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Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column

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Abstract

In this study, the ability of rice husk to adsorb methylene blue (MB) from aqueous solution was investigated in a fixed-bed column. The effects of important parameters, such as the value of initial pH, existed salt, the flow rate, the influent concentration of MB and bed depth, were studied. The Thomas model was applied to adsorption of MB at different flow rate, influent concentration and bed depth to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design using non-linear regression. The bed-depth/service time analysis (BDST) model was also applied at different bed depth to predict the breakthrough curves. The two models were found suitable for describing the biosorption process of the dynamic behavior of the rice husk column. All the results suggested that rice husk as adsorbent to removal MB from solution be efficient, and the rate of biosorption process be rapid. When the flow rate was 8.2 ml min^{-1} and the influent concentration of MB was 50 mg l^{-1}, the equilibrium adsorption biomass reached 4.41 mg g^{-1} according to Thomas model.
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Keywords: Rice husk; Methylene blue; Biosorption; Thomas model; BDST model

1. Introduction

Color is a visible pollutant and the presence of even a very minute amount of coloring substance makes it undesirable due to its appearance. The removal of color from dye-bearing effluents is a major problem due to the difficulty in treating such wastewaters by conventional treatment methods. The sorption technique is proved to be an effective and attractive process for the treatment of these dye-bearing wastewaters [1,2]. The most widely used and effective physical method in industry is activated carbon, although running costs are expensive [3]. If the adsorbent material used is of cheaper cost and does not require any expensive additional pretreatment step, this method will become inexpensive. In recent years, some papers had reported several kinds of agricultural by-product such as rice husk [4], cereal chaff [5], giant duckweed [6], sawdust [7] for the removal of methylene blue from its aqueous solutions. Methylene blue (MB) is selected as a model compound in order to evaluate the capacity of rice husk for the removal of MB from solutions. MB has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools, and coating for paper stock.

The sorption capacity parameter obtained from a batch experiment is useful in providing information about effectiveness of dye–biosorbent system. However, the data obtained under batch conditions are generally not applicable to most treatment system (such as column operations) where contact time is not sufficient long for the attainment of equilibrium. Hence, there is a need to perform equilibrium studies using columns.

Rice husk contains abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxy and amidogen, etc., which make adsorption processes possible [8,9]. Secondly, the yield of rice husk obtained from agriculture as a by-product is vastness.

The aim of this study is to develop a cheap technology for the removal of MB from wastewater. The objectives of present work were to investigate effects of the initial pH value, salt concentration, flow rate, influent concentration and bed depth on MB adsorption by husk bed column. Thomas model and BDST model was used to predict the performance.

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1.1. Thomas model

The data obtained in column in continuous mode studies was used to calculate maximum solid phase concentration of MB on biosorbent and the adsorption rate constant using the kinetic model developed by Thomas [10]. The Thomas solution is one of the most general and widely used methods in column performance theory. The expression by Thomas for an adsorption column is given as follows:

$$\frac{C_t}{C_0} = \frac{1}{1+\exp[k_{\mathrm{Th}}(q_0 x - c_0 V_{\mathrm{eff}})/v]} \quad (1)$$

where k_{Th} is the Thomas rate constant (ml min^{-1} mg^{-1}), q_0 the equilibrium MB uptake per g of the adsorbent (mg g^{-1}), x the amount of adsorbent in the column (g), V_{eff} the effluent volume (ml), C_0 the influent MB concentration (mg l^{-1}), C_t the effluent concentration at time t (mg l^{-1}) and 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 time t (min) is $t = V_{\mathrm{eff}}/v$.

The kinetic coefficient k_{Th} and the adsorption capacity of the column q_0 can be determined from a plot of C_t/C_0 against t at a given flow rate using non-linear regression.

1.2. The bed-depth/service time analysis (BDST) model

The BDST model is based on physically measuring the capacity of the bed at different breakthrough values. The BDST model works well and provides useful modeling equations for the changes of system parameters [11]. A modified form of the equation that expresses the service time at breakthrough, t, as a fixed function of operation parameters is BDST model [12,13]:

$$t = \frac{N_0}{C_0 F} Z - \frac{1}{K_{\mathrm{a}} C_0} \ln\left(\frac{C_0}{C_t} - 1\right) \quad (2)$$

where C_t is the effluent concentration of solute in the liquid phase (mg l^{-1}), C_0 the initial concentration of solute in the liquid phase (mg l^{-1}), F the influent linear velocity (cm min^{-1}), N_0 the adsorption capacity (mg g^{-1}), K_{a} the rate constant in BDST model (l mg^{-1} min^{-1}), t the time (min) and Z is the bed depth of column (cm).

