STUDY ON THE ADSORPTION OF REACTIVE ORANGE RO122 FROM AQUEOUS SOLUTION ONTO CROSSLINKED CHITOSAN-COATED DIATOMITE

NGHIÊN CỨU KHẢ NĂNG HẤP PHỤ THUỐC NHUỘM HOẠT TÍNH RO122 TRONG NƯỚC BẰNG VẬT LIỆU DIATOMITE PHỦ CHITOSAN KHÂU MẠCH

Le Thi Thi Ha[1], Lai Thi Hoan[2],
Nguyen Thi Cuc[3], Nguyen Thuy Ha[3], Ho Phuong Hien[3,*]

ABSTRACT

The preparation, characterization and RO122 adsorption of crosslinked chitosan coated diatomite (CS-GLA/DM) were investigated. The prepared crosslinked chitosan-coated diatomite was characterized using Fourier transform infrared (FT-IR) spectroscopy and Scanning electron microscope (SEM) techniques. The influences of sorbent dosages, pH, reaction time, reaction temperature and adsorption isotherms were studied. The optimum conditions for RO122 adsorption were pH 1.0, contact time of 50 mins with 0.2g of crosslinked chitosan coated diatomite. The maximum adsorption rate reached to 99.4%. Langmuir and Freundlich adsorption model were applied to describe the equilibrium isotherms. The equilibrium data were found to be fitted well to Langmuir isotherm and the maximum adsorption capacity was determined to be 163.9mg/g. The results suggested that crosslinked chitosan coated diatomite was a promising sorbent to remove dyes in textile wastewater.

Keywords: *Crosslinked chitosan coated diatomite, Reactive Orange RO122, adsorption.*

TÓM TẮT

Trong bài báo này, các đặc tính của vật liệu diatomite phủ chitosan khâu mạch (CS-GLA/DM) đã được phân tích bằng phương pháp phổ hồng ngoại (FT-IR), kính hiển vi điện tử quét (SEM). Các yếu tố ảnh hưởng đến hiệu suất hấp phụ thuốc nhuộm RO122 của vật liệu như khối lượng vật liệu, pH, thời gian và nhiệt độ của quá trình hấp phụ đã được khảo sát. Hiệu suất hấp phụ tối đa đạt 99,4% với 0,2g diatomite phủ chitosan khâu mạch trong điều kiện pH 1,0 sau 50 phút xử lí. Kết quả nghiên cứu cũng cho thấy sự hấp phụ tuân theo mô hình đẳng nhiệt hấp phụ Langmuir với dung lượng hấp phụ cực đại là 163,9mg/g. Với kết quả này, diatomite phủ chitosan khâu mạch hứa hẹn sẽ là vật liệu hấp dẫn trong việc ứng dụng vào xử lí môi trường nước đang bị ô nhiễm.

Từ khóa: *Diatomite phủ chitosan khâu mạch, thuốc nhuộm hoạt tính RO122, hấp phụ.*

[1]University of Transport and Communications, Campus in Ho Chi Minh City
[2]Faculty of Basic Sciences, University of Transport and Communications
[3]Faculty of Chemistry, Hanoi National University of Education
*Email: meek1512@yahoo.com

1. INTRODUCTION

The growing world economy, accompanied by population growth and rapid development of industries, has created enormous pressure on the environment. Large amounts of organic compounds in wastewater of several industries such as textile, food, cosmetic, pharmaceutical products… have released into the environment, existed in soil and water. Ultimately, they would adversely affect by human heath, causing serious illness [1].

Recently, several methods of dye removal from wastewater have been reported including filtration, ion exchange, precipitation, flocculation and adsorption [2]. Among these mentioned methods, adsorption has received much attention due to the low cost of commercial adsorbents, ease to operation and high efficiency [3].

Chitosan, natural polymeric material, is used widely for adsorption. Chitosan, the deacetylated form of chitin, generally exists in nature and possess special properties, such as non-toxicity, biological compatibility and biodegradability [4, 5]. Chitosan, due to its high contents of amino and hydroxyl groups, can adsorb dyes, metal ions, protein. However, pure chitosan is high cost, less chemical stable, forms gels at low pH [6]. This has limited the application of chitosan in adsorption. Several cross-linking reagents such as glutaraldehyde (GLA), epichlorohydrin (ECH) were applied to enhance chitosan resistance to acids.

