch mode studies was used to calculate the equilibrium MB adsorption quantity. It was calculated for adsorptive quantity of MB by using the following expression:

$$q_e = \frac{V(c_0 - c_e)}{m} \quad (17)$$

where  $V$  is the sample volume in l,  $c_0$  is the initial MB concentration in mg l<sup>-1</sup>,  $c_e$  is the equilibrium MB concentration in mg l<sup>-1</sup>, and  $m$  is the dry weight of zeolite in g.

### 2.2.4. Kinetic studies

Zeolite of 0.3 g was added to each 50 ml volume of MB solution. The initial concentrations of MB solution tested were 30, 55, 113 and 230 mg l<sup>-1</sup>, and the experiments were carried out at 298, 318 and 333 K in a constant temperature shaker bath, respectively. The samples were then collected at different time intervals and were centrifuged. The left out concentration in the supernatant solution was analyzed as said before.

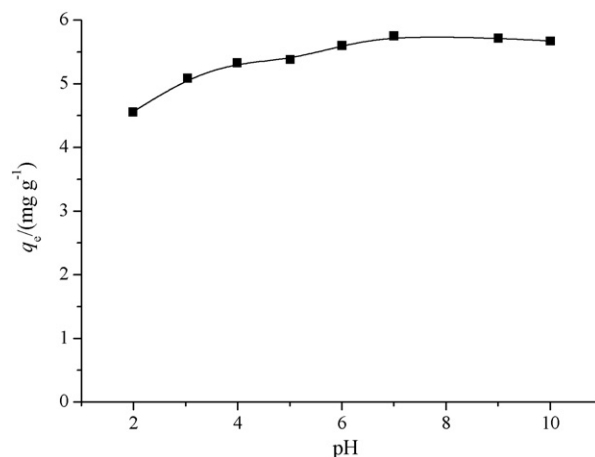


Fig. 1. The effect of initial pH on the equilibrium adsorption capacity of natural zeolite.

## 3. Results and discussion

### 3.1. The effect of pH

Fig. 1 shows the effect of solution pH on MB adsorption onto zeolite at various initial solution pH for an initial dye concentration of 30 mg l<sup>-1</sup> and zeolite dose of 6 g l<sup>-1</sup>.

From Fig. 1, the solution pH affected the values of  $q_e$ . When the value of pH was from 4 to 10, the adsorption quantity was approximately constant. As the initial pH of MB solution is near 7.5, the pH of experimental solution was not adjusted.

### 3.2. The effect of salt concentration on adsorption

Fig. 2 shows the effect of various concentration of NaCl and CaCl<sub>2</sub> solution on the amount of MB adsorbed onto per unit mass of zeolite for an initial MB concentration of 40 mg l<sup>-1</sup> and zeolite dose of 6 g l<sup>-1</sup>.

The wastewater containing dye has commonly higher salt concentration, and effect of ionic strength (or salt concentration) is of some importance in the study of dye adsorption onto adsorbents. From Fig. 2, NaCl and CaCl<sub>2</sub> existed in solution affected the MB adsorption onto zeolite. It was seen that the increase in the salt concentration resulted in a decrease of MB adsorption. This trend indicated that the adsorbing efficiency decreased when NaCl and