A plot of t versus bed depth, Z, should yield a straight line where N_0 and K, the adsorption capacity and rate constant, respectively, can be evaluated.

A simplified form of the BDST model is:

$$t = aZ - b \quad (3)$$

where

$$a = \frac{N_0}{C_0 F}, \qquad b = \frac{1}{K_{\mathrm{a}} C_0} \ln\left(\frac{C_0}{C_t} - 1\right) \quad (4)$$

The slope constant for a different flow rate can be directly calculated by Eq. (5) [12,13]:

$$a' = a\frac{F}{F'} = a\frac{v}{v'} \quad (5)$$

where a and F are the old slope and influent linear velocity, respectively, and a' and F' are the new slope and influent linear velocity. As the column used in experiment has the same diameter, the ratio of original (F) and the new influent linear velocity (F') and original flow rate (v) and the new flow rate (v') is equal.

For other influent concentrations, the desired equation is given by a new slope, and a new intercept given by:

$$a' = a\frac{C_0}{C'_0} \quad (6)$$

$$b' = b\frac{C_0}{C'_0}\frac{\ln(C'_0 - 1)}{\ln(C_0 - 1)} \quad (7)$$

where b', b are the new and old intercept, respectively, C'_0 and C_0 are the new and old influent concentration, respectively.

1.3. Error analysis

As different forms of the equation affected R^2 values more significantly during the linear analysis, the non-linear analysis might be a method of avoiding such errors [14,15].

In this paper, a non-linear χ^2 of determination test was used. The relative mathematical formula is:

$$\mathrm{SS} = \sqrt{\sum \frac{(y_{\mathrm{e}} - y_{\mathrm{c}})^2}{N}} \quad (8)$$

where y_{e} and y_{c} are the experimental value and calculated value according the model, respectively; N is the number of the experimental point. In order to confirm the best fit isotherm for the adsorption system, it is necessary to analyze the data using SS, combined the values of determined coefficient (R^2).

2. Materials and methods

2.1. Preparation of biomass

Fresh biomass of rice husk was collected from its natural habitats on the dead millet in the farmland, Zhengzhou City, China. It was washed a few times with distilled water, dried for 8 h at 60 °C in the oven. The biomass was sieved and a fraction of average particle size (0.5 mm) was used for column studies.

2.2. MB solution

The stock solutions of MB (500 mg l^{-1}) were prepared in distilled water. All working solutions were prepared by diluting the stock solution with distilled water to the needed concentration.

2.3. Methods of adsorption studies

Continuous flow sorption experiments were conducted in a glass column (1.5 cm internal diameter and 50 cm height). A series of experiments were conducted with various influent wastewater and rice husk columns. Rice husk was packed into a glass column (1.5 cm in diameter and 50 cm in height). Except the experiment of the effect of pH values and bed depth, the mass of rice husk in the column was 2.0 g and the value of pH was near 7.5. The pH of MB solution was adjusted by adding 0.1 mol l^{-1} nitric acid or NaOH solution. No other solution was provided in experiment except effect of salt concentration on biosorption. The MB solution was pumped to the column in a down-flow direction by a peristaltic pump at a certain rate. Samples were collected at regular intervals in all the adsorption. 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).

Also, the experiments of four different bed depth, 8.4 cm (1.3 g), 13 cm (2.0 g), 25.4 cm (4.0 g), 39 cm (6.0 g), were operated at the same influent MB concentration (50 mg ml^{-1}) and flow rate (8.2 ml min^{-1}), respectively.

3. Result and discussion

3.1. The effect of initial solution pH on breakthrough curve

In order to examine the pH variation as well as its effect on MB biosorption in columns, MB adsorption experiments were done at different values 5.0, 7.5 and 9.0. Fig. 1 shows the effect of pH values on adsorption of MB onto rice husk using a plot of dimensionless concentration (C_t/C_0) versus time (t).

As shown in Fig. 1, when the value of pH was 5.0, the value of C_t/C_0 reached 0.86 in 15 min. But the breakthrough curve of the pH 7.5 and 9.0 was not more than 0.52 and 0.40 in the same time, respectively. Obviously, with an increase of pH in the influent, the breakthrough curves shifted from left to right, which indicates that more MB can be removed. It would spend more time reaching the saturation, and the efficiency of biosorption was much higher. The results suggested that with the increasing of pH in experimental condition, the adsorption capacities increase. So the removal of MB from aqueous solution was more efficient at higher initial pH value.

