ADSORPTION OF REACTIVE DYE BY KERAMZITE BEADS IN A BATCH AND FIXED BED COLUMN MODE

KHẢO SÁT KHẢ NĂNG HẤP PHỤ THUỐC NHUỘM HOẠT TÍNH CỦA HẠT SỎI NHẸ KERAMZITE THEO MÔ HÌNH MẺ VÀ CỘT NHỒI CỐ ĐỊNH

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Received 27/10/2017, Peer reviewed 18/01/2018, Accepted for publication 23/02/2018

ABSTRACT

Keramzite gravel is widely used in construction and agriculture. Keramzite is used as material to produce light-weight concrete and fixed bed for the growing vegetables. This material is now known as a completely new and cheap absorbent material. Surprisingly, the adsorption capacity of the reactive dyes on the Keramzite gravel has been successful and is the precondition for the production of other gravel particles with higher toxicity. This research was carried out on the batch adsorption and the fixed bed column mode. The adsorption is well described with the Langmuir, Freundlich, and Bohart Adams model. Moreover, the adsorption isotherms were better described by the Langmuir equation than by the Freundlich equation. The results also indicated favorable adsorption nature and these dyes are favorably adsorbed on Karemzit and activated carbon. Optimal adsorption at pH 3 and 6, gravel size 5-10 mm,adsorption time 50 minutes, maximum adsorption capacity of 0.284 and 0.455 mg/g corresponding to SUNCION RED HE7B and SUNCION BLUE HEGN.

Keywords: *Batch adsorption; fixed bed column adsorption; Bohart Adam equation; reactive dye; Karemzit gravel.*

TÓM TẮT

Hạt sỏi Keramzit được sử dụng phổ biến trong lĩnh vực xây dựng và nông nghiệp. Keramzit được dùng để sản xuất bê tông nhẹ và giá thể trồng rau. Vật liệu này giờ đây được biết đến như là một vật liệu hấp phụ hoàn toàn mới và rẻ. Việc khảo sát khả năng hấp phụ thuốc nhuộm hoạt tính trên sỏi Keramzit đã thành công và là tiền đề cho việc tạo ra các hạt sỏi khác có khả năng hấp phụ độc tố cao hơn. Nghiên cứu này đã được tiến hành trên mô hình hấp phụ dạng mẻ và dạng cột nhồi cố định. Quá trình hấp phụ này được mô tả tương thích với mô hình Langmuir, Freundlich và Bohart Adams. Hơn nữa, mô hình Langmuir lại mô tả tương thích đẳng nhiệt hấp phụ hơn mô hình Freundlich. Các kết quả chỉ ra rằng bản chất hấp phụ này là tự nhiên và các thuốc nhuộm hoạt tính hấp phụ tốt trên sỏi keramzite và than hoạt tính. Quá trình hấp phụ tối ưu tại pH 3 và 6, cỡ sỏi 5 - 10 mm, thời gian hấp phụ 50 phút thì công suất hấp phụ cực đại đạt 0.284 và 0.455 mg/g tương ứng với thuốc nhuộm SUNCION RED HE7B và SUNCION BLUE HEGN.

Từ khóa: *Hấp phụ theo mẻ; hấp phụ cột nhồi cố định; mô hình Bohart Adam; thuốc nhuộm hoạt tính; sỏi Keramzit.*

1. INTRODUCTION

In recent years, Vietnamese country's economy has been constantly developing. Serious polluted industries including textile and dyeing industry which has a large production network and high economic growth rate. The dyestuff, textile industries release highly colored effluents that pose severe environmental hazards [1]. The factories of this industry category discharge large amounts of wastewater, so the treatment of wastewater with cost effective solutions is one of the current challenges.

