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Column absorption and regeneration behavior of a granular red mud for treating wastewater containing methylene blue

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ABSTRACT

This work focuses on the column absorption and regeneration behavior of a granular red mud (GRM) for absorbing methylene blue (MB) in wastewater. By investigating key parameters, such as packing column height of adsorbent, initial concentration of MB, and flow rate, on the adsorption effects of GRM, the results show that the GRM can effectively remove MB from wastewater. The breakthrough time of the absorption process can be as high as 330 min, when 20.5 cm GRM column was used, with initial concentration and flow rate of MB wastewater being 150 mg L^{-1} and 4 mL min^{-1}, respectively. The Thomas model is capable of describing the adsorption kinetics. Finally, for assessing the regeneration ability of the loaded GRM, a series of experiments of eluting the MB-loaded column with dilute nitric acid solution, whose pH value is about 3.0, were conducted. The results showed that the regeneration and re-adsorption effect of the GRM column is good.

Keywords: Granular red mud; Methylene blue; Adsorption column; Regeneration; Wastewater treatment

1. Introduction

Red mud (RM) is a solid waste residue formed after the caustic digestion of bauxite ores during the production of alumina. For every tonne of alumina produced, approximately one to two tonnes (dry weight) of bauxite residues, RM, is generated. Presently, all over the world, an excess of 2.7 billion tonnes of RM has been stored up. The number is increasing quickly at a speed of 120 million tonnes per year [1]. Currently, most RM produced from alumina plants is disposed in landfills or dumped into the sea. Due to its alkaline nature and the chemical and mineralogical species present in RM, this solid waste causes some impact on the environment [2]. The treatment and utilization of high volume RM waste has been a major challenge for the alumina industry.

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Currently, the comprehensive resource utilization of RM is reflected mainly in three aspects. The first is extraction of valuable metals such as iron [3,4], alumina [5,6], titanium, scandium, gallium [7], and other metals [8–11] from RM. The second is to use RM in the construction materials such as ceramics [12,13], cements [14], clay bricks [15], and glazes [16]. The last is to produce glass and glass–ceramics with RM [17–19].

In recent years, it has become a research trend to use RM as an adsorbent for wastewater treatment. RM has been studied for potential use as a low-cost sorbent for the removal of toxic heavy metals [20–22], metal ions [23–26], and inorganic anions [27–29], as well as organic compounds [30–32].

Studies about the utilization of RM in columns to remove wastewater are very rare; this is because RM particles are too fine to be used in the column technique. With our knowledge from the literature survey, it can be seen that the removal of dye from aqueous solutions, such as methylene blue (MB), in wastewater by using RM in the column absorption method has not been reported. Therefore, the objective of this study is to: (i) prepare the cement granular red mud (GRM) according to the method reported by Ju et al. [26]; (ii) perform column studies to investigate the influence of parameters, such as packing column height of adsorbent, initial concentration of MB, and flow rate, on the adsorption effect of a cement GRM; and (iii) perform column studies to examine the regeneration possibility of the GRM with a series of experiments.

2. Experimental

2.1. Materials

The fresh RM used in this study was obtained from an alumina plant in Henan province, China. Its water content is about 30%, and its initial pH value is about 12–14. The binder, a high-quality Portland cement, was obtained from a cement plant in Kunming, China. RM cake 1,000 g was directly mixed with 2 wt% cement for producing the GRM which was condensed in humid environment for 6 d, and then was used as an absorbent in the following experiments and research work. The properties of the GRM are as follows: particle size is less than 2 mm; the efflorescence rate is 4.83%; and the specific surface area is 17.42 $m^2 g^{-1}$.

All chemicals, including HNO_3, NaOH, $C_{16}H_{18}N_3SCl.3H_2O$ (methylene blue trihydrate), are of analytical grade.

2.2. Column absorption

The device connection diagram is shown in Fig. 1.

