

**EVALUATION OF THE BIOSORPTION
OF A SULFUR BROWN GD FROM AQUEOUS SOLUTIONS
BY THE RECYCLED ACID-WASHING ACTIVATED SLUDGE**
ĐÁNH GIÁ KHẢ NĂNG HẤP PHỤ SINH HỌC THUỐC NHUỘM SULFUR
BROWN GD CỦA BÙN HOẠT TÍNH ĐÃ QUA TÁI CHẾ VỚI AXIT

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ABSTRACT

The protection of the environment through the recycling of waste brought back many economic-social benefits. Demand for the recycling of the large quantity of activated sludge derived from biological treatment stage of the wastewater treatment plant has become urgent in recent years. This study examined successfully the batch biosorption of Sulfur Brown GD on the recycled material prepared by the acid washing biomass of activated sludge. The correlation coefficients (r^2) of both Langmuir and Freundlich isotherm parameters are higher than 0.91 with, and the estimated maximum adsorption capacity reached 7.99 mg/g. Besides, the kinetic parameters of the dye adsorption process is described suitably by the pseudo-second-order adsorption kinetics.

Keywords: Activated sludge; Acid washing; Biosorption; Sulfur dye; Adsorption.

TÓM TẮT

Việc bảo vệ môi trường thông qua việc tái chế chất thải đem lại nhiều lợi ích về kinh tế và xã hội. Nhu cầu tái chế lượng lớn bùn hoạt tính phát sinh từ công đoạn xử lý sinh học từ các nhà máy xử lý nước thải đã trở nên cấp thiết trong giai đoạn gần đây. Bài nghiên cứu này đã khảo sát thành công quá trình hấp phụ sinh học dạng mẻ đối với thuốc nhuộm sulfur Brown GD trên vật liệu bùn hoạt tính đã qua tái chế với axit. Các hệ số tin cậy r^2 của hấp phụ đẳng nhiệt Langmuir và Freundlich đều cao hơn 0.91 và công suất hấp phụ cực đại đạt 7.99 mg/g. Bên cạnh đó, thông số động học của quá trình hấp phụ thuốc nhuộm này được mô tả phù hợp bởi mô hình động học hấp phụ bậc hai.

Từ khóa: Bùn hoạt tính; rửa với axit; hấp phụ sinh học; thuốc nhuộm Sulfur; Adsorption.

1. INTRODUCTION

By many outstanding features in dyeing properties and good price, Sulfur dyes are widely used with a large quantity all over the world. However, wastes from the dyeing process of this dye cause significant harmful effects on the environment [1].

The formation and development of the industrial waste recycling is the target of

environmental protection strategy in Vietnam by 2020. The research activities and identification of the low cost and friendly adsorbent have been strongly concerned by many authors. Activated sludge in the waste-water treatment plant is a natural carbon source and local material. This sludge can be recycled into activated carbon through the chemical pretreatment methods [2]. Chemicals such as sulfuric acid, sodium

hydroxide [3], hydrogen peroxide [4] can be used to transform the sludge into activated carbon.

This article focuses on the use of the recycled acid-washing activated sludge (RAWAS) to adsorb sulfur Brown GD. The adsorption kinetics and isotherm in turn be applied to evaluate the adsorption ability of this material.

2. MATERIALS AND METHODS

2.1 Biosorbent preparation

The surface morphology of dried activated sludge with acid-washing step is more heterogeneous, rough and porous than the dried activated sludge [5]. Activated sludge in domestic wastewater treatment plant of Chiao Tung University (Hsinchu, Taiwan) was collected and transformed. This sludge is stirred with hydrochloric acid 1% (v/v) at the rate of 25g dried sludge per 1200 ml of acid. This sludge was then washed 4 times with distilled water. After water-washing, the clean sludge was dried at 50°C until a constant weight and sieved through a < 2 mm diameter.



Figure 1. Activated sludge was washed with 1% (v/v) hydrochloric acid

2.2 Sulfur dye and dyeing

Sulfur Brown GD (SBGD, CI 53210, MW 104.1 g/mol) was purchased from Ningbo New Dragon International Co., Ltd, and Sodium sulfide nonahydrate (Na₂S·9H₂O)

used for reducing process was purchased from Alfa Aesar. With the weight ratio of SBGD to sodium sulfide was 0.4, SBGD was dissolved completely in sodium sulfide solution and the pH value of this dye solution reached 11.0.

