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Short communication

Comparison of linear and nonlinear analysis in estimating the Thomas model parameters for methylene blue adsorption onto natural zeolite in fixed-bed column

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Abstract

Comparison analysis of linear least square method and nonlinear least square method for estimating the kinetic parameters was made using the experimental column data of methylene blue (MB) adsorption onto zeolite at different flow rates and initial concentration. The data were fitted to Thomas model equations using linear and nonlinear regressive analysis, respectively. The error analysis was performed. Present investigation showed that the linear and nonlinear methods are both suitable to predict the breakthrough curves using Thomas model parameters and the nonlinear method is better.

Keywords: Zeolite; Adsorption; Methylene blue; Thomas model; Linear analysis; Nonlinear 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 [1,2]. Adsorption techniques have proved to be an effective and attractive process for removal of non-biodegradable pollutants (including dyes) from wastewater [2–5]. Activated carbon is commonly used as adsorbent to remove dyes in wastewater as it has excellent adsorption ability [6,7], but the high cost limits its widespread use. If the adsorbent material is of inexpensive material and does not require any expensive additional pretreatment step, the adsorption process will become economically viable.

Natural zeolite, which exists and is easily obtained in many places, is vast and cheap. Zeolite has been used as an adsorbent for the removal of dyes, ammonia ions and heavy metals from aqueous solution [8–10]. 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 fixed-bed column. MB has wider applications, which include coloring paper, dyeing cottons, wools, and coating for paper stock. Many researchers have studied the adsorption process by different low-cost adsorbents, such as rice husk [11,12], sawdust [13], chaff [14], leaf [15], industry waste [16], activated carbon [17] and clays [18].

Adsorption model were often used to express the relative adsorptive behavior and predict the adsorptive curve. 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 [19,20]. However, depending on the way adsorptive equation is linearized, the error distribution changes the worse [21–25]. So, it will be an inappropriate technique to use the linearization method for estimating parameters of adsorptive models.

The data obtained from batch adsorptive system are not applicable to continuous adsorptive system, thus continuous sorption studies are needed (e.g. in fixed-bed columns). In order to describe the fixed-bed column behavior and to scale up it for industrial applications, an accurate model has to be used [26–28]. Thomas model is often adopted to predict the adsorptive curve of breakthrough in fixed-bed mode [29,30]. Although

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linear least-square regressive analysis is often used to obtain the Thomas model parameters [26–30], nonlinear regressive analysis is also adopted to determine the relative parameters [12,31]. But the comparison of linear and nonlinear method about Thomas model was not analyzed. Thus, in the present study, linear and nonlinear method is used to determine the Thomas model parameters and 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 was also analyzed.

1.1. Thomas model

The data obtained in column in continuous mode studies was used to calculate maximum solid phase concentration of MB on adsorbent and the adsorption rate constant using the kinetic model developed by Thomas [32]. The Thomas model is one of the most general and widely used models in column performance theory. The expression by Thomas for an adsorption column is given as follows:

$$\frac{c_t}{c_0} = \frac{1}{1+\exp(k_{\mathrm{Th}} q_0 x/v - k_{\mathrm{Th}} c_0 t)} \tag{1}$$

where k_{Th} is the Thomas rate constant (ml min^{-1} mg^{-1}); q_0 is the equilibrium MB uptake per g of the adsorbent (mg g^{-1}); x is the amount of adsorbent in the column (g); c_0 is the influent MB concentration (mg l^{-1}); c_t is the effluent concentration at time t (mg l^{-1}); v is the flow rate (ml min^{-1}). The value of c_t/c_0 is the ratio of effluent and influent MB concentrations. The value of t is the flow time (min, $t = V_{\mathrm{eff}}/v$, V_{eff} is effluent volume at time t).