Textile effluent treatment includes several physiochemical methods like filtration, specific coagulation, use of activated carbon, electron beam radiation and chemical flocculation [1]. However, these processes are cost as well as labor intensive and besides, less efficient. Adsorption is one of the most widely used technologies for removing pollutants from contaminated aqueous media [2]. It is preferred over other methods because of its relatively simple design, operation, cost effectiveness, and energy efficiency. In recent time, a lot of adsorption materials have high efficiency and low cost. Some of the cheaper adsorbents have been studied and are being used recently such as: coconut fibers, red mud, iron ore, cotton dust, etc. Keramzite is also a completely new adsorption material and has been studied to first applied in textile wastewater treatment process. The material used to make karemzite gravel is kaolinite clay. They are found popular in the Mekong Delta. This material, after being treated, removes impurities in the clay, drying the soil, grinding and sieving through 2 mm sieve, will continue to be mixed with coal and husk grind at 70:30. The mixture is dried at high temperature (1000 - 1200^{0}C) and rapid cooling to form Keramzite gravel. Therefore, the study on the adsorption of reactive dyes on Keramzite gravel will partly contribute to the study of cheap adsorbent which capture hazardous waste effectively.

This research aims to investigate the adsorption capacity of Keramzite gravel during the adsorption of reactive dyes. The adsorption isotherm model and the fixed-bed adsorption column model have been applied.

2. MATERIALS AND METHODS

2.1 Chemicals and materials

SUNCION RED HE7B, SUNCION BLUE HEGN are reactive dyes which were bought from Tan Phu Cuong Ltd., Co, made in Korea. Karemzite and activated carbon was bought from Vinh Cuu Ltd., Co.

2.2 Determination of dye concentration

Dye samples were prepared at a concentration of 10 mg/L, measured in turns with wavelengths from 200 to 900 µm. The optimum wavelength is the wavelength which obtained at the highest absorption. The optimal wavelengths of the RED and BLUE dye samples are 300 and 600 µm, respectively (**Figure 1**).

Figure 2 shows the concentration of dye determined based on absorbance. The dye solution were measured at the optimum wavelengths.

2.3 Adsorption studies

2.3.1 Batch adsorption

Adsorption experiments were performed by batch equilibration method.

The amount of dye adsorbed was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

Where q_e is the amount of dye adsorbed on karemzit (mg g^{-1}), C_0 and C_e are the dye concentrations in the solution initially and at equilibrium (mg L^{-1}), respectively, V is the volume of the solution (L), and m is the mass of adsorbent used (g).

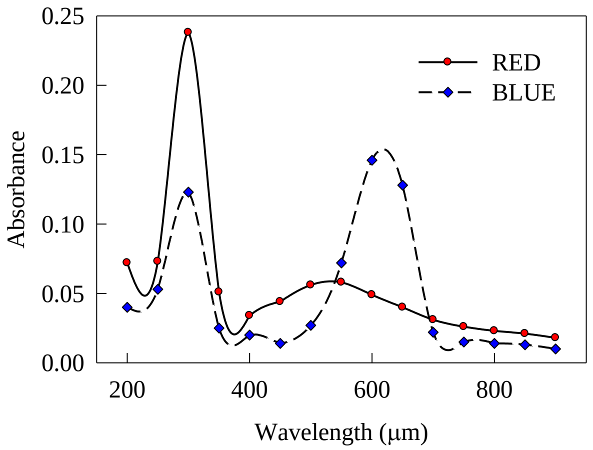


***Figure 1.** The optimum wavelengths of dye solution*

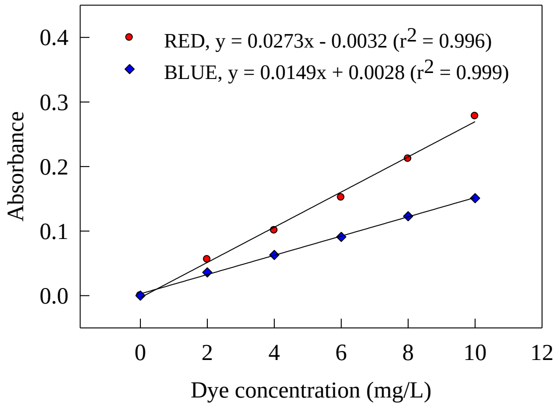


Figure 2. *The determination of dye concentration*

2.3.2 Fixed bed adsorption column

Bohart and Adams (1920) described the fixed bed adsorption column as the equation showed in below [3]:

$$Ln\left(\frac{C_0}{C_e}-1\right)=Ln\left(e^{\frac{KN_0L}{V}}-1\right)-KC_0t \qquad (2)$$