Several reasons may be attributed to MB adsorption behavior of the sorbent relative to solution pH. The surface of rice husk may contain a large number of active sites and MB uptake can be related to the active sites and also to the chemistry of the solute in the solution [16]. At higher pH the surface of rice husk particles may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction [4].

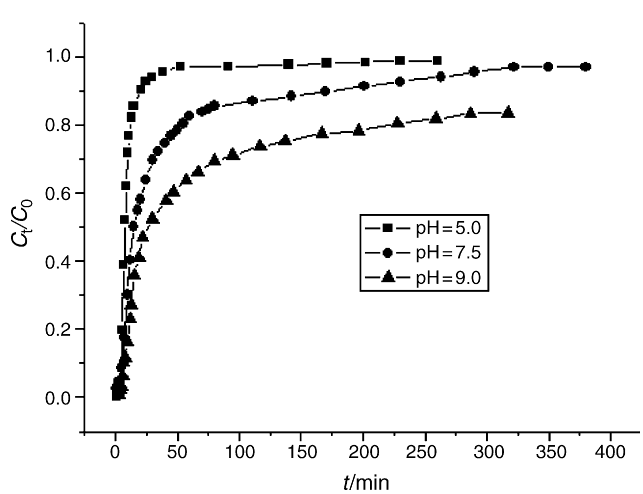

Fig. 1. Breakthrough curve of the effect of pH values on biosorption of MB onto rice husk (v = 8.2 ml min^{-1}, C_0 = 50 mg l^{-1}).

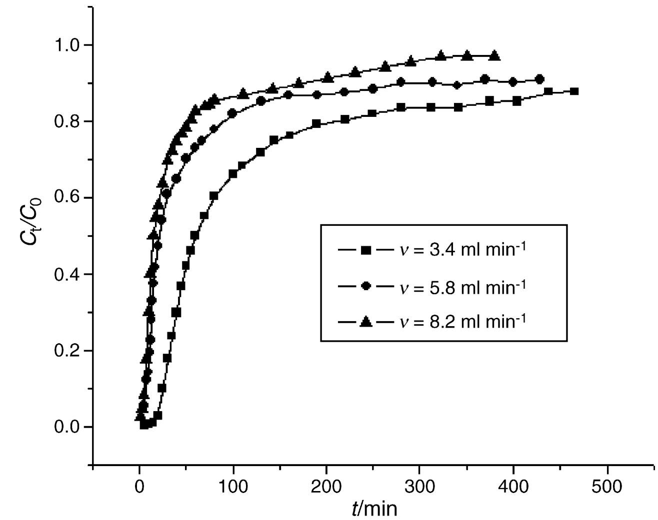

Fig. 2. Breakthrough curve of the effect of flow rate on MB biosorption onto rice husk (C_0 = 50 mg l^{-1}).

3.2. The effect of flow rate on breakthrough curve

To investigate the effect of flow rate on MB biosorption, the influent MB concentration was held constant at 50 mg l^{-1}, and the flow rate was 3.4, 5.8 and 8.2 ml min^{-1}, respectively. The breakthrough curves were shown in Fig. 2.

It was shown that breakthrough generally occurred faster with higher flow rate. Breakthrough time reaching saturation was increased significantly with a decreased in the flow rate. When at a low rate of influent, MB had more time to contact with rice husk that resulted in higher removal of MB ions in column. The variation in the slope of the breakthrough curve and adsorption capacity may be explained on the basis of mass transfer fundamentals. The reason is that at higher flow rate the rate of mass transfer gets increases, i.e. the amount of dye adsorbed onto unit bed height (mass transfer zone) gets increased with increasing flow rate leading to faster saturation at higher flow rate [11].

3.3. Effect of influent MB concentration on breakthrough curve

The effect of influent MB concentration on the shape of the breakthrough curves was shown in Fig. 3. As shown in Fig. 3, in the interval of 50 min, the value of C_t/C_0 reached 0.71, 0.78 and 0.86 when influent concentration was 35, 50 and 100 mg l^{-1}, respectively.