The linearized form of the Thomas model is as follows [27–30]:

$$\ln\left(\frac{c_0}{c_t} - 1\right) = \frac{k_{\mathrm{Th}} q_0 x}{v} - k_{\mathrm{Th}} c_0 t \tag{2}$$

The values of k_{Th} and q_0 can be determined from a plot of $\ln(c_0/c_t - 1)$ against t at a given flow rate using linear least-square regressive analysis or from a plot of c_t/c_0 against t using nonlinear regression analysis as the values of c_t/c_0 is within 0.05–0.95.

1.2. The error analysis

In order to confirm the fit model for the adsorption system, it is necessary to analyze the data using error analysis, combining the values of determined coefficient (R^2) from regressive analysis. The calculated expressions of some functions are as following [33–36]:

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

$$\mathrm{SSE} = \sum_{i=1}^{n} (y_{\mathrm{c}} - y_{\mathrm{e}})_i^2 \tag{3}$$

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

$$\mathrm{SAE} = \sum_{i=1}^{n} |(y_{\mathrm{c}} - y_{\mathrm{e}})_i| \tag{4}$$

(3) The average relative error (ARE)

$$\mathrm{ARE} = \frac{1}{n}\sum_{i=1}^{n} \left|\frac{y_{\mathrm{c}} - y_{\mathrm{e}}}{y_{\mathrm{e}}}\right| \tag{5}$$

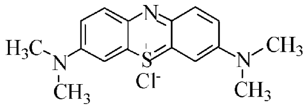
(4) The average relative standard error (ARS)

$$\mathrm{ARS} = \sqrt{\frac{\sum[(y_{\mathrm{c}} - y_{\mathrm{e}})/y_{\mathrm{e}}]^2}{n-1}} \tag{6}$$

where n is the number of experimental data points, y_{c} is the predicted (calculated) data with the Thomas model and y_{e} is the experimental data. In Eqs. (3)–(6), y represents the ratio of c_t/c_0.

2. Materials and methods

The dye used in column experiments was MB (C.I. no. 52015). MB has a molecular weight of 373.9 g mol^{-1}, which corresponds to methylene blue hydrochloride with three groups of water. The structure of MB is as following:



The stock solutions of MB were prepared in distilled water (1 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 are 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 in order to remove possible impurities that might induce clogging during the exchange in the column. After drying at 373 K in an oven, the sample was stored. Some of the specifications of this natural zeolite used in the present study are as following [37]: the analysis of XRD showed that the main composite of zeolite is clinoptilolite. The surface of zeolite is rough and it is composed of some elements, such as silicon, oxygen, aluminum and potassium, etc. The FT-IR spectra of zeolite composed of the peaks of sorbed water, vibration of framework and Si–O and A–O.

Column adsorption experiments were carried out using ten grams of zeolite, packed into a glass column (1.2 cm inner diameter and 30 cm in height) with a bed depth of 15 cm. The experiments were conducted by pumping a MB solution in down flow mode through the fixed-bed with a peristaltic pump at a specified flow rate. The temperatures of all experiments were 293 K. Samples were collected at regular intervals in all the adsorptive process. The concentration of MB in the effluent was analyzed using a UV spectrophotometer (Shimadzu Brand UV-3000) by monitoring the absorbance changes at a wavelength of maximum absorbance (668 nm).

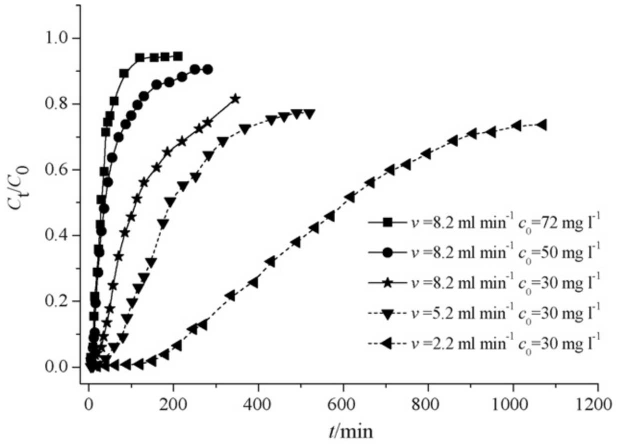


Fig. 1. Breakthrough curves of the effect of flow rate and initial MB concentration on MB adsorption onto zeolite.