$$t=\frac{N_0}{C_0V}D-Ln\left(\frac{C_0}{C_e}-1\right)/KC_0 \qquad (3)$$

$$N_0=aVC_0 \qquad (4)$$

$$K=\frac{Ln\left(\frac{C_0}{C_e}-1\right)}{bC_0} \qquad (5)$$

$$D=\frac{V}{KN_0}Ln\left(\frac{C_0}{C_e}-1\right) \qquad (6)$$

where, C_0 is the adsorbate concentration in the inflow to the column (mg/l), C_e is the breakthrough concentration in the effluent (mg/l), K is a velocity constant (m^3 of solution)/(kg of adsorbents)), N_0 is the adsorption capacity (kg of adsorbate/m^3 of adsorbent), D is the adsorbent height in the column (m), V is the lineal velocity (m/s), t is the time of operation (s).

As the inflow flow towards the columns was set at the beginning of the experiment to be 0.139 ml/s (0.5 L/hrs), and C_0 is the adsorbate concentration in the inflow to the column (10 mg/L), it was feasible to obtain the operation time (t) corresponding to each column before the C_e concentration was reached in its effluent. From these data, a straight line (3) is obtained by plotting (t) against the respective column height (D), the higher the column, the longer the operation time (t).

3. RESULTS AND DISCUSSION

3.1 Effect of pH on the adsorption capacity

Figure 3 shows the optimum pH of the RED and BLUE dye adsorption which are 3 and 6, respectively. The optimum pH 3 and 6 are then used for following experiments.

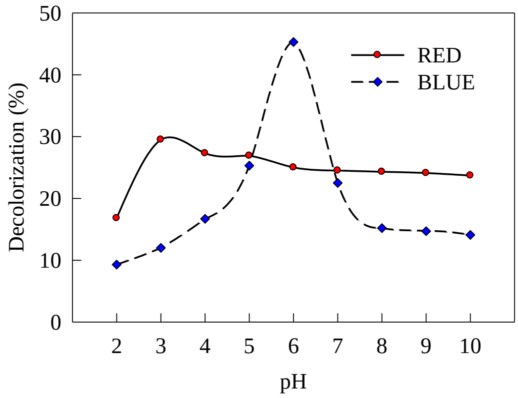


Figure 3. *The effect of pH on the dye adsorption*

3.2 Effect of adsorbent size on the adsorption capacity

Figure 4 displays the optimum gravel size of 5 – 10 mm. Maximum adsorption efficiency is at this particle size. A particle size of 5 – 10 mm is then used for subsequent experiments.

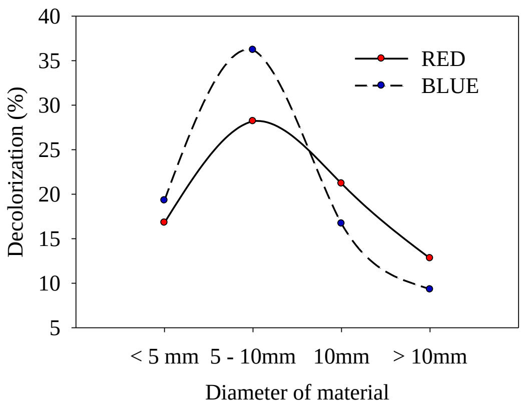


Figure 4. *The effect of adsorbent size on the dye adsorption*

3.3 Effect of adsorbent dose on the adsorption capacity

Figure 5 determines the color removal efficiency corresponding to the amount of adsorbent. The optimal adsorption amount of RED and BLUE dyes are 8g and 6g, respectively. At the same time, the optimum dosage of activated carbon (AC) the dye adsorption is 2g, and the decolourization efficiency of the activated carbon is twice higher than that Karemzite (Ka).