The procedures of column experiments are as follows:

At first, a certain amount of GRM was put into a 200 mL buret to form a GRM column, and a certain amount and concentration of MB solution was put into a 500 mL separatory funnel. Then, the switches of funnel and buret were turned into a certain angle to adjust the flow rate of the MB solution, which went through the GRM column for absorption and purification. After sampling from the absorbed MB solution, the samples were analyzed using the method of colorimetry. Finally, according to the relationship between the measured concentration ratio and the oscillation time, the adsorption rate curve was drawn.

The experimental parameters are MB initial concentration (100, 150, 200 mg L^{-1}), flow rate (1.5, 4, and 7 mL min^{-1}), and the amount of GRM (10, 20, and 30 g) corresponding to the adsorbent packing height of 9, 14, and 20.5 cm, respectively. According to the best experimental conditions for the batch technique of the removal of MB from solutions using thes GRM by Lu et al. method [33], the column systems were run using initial MB solutions with an initial pH 11.

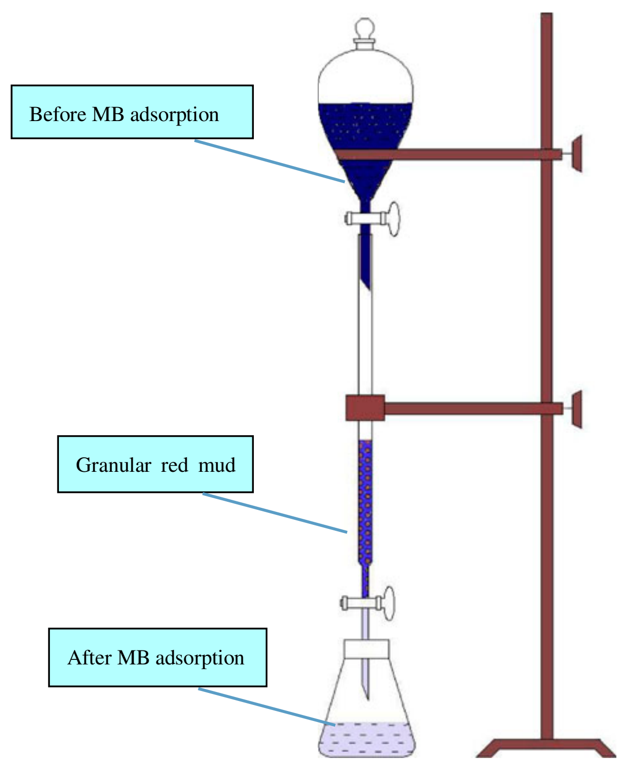

Fig. 1. Device connection diagram.

The amount of MB adsorbed was calculated with the following equation:

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

where q_t is the amount of dye adsorbed per unit weight of GRM at time "t" (mg g^{-1}); C_0 is the initial concentration of MB solution (mg L^{-1}); C_t is the concentration of MB in solution at certain time (mg L^{-1}); V is the MB solution volume (L); and m is the GRM dosage (g).

2.3. Regeneration

The device connection diagram is as illustrated in Fig. 1.

Two kinds of desorption methods are used during the experiments.

2.3.1. Continuous desorption

A large volume of nitric acid solution, whose pH value is 3, was used as the regeneration reagent at a flow rate of 4 mL min^{-1} to regenerate the MB-adsorbed column.

The Solution flowing out of the buret was sampled at a certain interval time. Then, the concentration of MB in the samples was determined to calculate the desorption amount of MB.

2.3.2. Piecewise desorption

Triplet nitric acid solution (pH 3) was used as the regeneration reagent, with a flow rate of 4 mL/min, to regenerate the MB absorbed column. Every 100 mL of the nitric acid solution was circulated for three times to wash out MB from the GRM column.

2.3.3. Sampling method:

During experiments (1) and (2), the solution flowing out of the buret was sampled at a certain interval time. Then, the concentration of MB in the samples was determined to calculate the desorption amount of MB.

3. Results and discussion

3.1. Effect of bed height and flow rate on the breakthrough curve

Breakthrough point is a parameter that indicates absorption limits of the GRM packing column [34]. In this article, we take $C_t/C_0 = 0.65$ as the breakthrough point.