2.3 Analytical and concentration measurement method of dye

The absorbance spectrum of SBGD was assessed using an UV/visible spectrophotometer (Jasco V650, Japan) over a broad concentration range. The concentration of SBGD was obtained through absorbance measurements at 467 nm [6].

2.4 Experiment method

Sulfur dye batch biosorption experiments were conducted by shaking 5g of RAWAS in 250ml of dye solution in an incubator with a rotary shaker at 200rpm at 30°C, pH 11.0. After each biosorption process, the sample was separated by centrifugation (10,000 x g for 10min) and supernatant was analyzed for remaining dye concentration using UV spectrophotometer by monitoring the absorbance at 467nm. Data from each experiment were replicated three times. The amount of dye adsorbed on dried activated sludge at equilibrium, q_e (mg/g), was calculated by the following equation:

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

wherein, C_0 and C_t (mg/l) are the concentration of SBGD at the initial and time t (mg/l), respectively, V is the volume of the solution (l), and m is the weight of adsorbent used (g).

3. RESULTS AND DISCUSSIONS

3.1 Biosorption kinetics

The pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models, which were tested to describe the biosorption

kinetics, are shown in Eq. (2) and Eq. (3), respectively [7]. Adsorption kinetics is an important analysis in the application of adsorption processes in water treatment. These parameters can be used to predict the speed of the capture of pollutants in aqueous solutions [8]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (3)$$

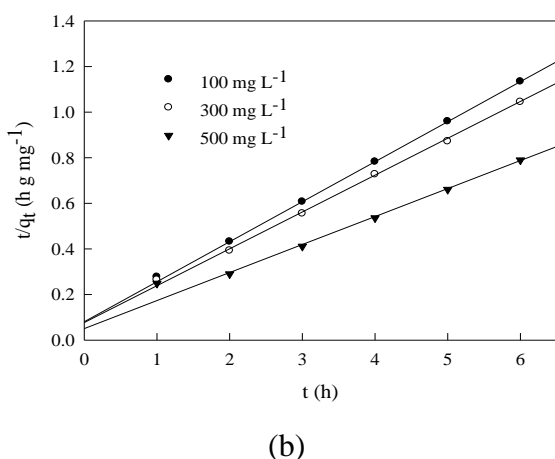
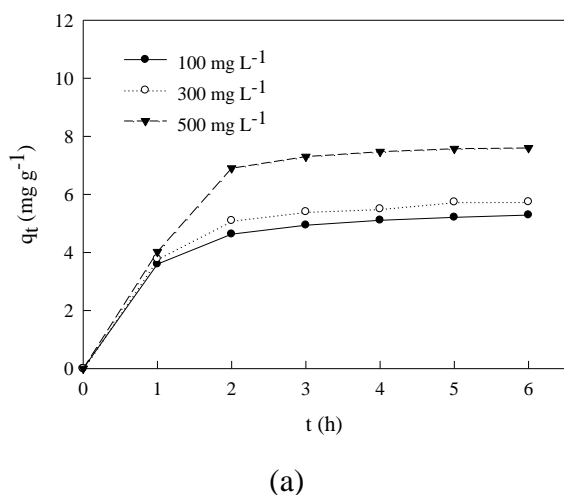


Figure 2. (a) Time changes of SBGD concentrations and (b) their pseudo-second-order kinetic plot during the adsorption of SBGD on RAWAS at 30°C

Table 1. Parameters of the PFO and PSO kinetic models for the adsorption of SBGD on RAWAS at 30°C^a.

C ₀	C _e	q _{e,exp}
100	52	5.32
300	90	5.75
500	321	7.62
Pseudo-first-order kinetic model		
k ₁	q _{e,cal}	r ²
0.0132	6.57	0.9845
0.0185	5.63	0.9479
0.0166	6.37	0.9920
Pseudo-second-order kinetic model		
k ₂	q _{e,cal}	r ²
0.0110	5.49	0.9940
0.0095	5.99	0.9930
0.0049	8.14	0.9800

^aUnit: C₀(mg/L); k₁ (g/mg/min);

k₂ (g/mg/min); q_{e,exp} (mg/g); q_{e,cal} (mg/g)

wherein, k₁ and k₂ are the pseudo-first-order and pseudo-second-order rate constant (g mg⁻¹ min⁻¹), respectively. The k₁ and k₂ values were calculated from the plot of ln(q_e-q_t) against t, and the plot of t/q_t against t, respectively.