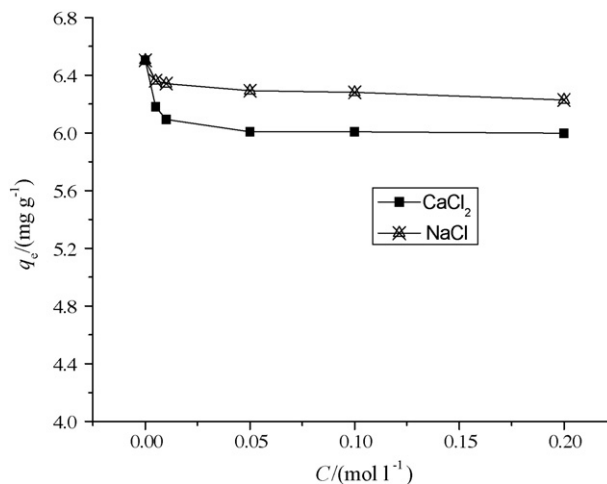
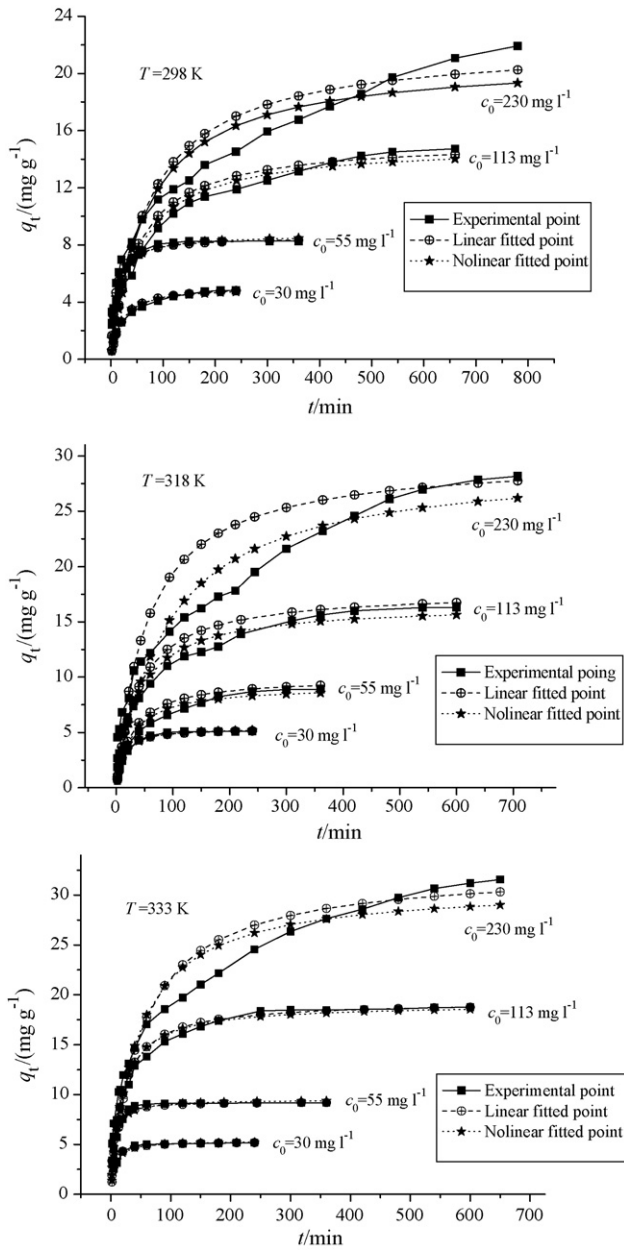


Fig. 2. Effect of salt concentration on MB adsorption.



**Fig. 3.** Effect of contact time on adsorption and comparison of experimental point and fitted point of pseudo-second-order model from linear and nonlinear method.

CaCl<sub>2</sub> concentration increased in the MB solution, which could be attributed to the competitive effect between MB ions and cations from the salt for the sites available for the adsorption process.

As Ca<sup>2+</sup> has more contribution to ionic strength and more positive charge than Na<sup>+</sup>, the effect of Ca<sup>2+</sup> on adsorption is more serious than Na<sup>+</sup>. But even at 0.20 mol l<sup>-1</sup> of salt, the decrease of values of *q<sub>e</sub>* was not more than 10%, so zeolite should be used to efficiently remove MB from aqueous solution with higher salt concentration.

### 3.3. The effect of contact time on adsorption

The effect of contact time on MB adsorption onto zeolite was shown in Fig. 3 at different conditions. It was seen from Fig. 3 that with the beginning of adsorption, values of *q<sub>t</sub>* (the adsorbed quantity of MB onto per unit mass of zeolite at given time, *t*) increased quickly. After 100 min, the values of *q<sub>t</sub>* gradually increased. To

820 min, adsorption nearly reached equilibrium. According to the results of the experiments, the agitation time was fixed at 14 h for the equilibrium study.

The results showed that kinetics of adsorption of MB consisted of two phases: an initial rapid phase where adsorption was fast and contributed significant to equilibrium uptake and a slower second phase whose contribution to the total MB adsorption was relatively small. The first phase was the instantaneous adsorption stage or external surface adsorption. The second phase was the gradual adsorption stage and finally the MB uptake reached equilibrium. It was also seen that equilibrium time occurred relatively earlier in the solution containing lower MB concentrations than the higher ones. The necessary time to reach equilibrium was variable according to the initial concentration. The adsorptive capacity of zeolite at equilibrium increased with the initial concentration increasing. This was obvious because more efficient utilization of the adsorption capacities of the adsorbent was expected due to a greater driving force by a higher concentration gradient pressure.