The breakthrough curve of the adsorption column for different packing layer heights is shown in Fig. 2. It was observed that with the increase in packing column height, the penetration point of breakthrough curve moved to the right. The breakthrough time of the absorption process can be as high as 330 min, when 20.5 cm GRM column was used, with the initial concentration and flow rate of MB wastewater being 150 mg L^{-1} and 4 mL min^{-1}, respectively.

The breakthrough curve of the adsorption column under different flow rates, 1.5, 4, and 7 mL min^{-1}, respectively, at column height of 14 cm, is shown in Fig. 3. It is shown that with the increase in flow rate, the penetration point of the breakthrough curve moved to the left. Thus, the breakthrough time of the GRM column was shortened.

3.2. Effect of MB initial concentration on breakthrough curve

The breakthrough curve of the adsorption column under different initial concentrations, 100, 150, and 200 mg L^{-1}, when the column height and flow rate was kept at 14 cm and 4 mL min^{-1}, respectively, is shown in Fig. 4. It can be seen that with the increase of initial MB concentration, the penetration point moved to the left and the curve becomes steep. When the MB initial mass concentration increased from 100 to 200 mg L^{-1}, the penetration time decreased from 320 to 146 min and the breakthrough time was shortened significantly.

3.3. Thomas model

Thomas model [28,35] can be used to estimate the equilibrium adsorption capacity and adsorption rate constant of the adsorbate. Its expression is as follows:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_T q_T m}{v} - k_T C_0 t \quad (2)$$

where C_t is the concentration of the solution after absorption at the sampling time (mg L^{-1}); C_0 is the initial concentration of the MB wastewater (mg L^{-1}); k_T is the rate constant (mL min^{-1} mg^{-1}); q_T is the total sorption capacity (mg g^{-1}); m is the amount of adsorbent in the adsorption column (g); v is the flow rate of the MB wastewater (mL min^{-1}); and t is the running time of adsorption column (min).

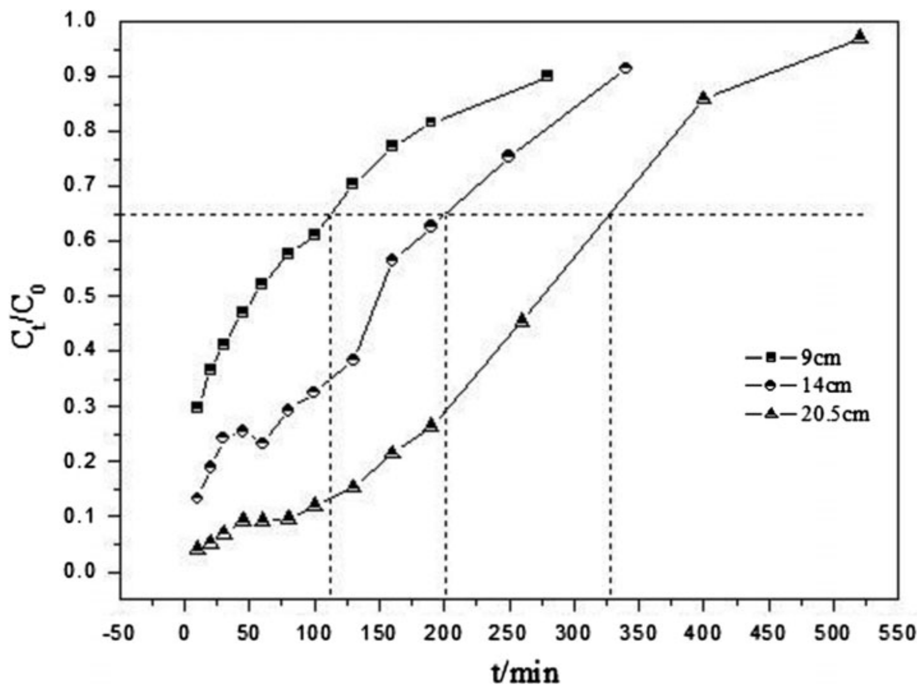

Fig. 2. The breakthrough curve of adsorption column for different packing column heights (MB initial concentration = 150 mg L^{-1}, flow rate = 4 mL min^{-1}).