According to the correlation coefficient (r²) in Table 1, the PFO model revealed more satisfactory fits (r² > 0.98) than the PSO. Regarding the speed of adsorption, the longer adsorption time occurred when the adsorption rate is smaller as well as the decreasing k₂q_e value happened with the increasing dye concentration [9].

3.2 Biosorption isotherm

Langmuir isotherm model described the monolayer adsorption of homogeneous structural materials. This equation allows estimation of the maximum adsorption capacity of the adsorbent [10]. Besides, the Freundlich isotherm model is applied for the heterogeneous systems or the uneven

distribution of enthalpy of adsorption [11] and for multilayer adsorption phenomena [12]. To assess the interaction between the dye molecules to the surface of the adsorbent, adsorption mechanism, estimated maximum adsorption capacity, these models were both applied in this study. The constants of Langmuir and Freundlich equations were calculated by using the linearized form equations given in Eqs. (3) and (5):

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{q_{\max} \times K_L} \right) \frac{1}{C_e} \quad (3)$$

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n} \right) \ln C_e \quad (5)$$

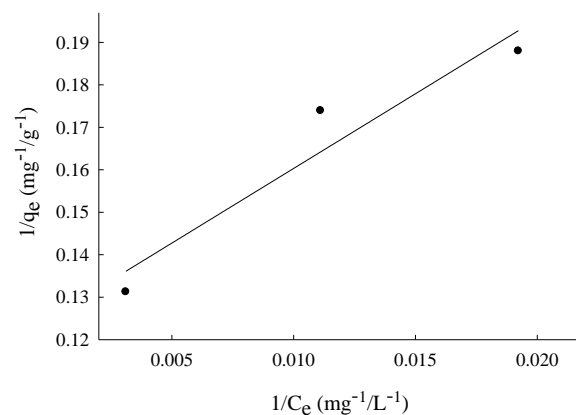
wherein, q_{\max} is the maximum capacity corresponding to complete monolayer coverage (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}); K_F is the Freundlich constant ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$) related to adsorption capacity and the constant n relates to the adsorption intensity. R_L value defined by Webber and Chakravorti [12] 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 ($R_L = 0$).

From Table 2 and Figure 3, the results show high correlation coefficients (> 0.91) of the Langmuir and Freundlich equations and the r^2 value of the Freundlich is higher than that of the Langmuir. Therefore, the biosorption isotherms were better described by the Freundlich equation than by the Langmuir equation. The value of $n > 1$ indicated that SBGD was favorably adsorbed on RAWAS [11]. Moreover, $0 < R_L < 1$ indicated favorable adsorption nature and the maximum adsorption capacity was 7.99 mg/g at 30°C .

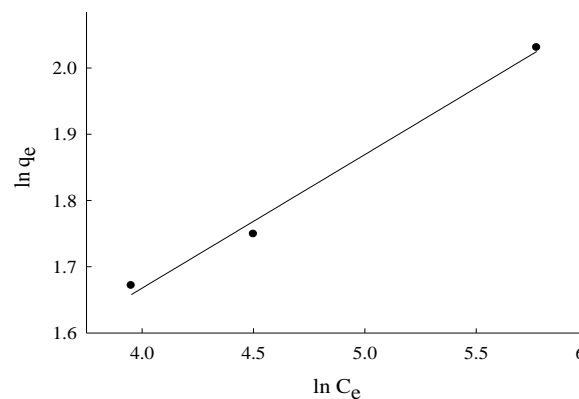
Table 2. Isotherm constants for the biosorption of SBGD on RAWAS at 30°C ^b

Langmuir	K_L	q_{\max}	r^2
	0.036	7.99	0.919
Freundlich	K_F	n	r^2
	2.37	4.96	0.992

^bUnit: K_L (L/mg); q_{\max} (mg/g);
 K_F ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$)



(a)



(b)

Figure 3. The linear plots of (a) Langmuir, (b) Freundlich equations

4. CONCLUSION

Activated sludge known as a popular waste in the waste-water treatment plant, proven in the effective biosorption of dye. Sulfur Brown GD was significantly adsorbed on the recycled acid-washing activated sludge. The isotherm data of sulfur dye to RAWAS fitted both the Langmuir and Freundlich models and the

kinetic data were well described by the pseudo second-order adsorption kinetics. Moreover, the speed of this biosorption decreased with the increasing dye concentration.

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