Diatomite is a siliceous sedimentary rock, natural source, used as an adsorbent, because of its unique physical and chemical properties, its abundance and low cost. Diatomite is porous, hollow surface, high melting point and chemical stable [7].

In order to improve the adsorption capacity of chitosan as well as to overcome disadvantages of chitosan, using diatomite- coated cross-linking chitosan was investigated. The aim of this work is to prepare crosslinked chitosan coated diatomite (CS-GLA/DM) and apply to adsorb RO122 from aqueous solution.

2. EXPERIMENTAL

2.1. Materials

Chitosan (CS) (fine powder, ivory white, 97% deacetylated, Thien Nguyen company, Vietnam) (average molecular weight = $2,0 \times 10^5$ Da). Phu Yen diatomite (DM) contains 71% SiO_2 in its chemical content. DM was ground into powder below 30 mesh and dried. Reactive Orange 122 (RO122) ($C_{31}H_{20}O_{16}S_5N_7Na_4Cl$; Vietnam), acetic acid > 99.5% (d = 1.05g/mL), glutaraldehyde 25% (GLA, d = 1.06g/mL), NaOH, H_2SO_4 98%.

2.2. Equipments

FT-IR spectra of the samples were recorded by FT-IR Prestige-21 spectrophotometer (Shimadzu, Japan) in the wave number range of 4000 - 400cm^{-1}. The general morphology of the samples was characterized by the scanning electron microscope (SEM, Hitachi S-4800, Japan). Absorbance of RO122 solution was determined by Biochrom S60 Spectrophotometer (England).

2.3. Synthesis of CS-GLA/DM [3]

Firstly, 1.00g of CS powder was dissolved in 40mL of 2.5wt.% acetic acid. 10.00g of DM was then dispersed in the solution. The mixture was stirred for 12 hours. Poured the mixture into 500mL of NaOH 1M and continuously stirred for 5 hours, result in the formation of the diatomite/chitosan composite. To remove any residual sodium hydroxide, the composite was washed many times with distilled water. Next, the composite was shaken in 200mL of GLA 1wt % for 12 hours at 60°C. After the cross-linking reaction, the composites were washed with distilled water to remove free GLA and dried at 100°C for 24 hours. CS-GLA/DM composite was ground into powder below 30 mesh and stored in a desiccator. In order to prove the role of GLA to enhance chitosan resistance to acids and increase its adsorption efficiency, CS/DM composite without the presence of GLA was also synthesized and applied for adsorption of RO122 from aqueous.

2.4. Experiment method

Concentration of RO122 in solution was determined by optical absorption method. The calibration curve for determining the concentration of RO122 at λ_{max} = 493nm was constructed as:

$$Abs = (0,0103 \pm 0,0002) \times C \text{ with } R^2 = 0.998.$$

Adsorption capacity of CS-GLA/DM was then calculated according to the following equation:

$$q_e = \frac{(C_o - C_e) \times V}{w}$$

where q_e (mg/g) is the adsorption capacity of CS-GLA/DM at equilibrium, V (mL) is the volume of the used RO122 solution, w (g) is the weight of the CS-GLA/DM composite, C_o (mg/L) is the initial RO122 concentration, C_e (mg/L) is the equilibrium RO122 concentration.

3. RESULTS AND DISCUSSION

3.1. Characterization of CS-GLA/DM

FT-IR spectra of natural diatomite DM and CS-GLA/DM were shown in Figure 1a. Absorption peaks at 2880cm^{-1} and 1383cm^{-1} were attributed to the stretching vibration of C-H and C-N of CS. It susgeted that CS was bonded or absorbed by the surface of DM. Figure 1b showed the FT-IR spectra of CS and CS-GLA/DM. An absorption peak at 1550cm^{-1} was attributed to the bending vibration of the amine -NH_2 group. The bands at 1550cm^{-1} of the FT-IR spectra of CS-GLA/DM disappeared. It can be assumed that the amine groups of CS were bound to the -CHO groups of GLA. The cross-linking would strengthen the stability of chitosan in acidic-solutions.
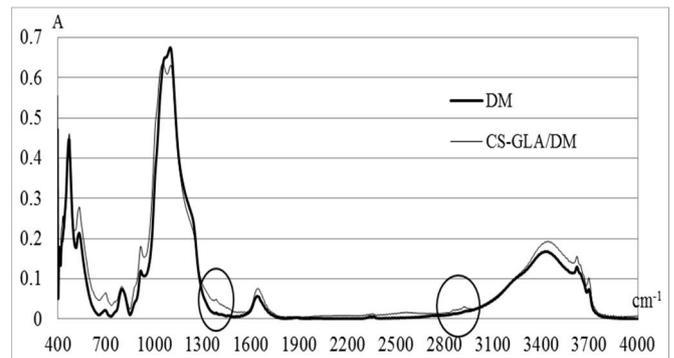