It is illustrated that the breakthrough time decreased with increasing influent MB concentration. At lower influent MB concentrations, breakthrough curves were dispersed

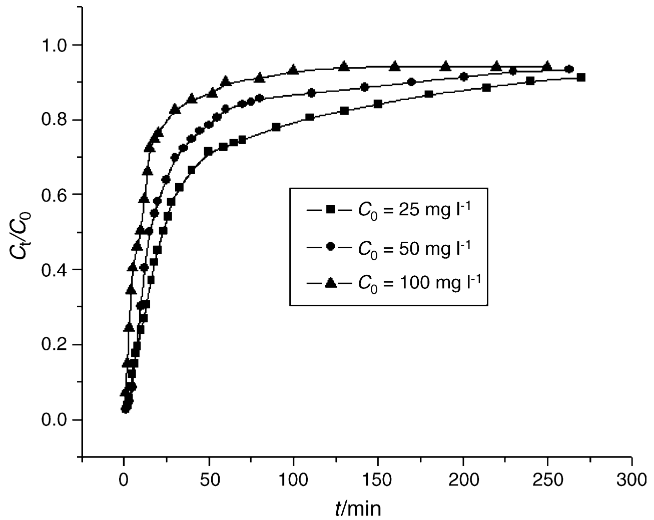

Fig. 3. Breakthrough curve of the effect of influent concentration on MB biosorption onto rice husk ($v = 8.2\,\mathrm{ml\,min^{-1}}$).

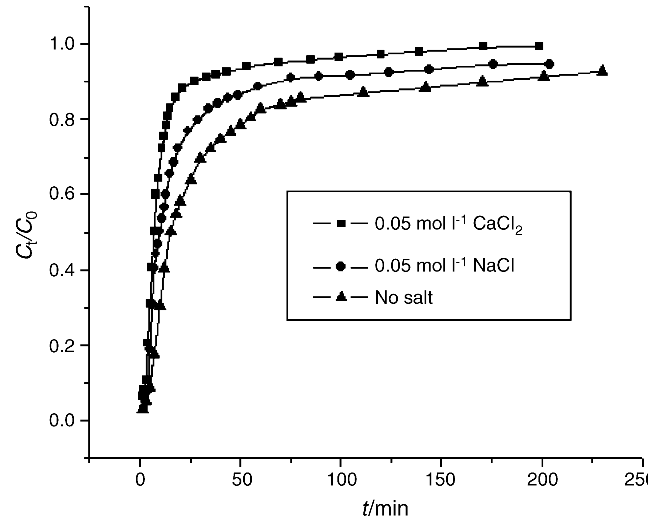

Fig. 4. Breakthrough curve of the effect of existed salt on MB biosorption onto rice husk ($C_0 = 50\,\mathrm{mg\,ml^{-1}}$, $v = 8.2\,\mathrm{ml\,min^{-1}}$).

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 [12]. This can be explained by the fact that more adsorption sites were being covered as the MB concentration increasing. The larger the influent concentration, the steeper is the slope of breakthrough curve and smaller is the breakthrough time. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time, or in other words, the diffusion process is concentration dependent. As the influent concentration increases, MB loading rate increases, so does the driving force increase for mass transfer, which in a decrease in the adsorption zone length [12].

3.4. The effect of salt concentration on breakthrough curve

To investigate the effect of salt concentration on MB biosorption, the influent MB concentration was held constant at $50\,\mathrm{mg\,l^{-1}}$, and the flow rate was $8.2\,\mathrm{ml\,min^{-1}}$. The breakthrough curves were shown in Fig. 4.

As shown in Fig. 4, the existence of salt in solution resulted in steeper slope and smaller breakthrough time, furthermore, the effect of $CaCl_2$ is stronger than the same concentration of NaCl.

The reason could be attributed to the competitive effect between MB ions and metal cations from the salt for the sites available for the sorption process. Another reason is that ionic strength increase, the activity of MB and the active sites decrease, so the adsorptive capacity of MB decreases. As Ca^{2+} has more contribution to ionic strength and more positive charge than Na^+, the effect of Ca^{2+} on adsorption is more serious than Na^+ at the same concentration [5]. But from Fig. 4, rice husk still had higher capacity of binding MB in salt-existed solution. So rice husk can be used to remove MB from aqueous solution with higher salt concentration.

3.5. The effect of different bed depth on breakthrough curve

Fig. 5 was the breakthrough curve at different bed depth at the same influent concentration ($C_0 = 50\,\mathrm{mg\,ml^{-1}}$) and flow rate ($v = 8.2\,\mathrm{ml\,min^{-1}}$), respectively.