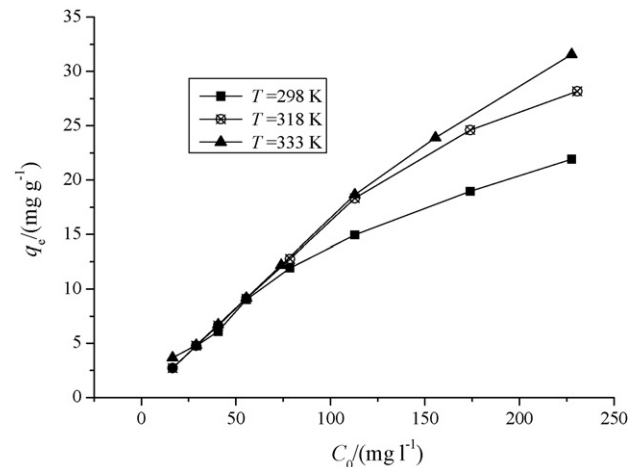
From Fig. 3, adsorption quantity increased with an increase in the temperature. This indicated that a higher temperature favored MB removal by adsorption on zeolite and the adsorption was controlled by an endothermic process.

### 3.4. The effect of initial concentration on temperature-dependent adsorption

The effect of the initial concentration of MB in the solutions on adsorption at 298, 318 and 333 K was shown in Fig. 4, respectively.

As seen from Fig. 4, equilibrium uptake increased with the increasing of initial MB concentrations at the range of experimental concentration. This is a result of the increase in the driving force from the concentration gradient. In the same conditions, if the concentration of MB in solution was bigger, the active sites of zeolite were surrounded by much more MB ions, the process of adsorption would carry out more sufficient. So the values of *q<sub>e</sub>* increased with the increase of initial MB concentrations. From Fig. 4, the adsorption capacity of MB onto zeolite was 21.0 mg g<sup>-1</sup> at 298 K. Compared to other adsorbents [16,28,29], the quantity of MB adsorption onto zeolite is not higher, but as natural materials, it is vast and cheap, so zeolite can be used to remove MB from solution.

The bigger adsorptive capacity of MB was also observed in the higher temperature range. This was due to the increasing tendency of MB to adsorb from the solution to the interface with an increase in temperature. The increase of the equilibrium adsorp-



**Fig. 4.** Effect of initial concentration on equilibrium adsorption uptake at different temperatures.

**Table 1**  
Isotherm parameters for MB adsorption onto zeolite

	Nonlinear method			Linear method		
	T = 298 K	T = 318 K	T = 333 K	T = 298 K	T = 318 K	T = 333 K
<b>Langmuir</b>						
$K_L$ ( $\text{mg g}^{-1}$ )	0.303	0.454	0.957	0.588	0.667	0.635
$q_m$ ( $\text{mg g}^{-1}$ )	19.94	24.14	29.18	16.37	20.7	35.1
$R^2$	0.935	0.926	0.944	0.981	0.994	0.970
<b>Freundlich</b>						
$K_F$	6.10	7.59	11.52	5.31	6.67	10.04
$1/n$	0.282	0.302	0.269	0.332	0.357	0.357
$R^2$	0.975	0.965	0.873	0.938	0.919	0.817
<b>Redlich–Peterson</b>						
A	18.02	30.11	31.70	12.5	14.8	30.5
B	2.11	2.87	1.29	1.21	0.86	1.49
g	0.795	0.779	0.948	0.843	0.914	0.848
$R^2$	0.990	0.976	0.947	0.994	0.995	0.943
<b>Koble–Corrigan</b>						
A	6.92	8.58	34.58	8.20	11.81	27.32
B	0.204	0.137	1.24	0.435	0.495	0.934
n	0.461	0.397	1.34	0.855	0.896	1.12
$R^2$	0.984	0.967	0.948	0.984	0.995	0.973
<b>Temkin</b>						
A	5.87	8.18	12.65	5.87	8.18	12.65
B	3.24	4.04	4.92	3.24	4.04	4.92
$R^2$	0.985	0.970	0.935	0.985	0.970	0.935

tion with increased temperature indicated that the adsorption of MB ions onto zeolite was endothermic in nature. So the adsorptive process may be chemical process. Other studies have the same results about the initial MB concentration on adsorption capacity [15,16,29–31].

### 3.5. Determination of adsorption isotherm parameters about MB/zeolite system

The analysis requires equilibrium to better understand the adsorption process. In this paper, the Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan and Temkin models were applied. An adsorption isotherm is characterized by certain constants which values express the surface properties and affinity of the adsorbent. It can also be used to find the adsorption capacity of adsorbent.