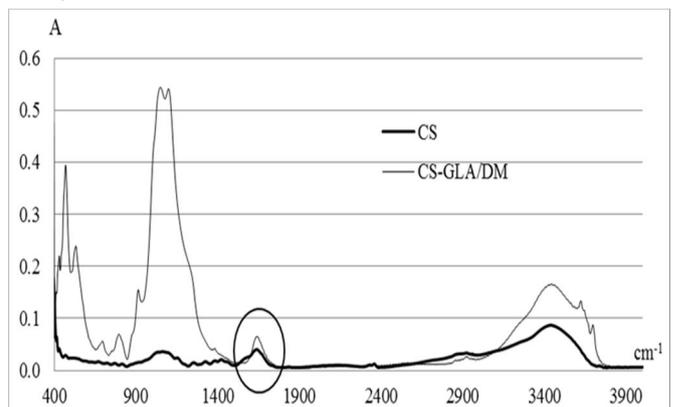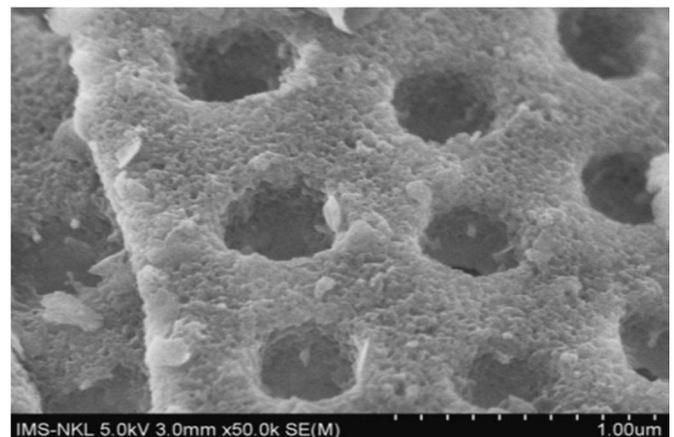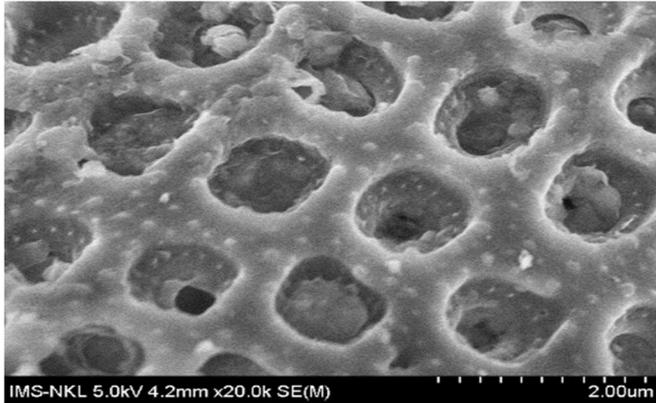Figure 1a. The FT- IR spectra of DM and CS-GLA/DM

Figure 1b. The FT-IR spectra of CS and CS-GLA/DM

a) DM

b) CS-GLA/DM

Figure 2. SEM image of DM and CS-GLA/DM

The SEM images of the CS-GLA/DM (Figure 2) showed that CS dispersed on the surface of DM. Figure 2 also indicated that the porous structure of DM was still maintained after loading with CS. The pore size of DM after being treated with acetic acid was increased in comparison with natural DM. It suggested that CS-GLA/DM was a potential adsorbent for RO122 removal in aqueous solution.

3.2. Adsorption of RO122 from aqueous onto CS-GLA/DM

3.2.1. The comparision of RO122 adsorption by using CS-GLA/DM; CS/DM and DM

Prepared 3 samples, each containing 50 mL RO122 solution concentration of 400 mg/L. The first sample was added 0.2g of CS-GLA/DM, the two others were added 0.2g of CS/DM and 0.2g of DM, respectively. The pH value of 1.0 was maintained in these samples. The solutions were shaken at 160rpm, at room temperature. The residual RO122 concentration in solution after 50 mins of treatment and the removal percentage of RO122 were shown in Table 1.