From Fig. 5, as the bed height increases, MB had more time to contact with rice husk that resulted in higher removal efficiency of MB ions in column. So the higher bed column results in a decrease in the solute concentration in the effluent at the same time. The slope of breakthrough curve decreased with increasing bed height, which resulted in a broadened mass transfer zone. High uptake was observed at the highest bed height due to an increase in the surface area of biosorbent, which provided more binding sites for the sorption [17,18].

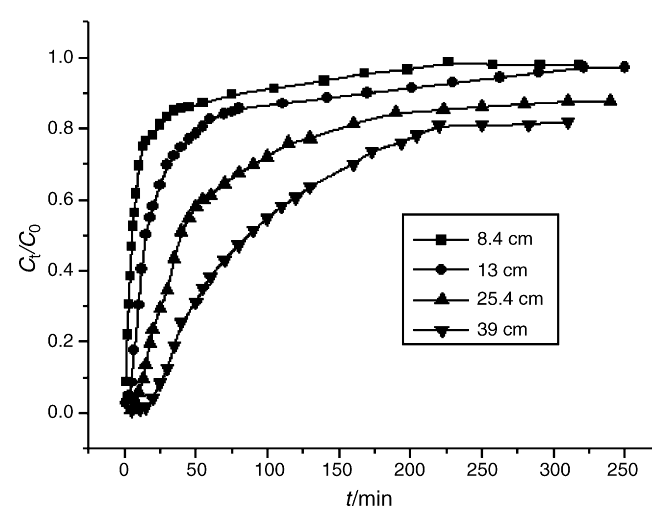

Fig. 5. Breakthrough curve of the effect of different bed depth on MB biosorption onto rice husk ($C_0 = 50\,\mathrm{mg\,ml^{-1}}$, $v = 8.2\,\mathrm{ml\,min^{-1}}$).

Table 1
Calculated constants of BDST model for the adsorption of MB using linear regression analysis ($C_0 = 50\,mg\,l^{-1}$, $v = 8.2\,ml\,min^{-1}$)

C_t/C_0	a ($min\,cm^{-1}$)	b (min)	K_a ($l\,mg^{-1}\,min^{-1}$)	N_0 ($mg\,l^{-1}$)	R^2	SS
0.2	1.08 ± 0.08	7.31 ± 1.8	0.00379 ± 0.00072	251 ± 18	0.990	3.27
0.4	1.97 ± 0.12	13.7 ± 3.0	0.000590 ± 0.000112	458 ± 28	0.992	8.24
0.6	3.34 ± 0.27	22.3 ± 6.5	−0.000364 ± 0.000120	776 ± 62	0.987	40.0

Table 2
Predicted breakthrough time based on the BDST constants for a new flow rate ($C_0 = 50\,mg\,l^{-1}$)

C_t/C_0	a ($min\,cm^{-1}$)	b (min)	v	v'	a'	Z (cm)	t_c (min)	t_e (min)
0.2	1.081	7.313	8.2	3.4	2.607	13	26.6	28
0.4	1.972	13.75	8.2	3.4	4.731	13	48.2	47.5
0.6	3.342	22.29	8.2	3.4	8.304	13	83.1	80

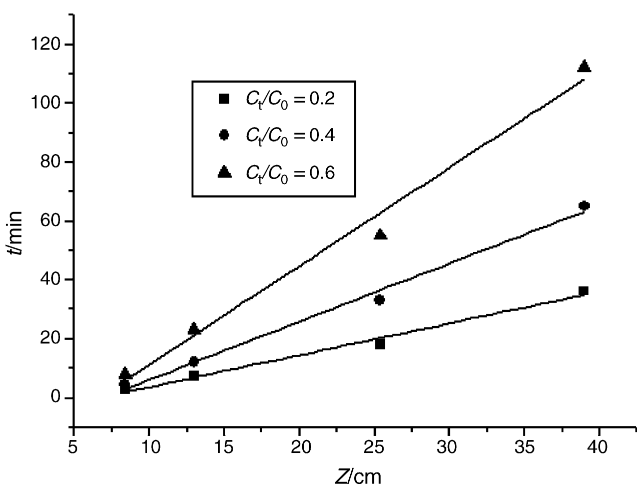

Fig. 6. Isoremoval lines for 0.2, 0.4 and 0.6 breakthrough for different bed height ($C_0 = 50\,mg\,l^{-1}$, $v = 8.2\,ml\,min^{-1}$).