The linear regressive method of least squares is used for finding the parameters of the isotherms. The relative parameters were obtained according to the intercept and slope from the plots between  $1/q_e$  versus  $1/c_e$ ,  $\ln q_e$  versus  $\ln c_e$ ,  $\ln(Ac_e/q_e - 1)$  versus  $\ln c_e$ ,  $1/q_e$  versus  $1/c_e^n$  and  $q_e$  versus  $\ln c_e$ , respectively.

The nonlinear regressive method of least sum squares of difference between calculated data and experimental data was used to determine the isotherm parameters with Origin 7.0. The isotherm parameters and coefficients of determination ( $R^2$ ) from linear method and nonlinear method were all listed in Table 1, respectively.

From Table 1, the parameters about same isotherm at one temperature were different using linear method and nonlinear method, respectively. All values of  $R^2$  in Table 1 were bigger than 0.9 except Freundlich model at 333 K (bigger than 0.81). So the five isotherms were all used to fit the experimental data. This showed that the adsorption process might be a heterogeneous adsorption. At the same temperature, the value of  $R^2$  from Redlich–Peterson was biggest.

As shown in Table 1, the constants of  $K_a$ ,  $q_m$  and  $K_F$  were all increased with increasing temperature. These results indicated that MB can be easy uptake by zeolite from aqueous solutions. The adsorptive capacity increased with increasing temperature.

**Table 2**  
Pseudo-second-order parameters for the adsorption MB at different conditions from linear method

	$c_0$ ( $\text{mg l}^{-1}$ )			
	30	55	113	230
<b>298 K</b>				
$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	0.00978	0.00392	0.00136	0.000627
$q_{e(\text{theo})}$ ( $\text{mg g}^{-1}$ )	5.19	8.47	15.38	22.12
$q_{e(\text{exp})}$ ( $\text{mg g}^{-1}$ )	4.81	8.27	14.9	22.0
$R^2$	0.9980	0.9937	0.9926	0.9740
<b>318 K</b>				
$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	0.0196	0.0141	0.00148	0.000627
$q_{e(\text{theo})}$ ( $\text{mg g}^{-1}$ )	5.25	8.53	17.18	29.85
$q_{e(\text{exp})}$ ( $\text{mg g}^{-1}$ )	5.15	8.90	16.35	28.40
$R^2$	0.9994	0.9995	0.9949	0.9704
<b>333 K</b>				
$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	0.0405	0.0305	0.00281	0.000606
$q_{e(\text{theo})}$ ( $\text{mg g}^{-1}$ )	5.27	9.29	19.34	32.68
$q_{e(\text{exp})}$ ( $\text{mg g}^{-1}$ )	5.17	9.20	18.70	31.60
$R^2$	0.9998	0.9998	0.9996	0.9889

Langmuir constant,  $q_m$ , represents the monolayer saturation at equilibrium. The other mono-component Langmuir constant  $K_L$  indicates the affinity for the binding of MB. A high  $K_L$  value indicates a high affinity. From Table 1, the monolayer or maximum adsorption capacity of zeolite ( $q_m$ ), obtained from linear method or nonlinear method, increased with temperature increasing. The values of  $q_m$  obtained from nonlinear regressive were 19.94, 24.14 and 29.18  $\text{mg g}^{-1}$  at 298, 318, 333 K, respectively.

The Freundlich model does not describe the saturation behavior of the adsorbent as well as Langmuir model. From Table 1, all measured values of  $K_F$  showed easy uptake of MB with high adsorptive capacity of zeolite and significant differences in adsorption capacities due to temperature. The obtained values of  $1/n$  ( $0.1 < 1/n < 1$ ) indicated a higher adsorb ability of MB at all temperatures studied [32]. The results also indicated that with the temperature increasing, the ability of adsorption increased.

Relevant adsorption parameters were also calculated according to the three-parameter isotherm of Redlich–Peterson and Koble–Corrigan at different temperatures. Examination of the data showed that the two isotherms were appropriate descriptions of the data for MB adsorption over the concentration ranges studied. The constants  $g$  and  $n$  were near to 1, and these indicate the isotherms were approaching the Langmuir form.