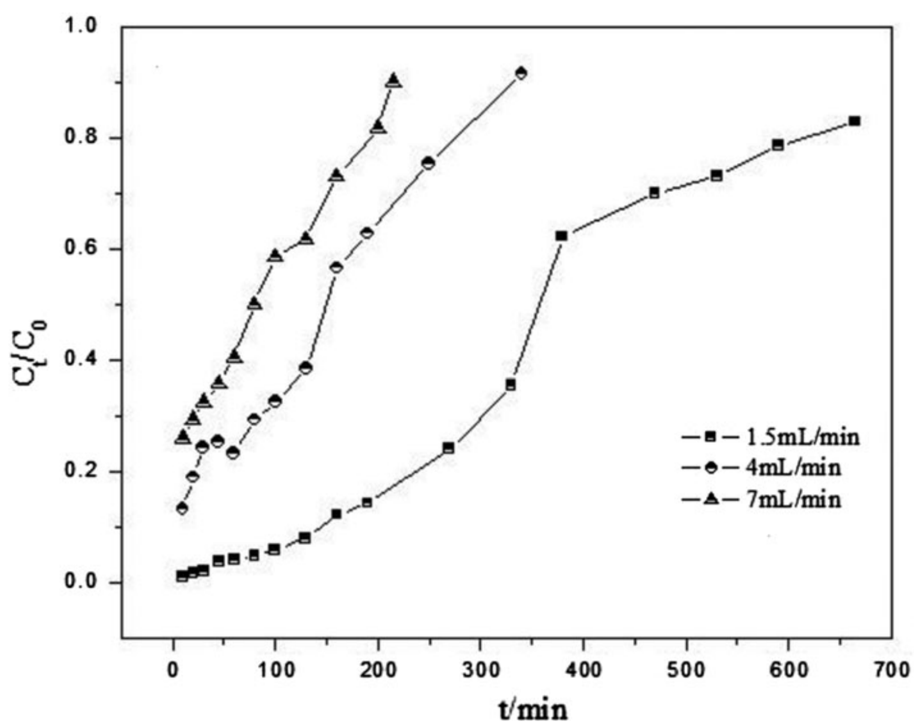

Fig. 3. The breakthrough curve of GRM column at different flow rates (MB initial concentration = 150 mg L^{-1}, column height = 14 cm).

Using the formula (2) in the experimental data in Figs. 2–4, the linear relationship of "t" and "$\ln(C_0/C_t - 1)$" and their regression diagram were obtained and drawn in Figs. 5–7. Then, according to the intercept and slope of the regression lines, the Thomas constants can be calculated as shown in Table 1.

These results shown that, with the increase in the flow rate from 1.5 to 7 mL min^{-1}, the adsorption rate