3. Results and discussion

3.1. The effect of flow rate on breakthrough curve

To investigate the effect of flow rate on MB adsorption, the influent MB concentration was held constant at 30 mg l^{-1}, and the flow rate was 2.2, 5.2 and 8.2 ml min^{-1}, respectively. The breakthrough curves were shown in Fig. 1. As shown in Fig. 1, in the interval of 100 min, the value of c_t/c_0 reached 0.008, 0.19 and 0.45 when the flow rate was 2.2, 5.2 and 8.2 ml min^{-1}, respectively.

It was shown that breakthrough generally occurred faster with higher flow rate. Breakthrough time reaching saturation was increased significantly with a decrease in the flow rate. When at a low rate of influent, MB had more time to contact with zeolite and it resulted in higher removal of MB ions from solution in column. The variation in the slope of the breakthrough curve and adsorption capacity may be explained on the basis of mass transfer fundamentals [38].

3.2. Effect of influent MB concentration on breakthrough curve

The effect of influent MB concentration on the shape of the breakthrough curves at the same flow rate (8.2 ml min^{-1}) was shown in Fig. 1. As shown in Fig. 1, in the interval of 50 min, the value of c_t/c_0 reached 0.18, 0.60 and 0.77 when influent concentration was 30, 50 and 72 mg l^{-1}, respectively.

It was illustrated that the breakthrough time decreased with increasing influent MB concentration. At lower influent MB concentrations, breakthrough curves were dispersed and breakthrough occurred slower. As influent concentration increased, sharper breakthrough curves were obtained. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time. Similar results have been reported by other researchers [26,27].

3.3. Comparison of the Thomas models by linear and nonlinear regressive analysis

Tables 1 and 2 listed the model parameters of Thomas model and values of R^2, SSE, SAE, ARE, ARS by linear and nonlinear regression analysis using least square method, respectively. Fig. 2 showed the experimental points, linear predicted points and nonlinear predicted points in different conditions according to the parameters of Thomas model in Tables 1 and 2. The values of equilibrium uptake per gram of the adsorbent (q_0, mg g^{-1}) from experiment were also listed in Tables 1 and 2.

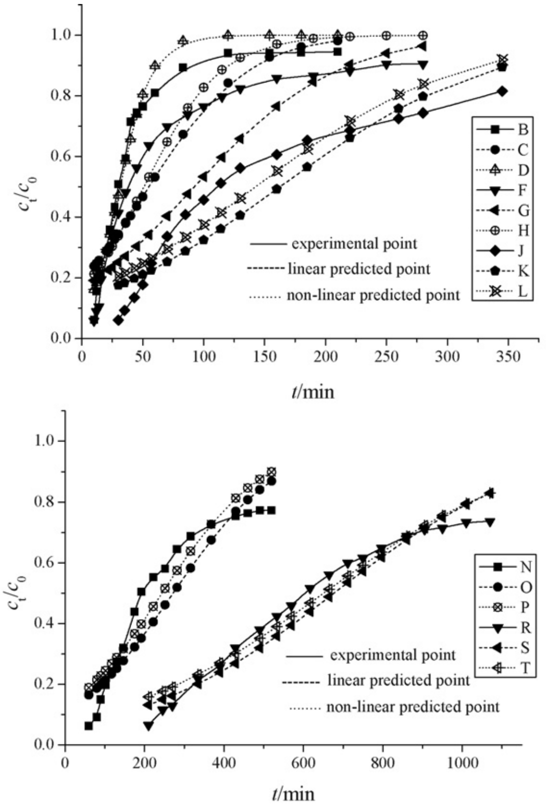
As seen from Tables 1 and 2, with the flow rate and initial concentration increasing, the values of k_{Th} became bigger, while the q_0 of equilibrium was decreasing. The capacity of MB adsorption onto zeolite was smaller compared to other adsorbents from