**Table 3**  
Pseudo-second-order parameters for the adsorption MB at different conditions from nonlinear method

	$c_0$ ( $\text{mg l}^{-1}$ )			
	30	55	113	230
<b>298 K</b>				
$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	0.0110	0.0113	0.00134	0.000691
$q_{e(\text{theo})}$ ( $\text{mg g}^{-1}$ )	5.08	8.70	15.07	21.03
$q_{e(\text{exp})}$ ( $\text{mg g}^{-1}$ )	4.81	8.27	14.91	22.00
$R^2$	0.974	0.977	0.960	0.910
<b>318 K</b>				
$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	0.0164	0.00415	0.00162	0.000380
$q_{e(\text{theo})}$ ( $\text{mg g}^{-1}$ )	5.24	9.21	16.60	29.49
$q_{e(\text{exp})}$ ( $\text{mg g}^{-1}$ )	5.15	8.90	16.35	28.40
$R^2$	0.992	0.954	0.962	0.909
<b>333 K</b>				
$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	0.0328	0.0207	0.00296	0.000751
$q_{e(\text{theo})}$ ( $\text{mg g}^{-1}$ )	5.35	9.51	19.09	30.92
$q_{e(\text{exp})}$ ( $\text{mg g}^{-1}$ )	5.17	9.20	18.70	31.60
$R^2$	0.980	0.981	0.981	0.928

The Temkin parameters  $A$  and  $B$  were also listed in Table 1. Similar to the parameters of Redlich–Peterson and Koble–Corrigan models, the value of  $A$  and  $B$  became larger with an increase in temperature.

Although some researchers have studied the characteristic of MB adsorption onto zeolite [17,33], and also discussed the isotherms. But the parameters of isotherms were from linear regressive analysis. This paper had some difference in the mathematical methods and research contents.

### 3.6. Determination of pseudo-second-order parameters about MB/zeolite system

The parameters of pseudo-second-order model were listed in Table 2 according to Eq. (12). Table 3 listed the relative parameters using nonlinear least-squares regressive analysis according to Eq. (11).

From Tables 2 and 3, the values of  $R^2$  from linear method are highest, while those from nonlinear are higher. So the two methods were both used to predict the adsorption process. The equilibrium adsorption capacities increased with an increase in MB initial con-

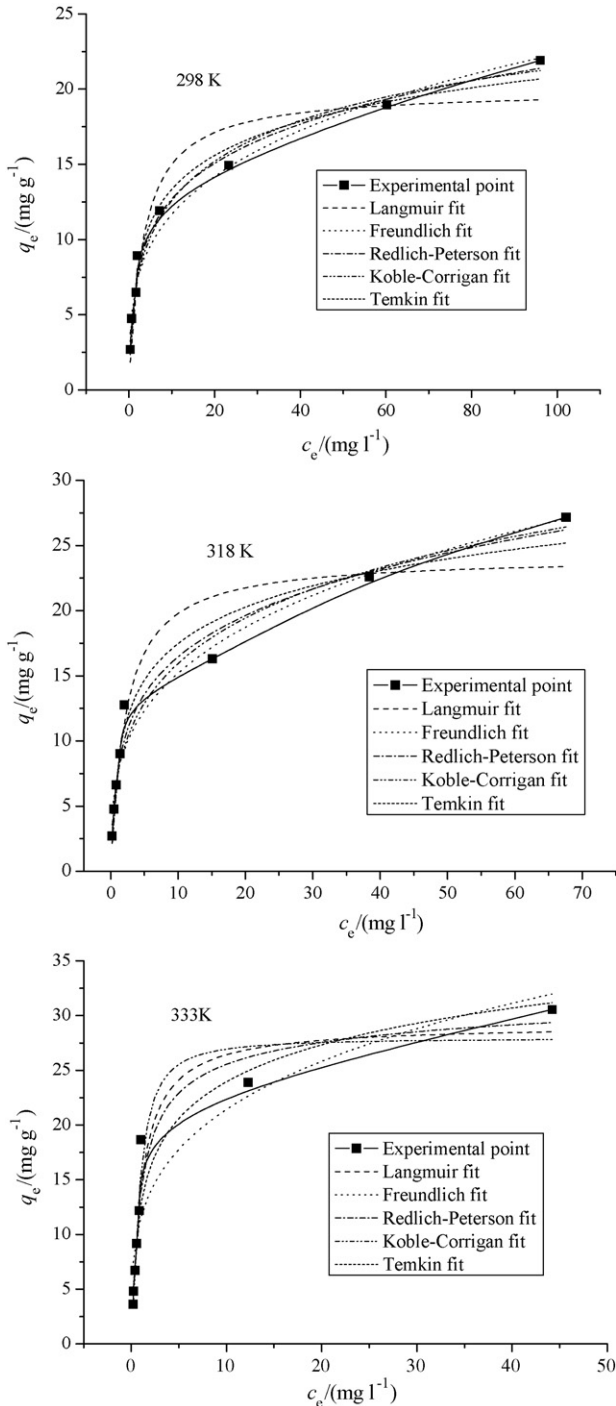


Fig. 5. The experimental points and nonlinear fitted curves from isotherms.