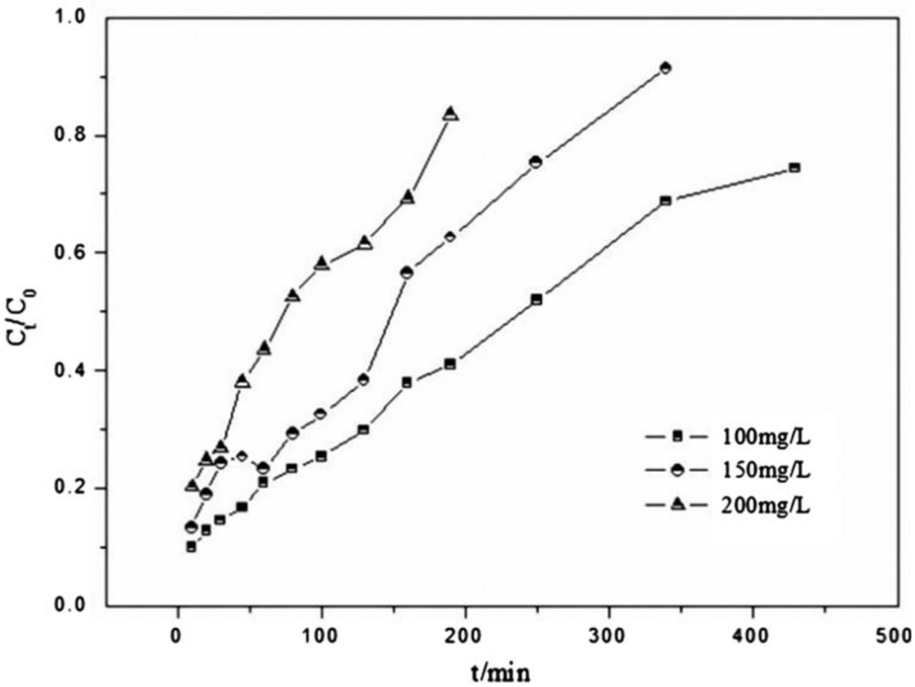

Fig. 4. The breakthrough curve of adsorption column under different initial concentrations (packing column adsorbent height = 14 cm, flow rate = 4 mL min^{-1}).

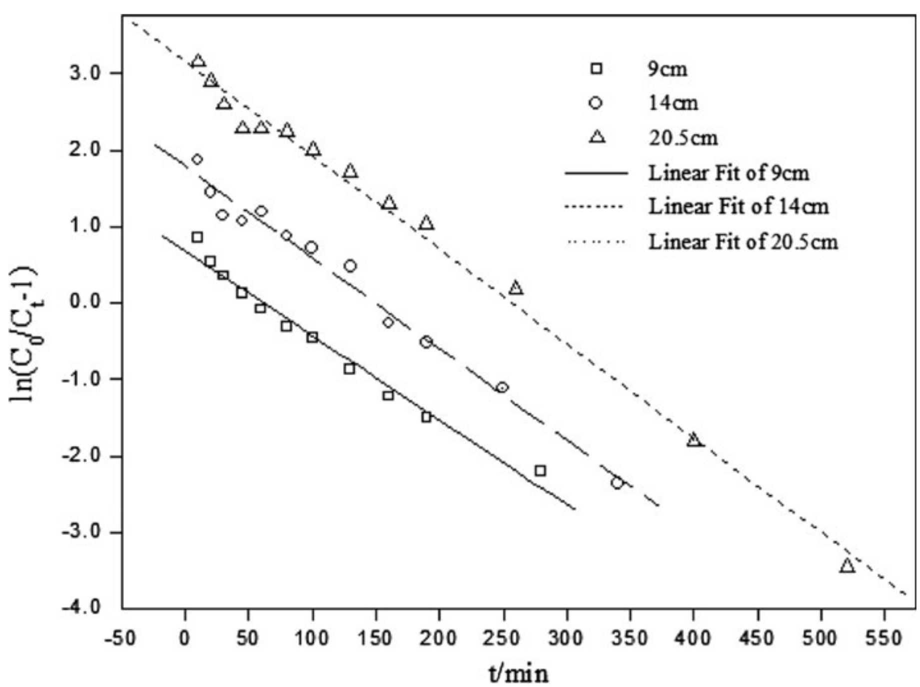

Fig. 5. The solution of Thomas model parameters for different bed heights.