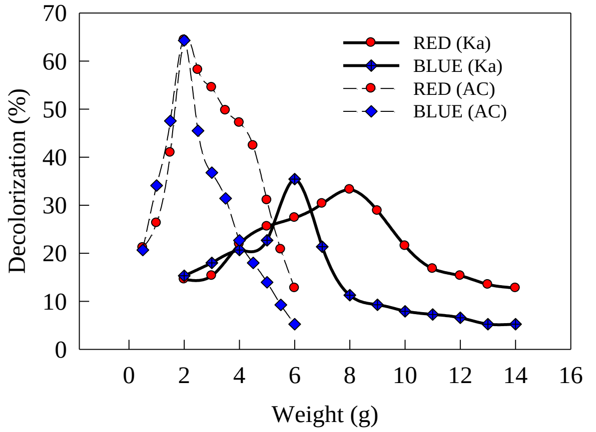


Figure 5. *The effect of adsorbent dosage on the dye adsorption*

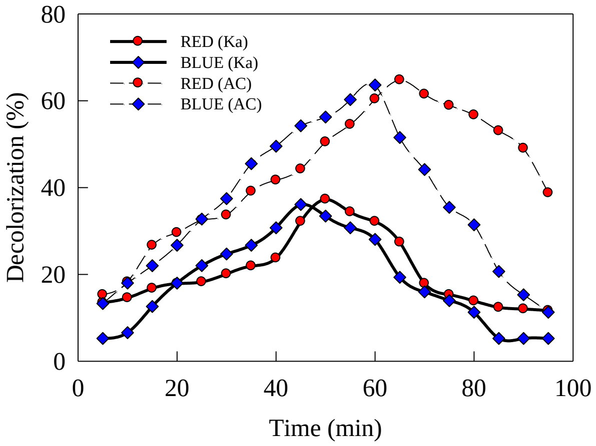


Figure 6. *The effect of time on the dye adsorption*

3.4 Effect of time on the adsorption capacity

Figure 6 shows the optimum time in the adsorption Karemzite (Ka) and activated carbon (AC) is approximately 50 minutes, and 65 minutes, respectively. Besides, the decolourizations are 38% and 65%, respectively.

3.5 Adsorption isotherm

Langmuir isotherm model described the monolayer adsorption of homogeneous structural materials. This equation allows to estimate the maximum adsorption capacity of the adsorbent [4]. Besides, the Freundlich isotherm model is applied for the heterogeneous systems or the uneven distribution of enthalpy of adsorption [5] and for multilayer adsorption phenomena [6]. To assess the interaction between the dye molecules to the surface of the adsorbent, adsorption mechanism, estimated maximum adsorption capacity, these models are both applied in this study. The constants of Langmuir and Freundlich equations are calculated by using the linearized form equations given in Eqs. (7) and (9):

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{q_{\max} \times K_L}\right)\frac{1}{C_e} \quad (7)$$

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \quad (9)$$

Where $q_{\max}$ is the maximum capacity corresponding to complete monolayer coverage (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}); K_F is the Freundlich constant ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1}) related to adsorption capacity and the constant n relates to the adsorption intensity . R_L value was defined by Webber and Chakkravorti [6] is a dimensionless constant, commonly known as separation factor, R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Table 1. *Isotherm constants for the adsorption of reactive dyes on Karemzite and Activated carbon at 30^0C^a*

Langmuir				
Absorbent	*Dye*	q_{max}	K_L	r^2
Ka	*RED*	*0.284*	*0.013*	*0.995*
	BLUE	*0.455*	*0.012*	*0.997*

AC	*RED*	*2.606*	*0.022*	*0.996*
	BLUE	*1.259*	*0.045*	*0.994*
Freundlich				
Absorbent	*Dye*	*n*	K_F	r^2
Ka	*RED*	*1.524*	*0.011*	*0.969*
	BLUE	*1.542*	*0.012*	*0.974*
AC	*RED*	*1.537*	*0.106*	*0.973*
	BLUE	*2.001*	*0.123*	*0.983*

[a]Unit: K_L (l/mg); q_{max} (mg/g); K_F ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1})

From **Table 1** and **Figure 7**, the results show high correlation coefficients (> 0.91) of the Langmuir and Freundlich equations and the r^2 value of the Langmuir is higher than of the Freundlich. Therefore, the adsorption isotherms were better described by the Langmuir equation than by the Freundlich equation. The value of $n > 1$ indicates that these dyes are favorably adsorbed on Karemzit and activated carbon [5]. Moreover, $0 < R_L < 1$ indicates favorable adsorption nature and the maximum adsorption capacity was 0.46 mg/g (BLUE on Karemzit) and 2.61 mg/g (RED on Activated carbon) at 30^0C.