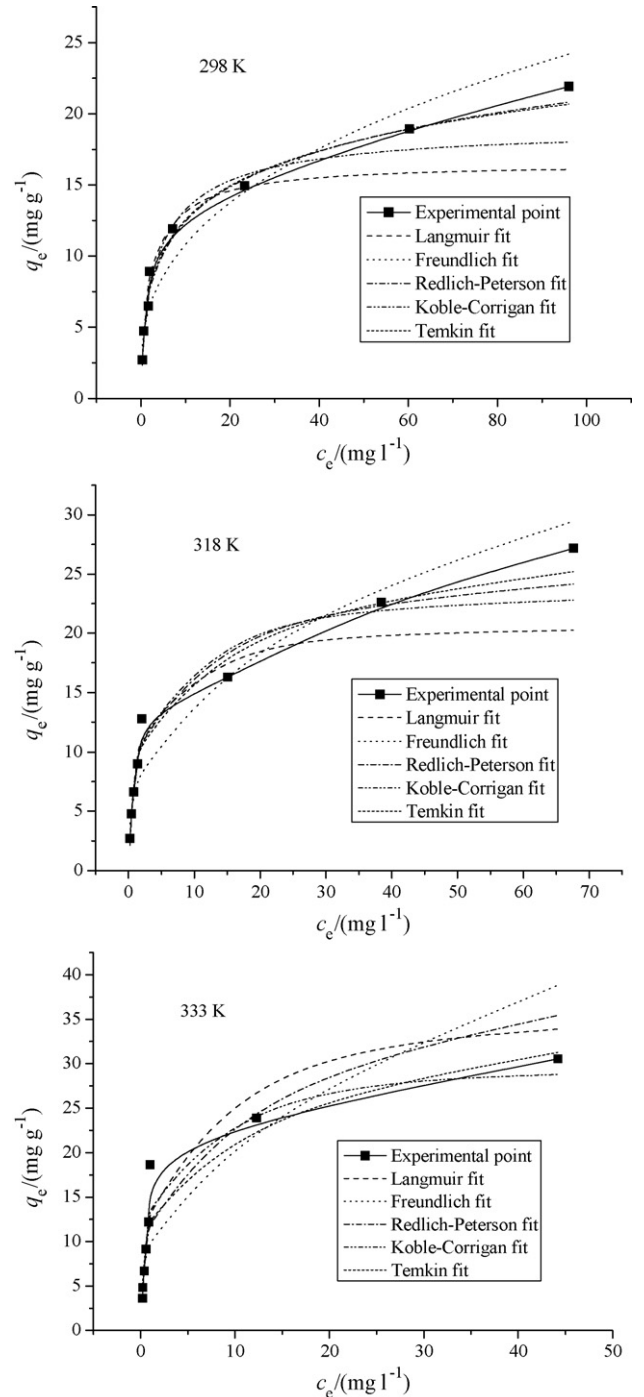


Fig. 6. The experimental points and linear fitted curves from isotherms.

**Table 4**  
Values of four different errors about isotherm equations

Isotherms	Nonlinear method				Linear method			
	SSE	SAE	ARE	ARS	SSE	SAE	ARE	ARS
<b>298 K</b>								
Langmuir	21.36	10.92	0.158	0.204	47.78	12.49	0.110	0.158
Freundlich	8.11	6.51	0.150	0.269	17.45	9.57	0.130	0.187
Redlich–Peterson	3.27	4.48	0.0724	0.101	4.39	5.02	0.0661	0.0817
Koble–Corrigan	5.29	5.69	0.105	0.164	22.34	10.12	0.101	0.119
Temkin	5.01	5.46	0.0783	0.0978	5.01	5.48	0.0783	0.0978
<b>318 K</b>								
Langmuir	39.49	11.77	0.118	0.157	63.27	14.51	0.100	0.133
Freundlich	18.74	8.97	0.187	0.327	30.64	12.58	0.161	0.228
Redlich–Peterson	12.83	7.81	0.109	0.156	23.77	8.86	0.0701	0.104
Koble–Corrigan	17.61	9.49	0.164	0.267	36.84	10.92	0.0815	0.120
Temkin	15.99	8.61	0.0968	0.126	15.99	8.62	0.0968	0.126
<b>333 K</b>								
Langmuir	38.03	14.18	0.149	0.180	88.96	16.99	0.118	0.167
Freundlich	84.35	20.67	0.332	0.501	156.7	24.82	0.242	0.318
Redlich–Peterson	35.54	13.30	0.157	0.201	81.53	17.53	0.131	0.179
Koble–Corrigan	34.21	13.87	0.125	0.141	37.81	12.37	0.103	0.128
Temkin	41.50	12.22	0.152	0.210	41.50	12.22	0.152	0.210

centration. However, the values of  $k_2$  were found to decrease for the increase in the initial concentration at the same temperature. With temperature increasing, both the values of  $q_e$  and  $k_2$  increased. The findings clearly again indicated that the higher temperature favored the MB adsorption on zeolite. Also, the relative parameters were different from linear method and nonlinear method. This showed that the predictive point using parameters from linear method was not same to the predictive point from nonlinear method.