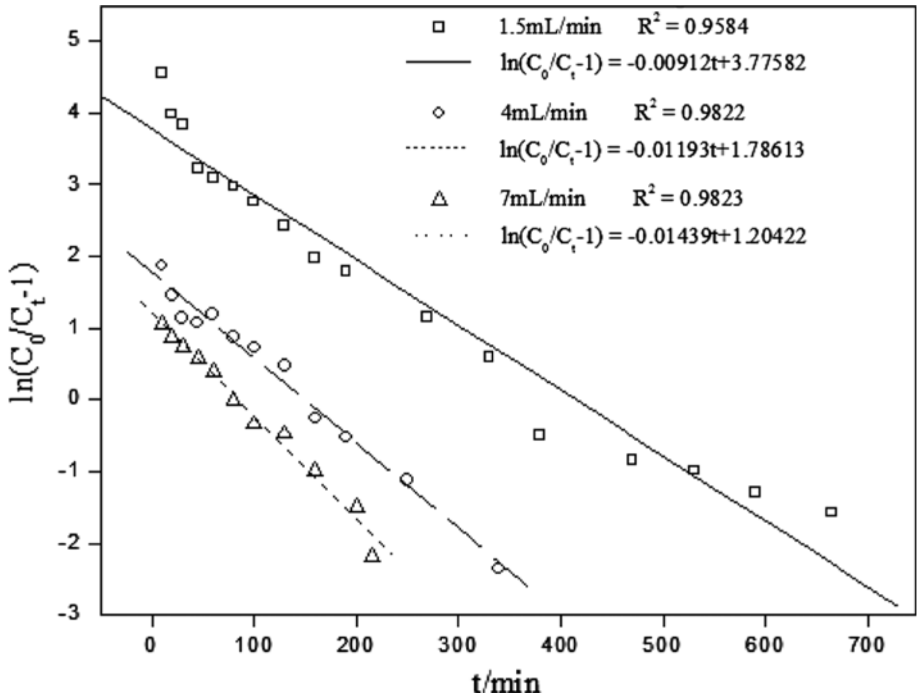

Fig. 6. The solution of Thomas model parameters for different flow rates.

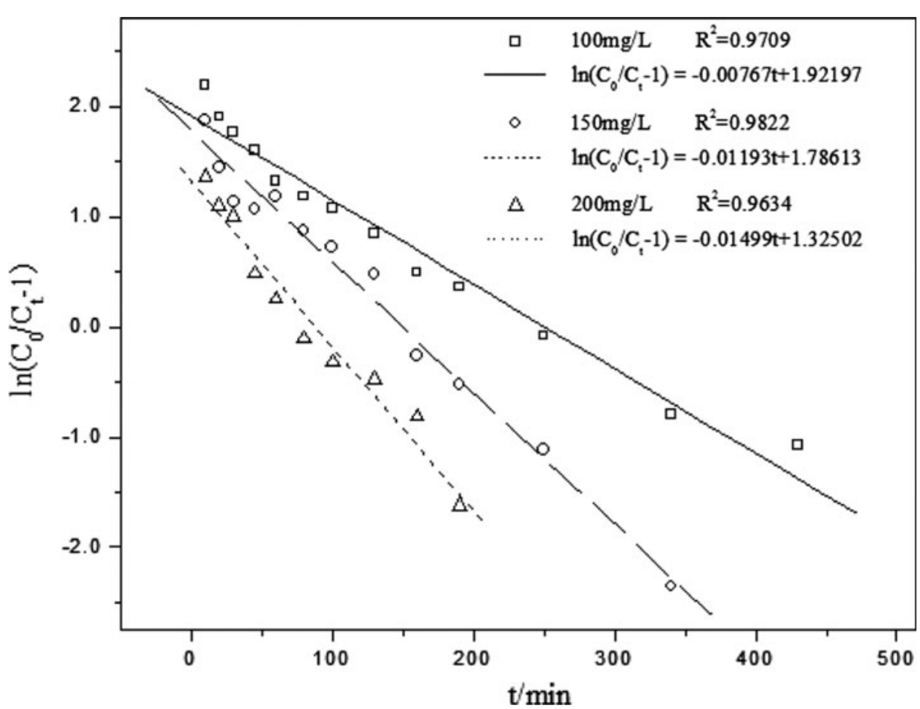

Fig. 7. The solution of Thomas model parameters for different MB initial concentrations.

Table 1
The Thomas constants in different conditions

C_0 mg L^{-1}	v mL min^{-1}	Z cm	K_T mL min^{-1} mg^{-1}	q_T mg g^{-1}	R^2
150	4	9	0.0738	3.6905	0.9772
150	4	20.5	0.0823	5.1306	0.9918
150	4	14	0.0795	4.4915	0.9822
150	1.5	14	0.0608	4.6577	0.9584
150	7	14	0.0959	4.3934	0.9823
100	4	14	0.0767	5.0117	0.9709
200	4	14	0.0750	3.5357	0.9634

constant increased from 0.0608 to 0.0959 mL min^{-1} mg^{-1}, which means that the quicker the flow rate of the MB solution, the less the mass transport resistance is, and the shorter the breakthrough time is.