Table 1
Model parameters by linear regression analysis with the Thomas model for adsorption of MB onto zeolite

c_0 (mg l^{-1})	v (ml min^{-1})	Linear analysis							
		k_{Th} (ml min^{-1} mg^{-1})	$q_{0\text{-c}}$ (mg g^{-1})	R^2	SSE	SAE	ARS	ARE	$q_{0\text{-e}}$ (mg g^{-1})
30	2.2	0.134	4.47	0.921	0.0538	0.902	0.276	0.164	4.36
30	5.2	0.255	4.25	0.835	0.143	1.38	0.500	0.282	3.96
30	8.2	0.390	4.00	0.804	0.145	1.36	0.592	0.349	3.61
50	8.2	0.350	3.79	0.719	0.570	2.83	0.691	0.429	2.46
72	8.2	0.358	3.25	0.723	0.547	2.44	0.780	0.398	1.83

Table 2
Model parameters by nonlinear regression analysis with the Thomas model for adsorption of MB onto zeolite

c_0 (mg l^{-})	v (ml min^{-1})	Nonlinear analysis							
		k_{Th} (ml min^{-1} mg^{-1})	$q_{0\text{-c}}$ (mg g^{-1})	R^2	SSE	SAE	ARS	ARE	$q_{0\text{-e}}$ (mg g^{-1})
30	2.2	0.126	4.30	0.955	0.0418	0.748	0.379	0.181	4.36
30	5.2	0.264	3.81	0.897	0.114	1.25	0.613	0.311	3.96
30	8.2	0.400	3.51	0.878	0.115	1.24	0.748	0.393	3.61
50	8.2	0.640	2.39	0.891	0.185	1.77	0.769	0.379	2.46
72	8.2	0.733	2.04	0.969	0.0468	0.730	0.648	0.257	1.83



B, C, D: v =8.2 ml min^{-1}, c_0=72 mg l^{-1}; F, G, H: v =8.2 ml min^{-1}, c_0=50 mg l^{-1}; J, K, L: v =8.2 ml min^{-1}, c_0=30 mg l^{-1}; N, O, P: v =5.2 ml min^{-1}, c_0=30 mg l^{-1}; R, S, T: v =2.2 ml min^{-1}, c_0=30 mg l^{-1}

Fig. 2. Comparison of experimental points, linear predicted points and nonlinear predicted points.

the values of q_0 listed in Tables 1 and 2 [39], but the natural zeolite is very cheap, so it is still considered as adsorbent to remove dyes from solution.

The results demonstrate that the values of the constant k_{Th} and q_0 obtained by nonlinear regression are not all consistent and have no similarity with the linear transform values. The same parameter values are somewhat close to those obtained by linearization, such as the SSE and SAE set at 30 mg l^{-1} initial concentration.

Considering determined coefficients at the same condition, the value of R^2 from nonlinear regressive method was larger than that from linear regressive method and the error values of SSE and SAE from nonlinear method were lower at all experimental conditions. But concerning the values of ARE and ARS, the two methods were not consistent. Compared to the values of $q_{0-\text{e}}$ and $q_{0-\text{c}}$ listed in Tables 1 and 2, the difference of $q_{0-\text{e}}$ from the experiment and $q_{0-\text{c}}$ from nonlinear was smaller.

From Fig. 2, both linear methods and nonlinear methods are suitable for predicting the dynamic behavior of the column with respect to flow rate and inlet MB concentration. Furthermore, the nonlinear regressive method was more effective in predicting the sorption kinetics than linear method from the values of R^2, SSE, SAE and the difference of $q_{0\text{-e}}$ and $q_{0\text{-c}}$. This conclusion is the same as with other research results [21,22,24,39].

4. Conclusion

On the base of the experimental results of this investigation, the following conclusion can be drawn:

(a) Variables, such as influent concentration and flow rate, can affect the breakthrough curve.
(b) Natural zeolite as low-cost adsorbent to removal of MB from solution was efficient.
(c) The linear method and nonlinear method are both used to predict the breakthrough curve using the Thomas model. But the nonlinear is more effective.

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