Comparison of difference between values of equilibrium adsorption quantity ( $q_e$ ) from experiment and calculation (obtained from linear method or nonlinear method), some of the value of difference from experiment and linear method is larger, some is opposite. So it cannot be concluded whether linear method or nonlinear method is better from the difference.

### 3.7. Error analysis

#### 3.7.1. The adsorption isotherm

In order to assess different isotherms and their ability to correlate with experimental results, the fitted plots from each isotherm were shown with the experimental data for adsorption of MB onto zeolite at the temperature 298, 318 and 333 K in Figs. 5 and 6. The

values of different errors from linear method and nonlinear method were all listed in Table 4.

The values of SSE, SAE, ARE, ARS about Redlich–Peterson model from linear method or nonlinear method were smallest among the five isotherms, respectively. So it could be concluded that the Redlich–Peterson model be best to fit the experimental data according to  $R^2$ , Figs. 5 and 6 and error values. Among five isotherms, the Freundlich equation was poorest fit according to values of ARE and ARS from linear and nonlinear method, while the Langmuir equation was poor fit according to values of SSE and SAE.

From Tables 1 and 4, the parameters and error values about Temkin equation from nonlinear method was equal to those from linear method. This was because the form of equation is not transformed using linear method. As the forms of linear equation of other four isotherms were transformed from the original equations, respectively, the relative parameters of isotherms from nonlinear method are different to those from linear method. Furthermore, there were difference about the values of each error function between nonlinear method and linear method. Both linear method and nonlinear method can be used to predict the adsorption process as all values of  $R^2$  is larger. From Table 4, if the values of SSE and SAE (absolute error) are expected as limited condition, the nonlin-

**Table 5**  
Error analysis using parameters from linear method and nonlinear method about pseudo-second-order model

	Linear method				Nonlinear method			
	$c_0 = 30 \text{ mg l}^{-1}$	$c_0 = 50 \text{ mg l}^{-1}$	$c_0 = 113 \text{ mg l}^{-1}$	$c_0 = 233 \text{ mg l}^{-1}$	$c_0 = 30 \text{ mg l}^{-1}$	$c_0 = 50 \text{ mg l}^{-1}$	$c_0 = 113 \text{ mg l}^{-1}$	$c_0 = 233 \text{ mg l}^{-1}$
<b>298 K</b>								
SSE	0.397	1.98	14.11	63.15	0.369	1.43	12.69	56.33
SAE	1.55	4.13	13.9	31.1	1.45	3.15	12.9	28.4
ARE	0.0552	0.0654	0.148	0.206	0.0539	0.0508	0.144	0.194
ARS	0.110	0.116	0.255	0.306	0.0985	0.112	0.251	0.302
<b>318 K</b>								
SSE	0.209	6.72	25.32	246.6	0.118	3.85	13.96	102.4
SAE	1.09	8.45	18.6	57.7	1.03	6.25	14.0	39.84
ARE	0.0288	0.146	0.135	0.228	0.0264	0.124	0.124	0.197
ARS	0.0479	0.397	0.213	0.312	0.0342	0.215	0.211	0.302
<b>333 K</b>								
SSE	0.331	2.77	8.88	111.1	0.161	1.02	8.47	100.3
SAE	1.10	4.41	9.70	39.7	1.07	3.08	9.62	38.6
ARE	0.0291	0.0507	0.0624	0.160	0.0237	0.0307	0.0622	0.148
ARS	0.0580	0.0846	0.130	0.257	0.0338	0.0449	0.125	0.240

ear method is better than linear method. But if values of ARE and ARS (relative error) are expected to be lower, the linear method is better than nonlinear method.

### 3.7.2. The adsorption kinetic

The values of different errors from linear method and nonlinear method about pseudo-second-order model were both listed in Table 5, respectively.

From Table 5, the values of SSE, SAE, ARE and ARS from nonlinear method were all smaller than those from linear method, respectively. It could be referred that the nonlinear method may be better to predict the kinetic process of MB adsorption onto zeolite than the linear method. The comparison of experimental points and fitted points were also shown in Fig. 1. Some researches had the same results [7,8].