3.4. BDST Model

The height of the adsorbent in the adsorption column is a key factor that affects the processing efficiency, running costs, and operation duration. This relationship can be represented with BDST model [36]. Its linear form can be expressed as follows:

$$t = \frac{N_0}{C_0 F} Z - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_t} - 1\right) \quad (3)$$

where F is the flow rate (cm min^{-1}); N_0 is the adsorption capacity of adsorption column (mg L^{-1}); K_a is the velocity constant (L min^{-1} mg^{-1}); t is the running time (min); Z is the height of adsorption column (cm); C_t, C_0 is the same as above.

According to Eq. (3) and the experiment data, by fitting "t" with "Z" using linear regression, Fig. 8 and Table 2 are obtained. The "R^2" is as high as 0.9992, which means that the BDST model is effective to their relationship.

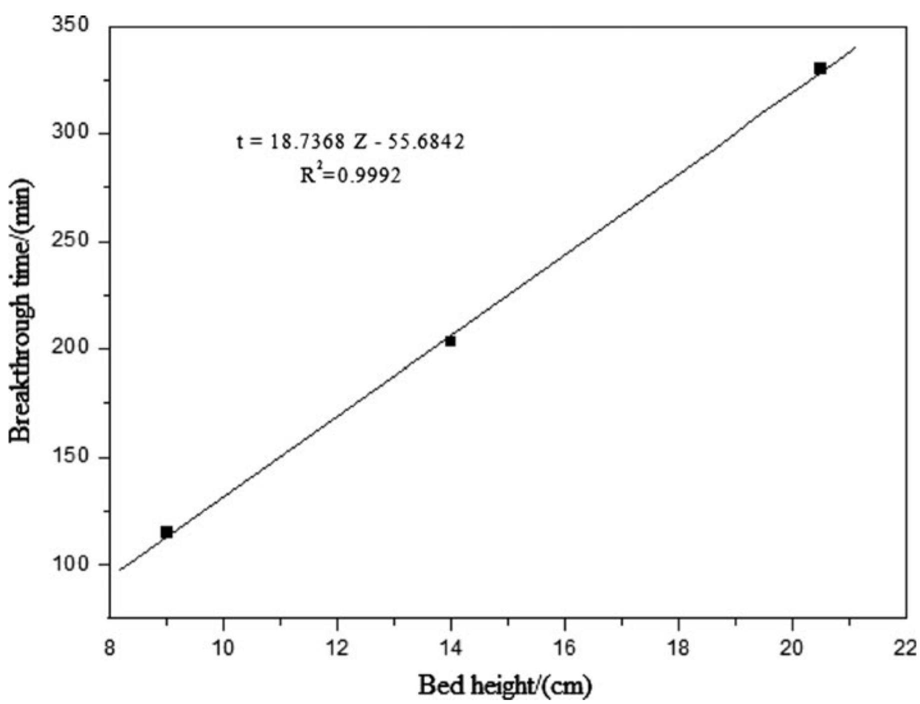

Fig. 8. The solution of BDST model parameters.

Table 2
The contrast of theory breakthrough time between experiment breakthrough time

	Breakthrough time/(min)		
Bed height/(cm)	Test	Theory	Error/(%)
9	115	112.98	1.76
14	203	206.68	1.81
20.5	330	328.49	0.45

3.5. Regeneration of GRM column

3.5.1. Determination of regeneration effect

Regeneration property is an important criterion for thorough evaluation of the performance of an adsorbent. In this work, the regeneration ratio η is determined from formula (4):

$$\eta = \frac{m_{n+1}}{m_n} \quad (4)$$

where η is the regeneration ratio (%); m_n is the adsorption amount of the adsorbent after n times of regeneration (mg g^{-1}); m_{n+1} is the adsorption amount of the adsorbent after $n + 1$ times of regeneration (mg/g).