3.6. Modeling of different bed depth column study results about: BDST model

The lines of t–Z at values of C_t/C_0 0.2, 0.4 and 0.6 were shown in Fig. 6, respectively. The related constants of BDST according the slopes and intercepts of lines are listed in Table 1. The uncertainties of the relative parameters are also listed in Table 1.

From Table 1, as the value of C_t/C_0 increased, the rate constant of K_a decreased while the adsorption capacity of the bed per unit bed volume, N_0, increased. From the values of R^2 and SS, it indicated the validity of BDST model for the present system. The BDST model constants can be helpful to scale up the process for other flow rates and concentration without further experimental run.

The BDST equation obtained at flow rate $8.2\,ml\,min^{-1}$ and influent concentration $50\,mg\,l^{-1}$ was used to predict the adsorbent performance at lower flow rates of $3.4\,ml\,min^{-1}$ and influent concentration of $35\,mg\,l^{-1}$, respectively. The predicted time (t_c) and experimental time (t_e) were shown in Tables 2 and 3, respectively. From Tables 2 and 3, good prediction has been found for the case of changed feed concentration and flow rate. Thus, model and the constants evaluated can be used to design columns over a range of feasible flow rates and concentrations at $C_t/C_0 = 0.2$, 0.4 and 0.6, respectively.

These results indicate that the equation can be used to predict adsorption performance at other operating conditions for adsorption of MB onto rice husk.

3.7. Modeling of column study results: Thomas model

Thomas model was applied to the experimental data with respect to flow rate, influent concentration of MB and bed depth. A non-linear regression analysis was used on each set of data to determine the Thomas model parameters of q_0 and k_{Th}. The determined coefficients and the SS were also obtained using non-linear regression analysis according Eq. (1). The results were listed in Table 4. They were all fits with higher determined coefficients (R^2) ranging from 0.81 to 0.95 and lower SS (smaller than 0.05).

As shown in Table 4, as the influent concentration increased, the value of q_0 increased but the value of k_{Th} decreased. The reason is that the driving force for biosorption is the concentration difference between the dye on the biosorbent and the dye in the solution [19–21]. Thus the high driving force due to the higher MB concentration resulted in better column performance. With flow rate increasing, the value of q_0 decreased but the value of k_{Th} increased. As the bed depth increased, the value of q_0

Table 3
Predicted breakthrough time based on the BDST constants for a new influent concentration ($v = 8.2\,ml\,min^{-1}$)

C_t/C_0	a ($min\,cm^{-1}$)	b (min)	C_0	C'_0	a'	b'	Z (cm)	t_c (min)	t_e (min)
0.2	1.081	7.313	50	35	1.54	9.47	13	10.5	8.0
0.4	1.972	13.75	50	35	2.8	17.3	13	19.2	17.5
0.6	3.342	22.29	50	35	4.92	32.2	13	31.8	30

Table 4
Calculated constants of Thomas model at different conditions using non-linear regression analysis

C_0 (mg l^{-1})	v (ml min^{-1})	Z (cm)	k_{Th} (ml min^{-1} mg^{-1})	q_0 (mg g^{-1})	R^2	SS
35	8.2	13	2.89 ± 0.19	4.16 ± 0.61	0.862	0.0115
50	8.2	13	2.69 ± 0.45	4.41 ± 0.45	0.839	0.0122
100	8.2	13	2.55 ± 0.16	4.70 ± 0.45	0.945	0.0367
50	3.4	13	2.18 ± 0.38	4.81 ± 0.47	0.846	0.0154
50	5.8	13	2.46 ± 0.37	4.57 ± 0.36	0.915	0.0139
50	8.2	8.4	3.06 ± 0.55	3.23 ± 0.50	0.867	0.0186
50	8.2	25.4	1.06 ± 0.21	5.32 ± 0.53	0.828	0.0198
50	8.2	39	0.876 ± 0.184	6.63 ± 0.45	0.813	0.0207

increased significantly while the value of k_{Th} decreased significantly. So higher flow rate and lower influent concentration have disadvantage to adsorption of MB on rice husk column.

4. Conclusion

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

(a) Variables, such as pH, influent concentration, flow rate and existed salt, can affect the breakthrough curve.
(b) Rice husk as adsorbent to removal MB from solution was proved efficiently.
(c) The Thomas model and BDST model adequately described the adsorption of MB onto rice husk by column mode.

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