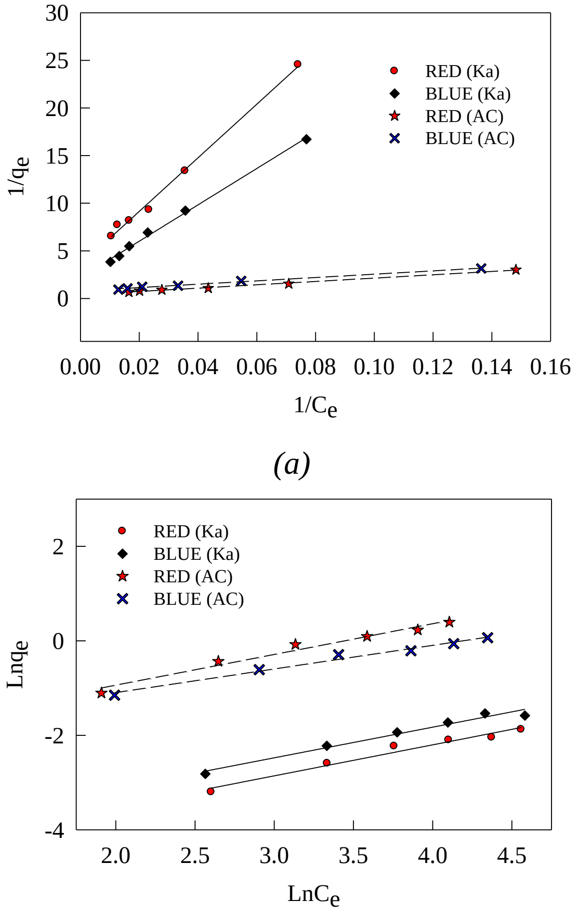
3.6 Fixed bed adsorption column study

The straight line (3) fittings made it possible to obtain the characteristic parameters corresponding to the operated fixed bed system that are shown in **Table 2** and **Figure 8**. The slopes of these straight lines are (N_0/C_0V) and, the y-axis occurring at the point – Ln [(C_0/C_e) – 1]/KC_0, it has been feasible to calculate the adsorption capacity (N_0), the velocity constant (K) and the critical height (D_e).

Table 2. *Characteristic parameters corresponding to the operated fixed bed adsorption systems* [b]

Absorbent	*Dye*	N_0	K_{BA}	*D*	r^2
Ka	*RED*	*4.03*	*0.037*	*0.026*	*0.96*
	BLUE	*4.50*	*0.022*	*0.039*	*0.94*
AC	*RED*	*5.57*	*0.045*	*0.016*	*0.95*
	BLUE	*6.31*	*0.016*	*0.042*	*0.92*

[b]Unit: N_0 (kg/m^3), K_{BA} (m^3/kg), D (m)



(a)

(b)

Figure 7. *The linear plots of (a) Langmuir, (b) Freundlich equations*

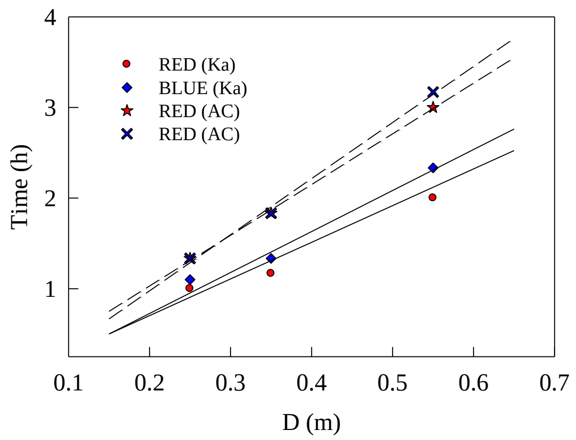


Figure 8. *Linear fittings to continuous adsorption data corresponding to the dye adsorption in columns according to Bohart and Adams equation.*

4. CONCLUSIONS

Keramzite gravel, in addition to the ability to grow plants or construction materials, also has the ability to absorb toxic substances. The adsorption capacity of Keramzite is low compared to traditional adsorbents such as activated carbon. However, Keramzite gravel can be manufactured with a number of innovative steps such as changing the drying temperature or adding baking additives into the production of the gravel to increase the pore size as well as enhance the adsorption capacity. The isotherm adsorption was simulated in accordance with the Langmuir model rather than the Freundlich model.

ACKNOWLEDGMENTS

I am really thankful to the support of HCMUTE and my students who took their time and patient to do the experiments.

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