3.5.2. The regeneration effect

According to the regeneration experiments during the first and second cycle, the results are shown in Fig. 9.

It is shown in Fig. 9 that the regeneration ratios of GRM adsorption column in the first and second cycles were 67.04 and 44.96%, respectively.

Additionally, the use of the dilute nitric acid solution (pH 3) can desorb the adsorption column which has been adsorbed. The calculation results show that the desorption rate of continuous desorption method and piecewise desorption method were 83.27 and 71.968%, respectively after 160 min. Although the effect of continuous desorption method is better than piecewise desorption method, the piecewise method can save the cost of nitric acid solution. Thus, these two desorption methods may be combined appropriately in use.

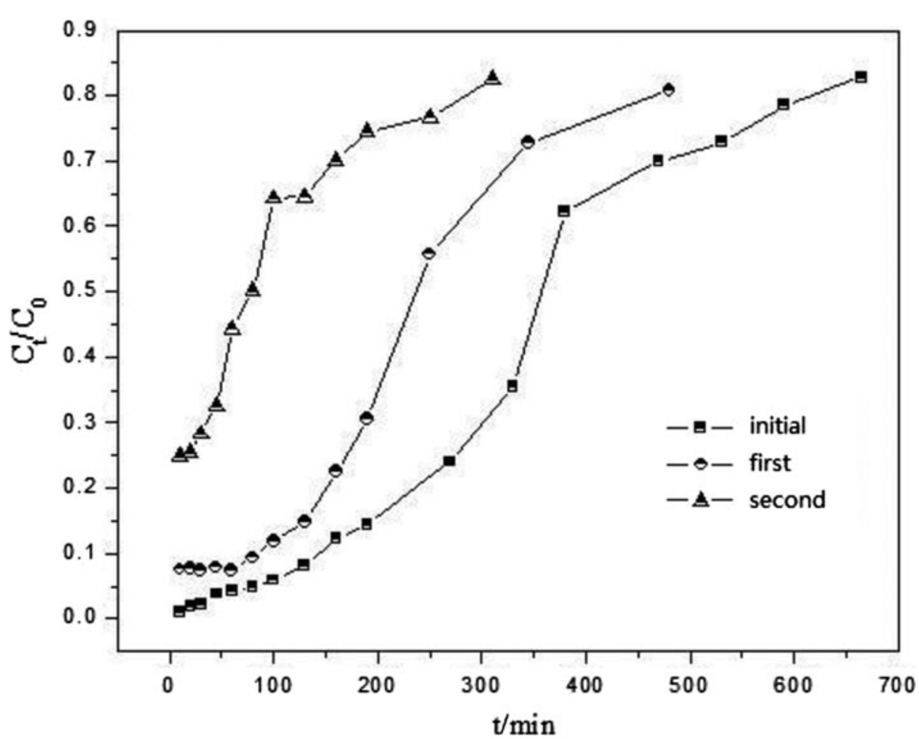

Fig. 9. The reuse effect of regeneration column.

4. Conclusions

Wet RM is directly mixed with 2 wt% cement and GRM adsorbent is produced using granulating machine. The GRM can effectively remove MB from wastewater. The results show that the column adsorption capacity increases with increasing bed height, but decreases with increasing influent concentration and flow rate. The Thomas model is capable of describing the adsorption kinetics. The maximum capacity of column adsorption experiments was about 5.13 mg MB per gram of GRM for flow rate of 4 mL/min, initial concentration of 150 mg/L, and bed height of 20.5 cm. The BDST model shows a very good fit with experimental data and can be used for the prediction of experimental results as well. Furthermore, two kinds of different desorption methods are compared and the most economical method of desorption was found in regeneration experiments. Therefore, the application of the column adsorption–regeneration treatment for adsorptive removal of MB is certainly feasible. The GRM can be used as an absorbent with low cost and high efficiency for removal of MB from wastewater.

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