## 3.8. Calculation of thermodynamic parameters

### 3.8.1. Calculation of the change free energy change ( $\Delta G^\circ$ )

To estimate the effect of temperature on the adsorption of MB onto zeolite, the free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) were determined. The adsorption process can be summarized which represents a heterogeneous equilibrium. The apparent equilibrium constant ( $K'_c$ ) of the biosorption is defined as [32,34]:

$$K'_c = \frac{c_{ad,e}}{c_e} \quad (18)$$

where  $c_{ad,e}$  is the concentration of MB on the adsorbent at equilibrium ( $\text{mg l}^{-1}$ ). The value of  $K'_c$  in the lowest experimental MB concentration can be obtained [34]. The  $K'_c$  value is used in the following equation to determine the change of Gibbs free energy of adsorption ( $\Delta G^\circ$ ):

$$\Delta G^\circ = -RT \ln K'_c \quad (19)$$

The change of enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) can be obtained from the slope and intercept of a van't Hoff equation of  $\Delta G^\circ$  versus  $T$ :

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (20)$$

where  $\Delta G^\circ$  is standard Gibbs free energy change, J;  $R$  is universal gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $T$  is absolute temperature, K.

Values of the standard Gibbs free energy change for the adsorption process obtained from Eq. (19) were listed in Table 6.

The negative  $\Delta G^\circ$  values of MB adsorption onto zeolite was due to the fact that the adsorption processes were spontaneous with a high preference of MB onto zeolite and the negative value of  $\Delta G^\circ$  decreases with an increase in temperature, indicating that the spontaneous nature of adsorption of MB were inversely proportional to the temperature and higher temperature favored the adsorption.

The standard enthalpy and entropy changes of adsorption determined from Eq. (20) were  $12.9 \text{ kJ mol}^{-1}$  and  $0.0758 \text{ kJ mol}^{-1} \text{ K}^{-1}$ , respectively. The positive value of  $\Delta H^\circ$  confirmed the endothermic character of adsorption on MB/zeolite system whereas the positive  $\Delta S^\circ$  values confirmed the increased randomness at the solid–solute

interface during adsorption. The low value of  $\Delta S^\circ$  also indicated that no remarkable changed on entropy occurs.

### 3.8.2. Estimation of activation energy

The magnitude of activation energy may give an idea about the type of sorption. There are two main types of adsorption: physical and chemical. Activated chemical adsorption means that the rate varies with temperature according to a finite activation energy ( $8.4\text{--}83.7 \text{ kJ mol}^{-1}$ ) in the Arrhenius equation. In nonactivated chemical adsorption, the activation energy is near zero [32].

The activation energy for MB adsorption was calculated by the Arrhenius equation [32,34]:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (21)$$

where  $k_0$  is the temperature independent factor in  $\text{g mg}^{-1} \text{ min}^{-1}$ ;  $E_a$  is the apparent activation energy of the reaction of adsorption in  $\text{kJ mol}^{-1}$ ;  $R$  is the gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $T$  is the adsorption absolute temperature, K. The linear form is

$$\ln k = \frac{-E_a}{RT} + \ln k_0 \quad (22)$$

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

The values of rate constant obtained nonlinear analysis according to the pseudo-second-order can be used to calculate the activation energy of sorption 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. (22) and was found to be 25.1, 22.0, 17.8 and  $16.2 \text{ kJ mol}^{-1}$  at the initial concentration of 30, 55, 113 and  $230 \text{ mg l}^{-1}$ , respectively. The values are of the same magnitude as the activation energy of activated chemical sorption. The positive values of  $E_a$  suggested that rise in temperature favor the adsorption and adsorption process may be an endothermic in nature.

## 4. Conclusion

Present study showed that all the five isotherms, Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan and Temkin equation, could represent the equilibrium adsorption of MB onto natural zeolite. The kinetic process can be predicted by pseudo-second-order model. Both linear method and nonlinear method were suitable to predict the adsorption process. The Redlich–Peterson equation was best fitted to the equilibrium data from two methods. Nonlinear method was better than linear method about pseudo-second-order model. The thermodynamics parameters indicated spontaneous and endothermic process. Rise in temperature favored the adsorption.

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**Table 6**

Thermodynamic parameters of MB adsorption on zeolite

	T (K)		
	298	318	333
$\Delta G^\circ$ ( $\text{kJ mol}^{-1}$ )	−9.60	−11.3	−12.2
$\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )		12.9	
$\Delta S^\circ$ ( $\text{kJ mol}^{-1} \text{ K}^{-1}$ )		0.0758	



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