Table 1. The residual RO122 concentration in solution and the removal percentage of RO122 after 50 mins of treatment

Absorbent	DM	CS/DM	CS-GLA/DM
C_{RO122} (mg/L)	390.9	46.9	2.5
Removal %	2.3	88.3	99.4

The results of Table 1 showed that the RO122 removal efficiency of CS-GLA/DM was higher than that of CS/DM and DM. Therefore, CS-GLA/DM was selected for the further experiments.

3.2.2. Effect of time on adsorption

The effect of contact time on the sorption process was performed as follows: 50mL of the RO122 solution concentration of 400mg/L taken and 0.2g CS-GLA/DM was added subsequently. pH of the solution was adjusted to pH = 1.0. The sample was shaken at 160rpm using orbitex shaker. The effect of contact time on the removal percentage of RO112 was shown in Figure 3. The results showed that the adsorption happened very quickly in the first hour, as shown by the large slope of the graph. As

adsorption time increased, the slope of the graph decreases. The reason was that in the early time, the surface area of the adsorbent material was larger, then gradually decreased over time to saturation. The absorption reached equilibrium after about 50 mins, at which the adsorption capacity of CS-GLA/DM was 99.4mg/g and the removal efficiency reached to 99.4%. After 50 mins, the differences in adsorption values were very small. Therefore, the optimum adsorption time was 50 mins.
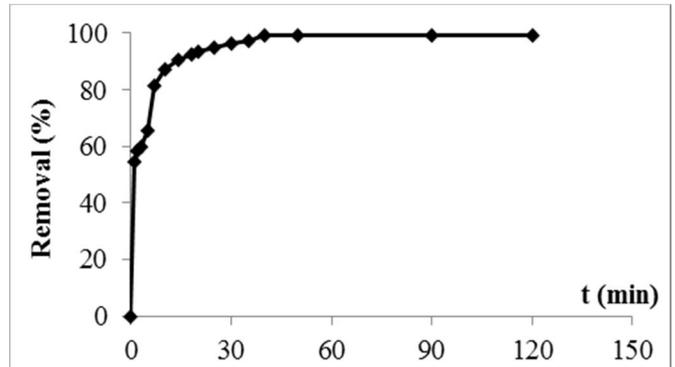

Figure 3. Effect of contact time on the RO122 removal

3.2.3. Effect of adsorbent dosage

Prepared 6 samples, each containing 50mL RO122 solution concentration of 400mg/L. The CS-GLA/DM amount used to process the samples was changed to 0.1; 0.2; 0.3; 0.4; 0.5g. The pH value of 1.0 was maintained constant in all samples. The solutions were shaken at 160 rpm, at room temperature. The residual RO122 concentration in solution after treatment 50 mins was shown in Figure 4.
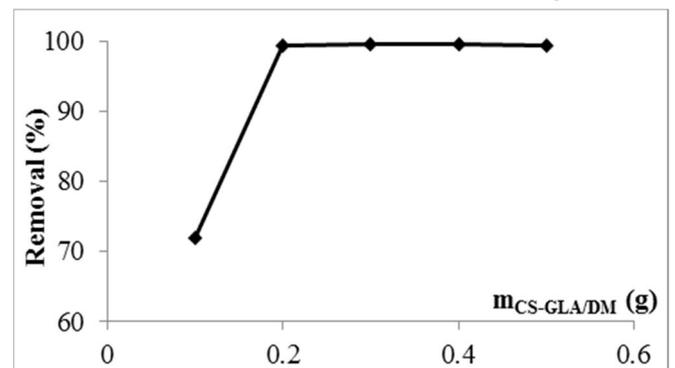

Figure 4. Effect of adsorbent dosage on the RO122 removal

The results of Figure 4 showed that as the CS-GLA/DM amount increases, the removal efficiency rate was higher. The number of adsorption sites on the surface of the absorbent increased with increasing dose. The removal was not affected by increasing dose over 0.2g. Therefore, the dosage of 0.2g of CS-GLA/DM was selected for the further experiments.

3.2.4. Effect of pH on adsorption

The effect of pH on adsorption was investigated by varying the pH from 2.07 to 5.7 under the following conditions: 50mL of the RO122 solution concentration of 400mg/L, 0.2g of adsorbent dosage.

Figure 5 showed the RO122 adsorption rate after 50 mins of CS-GLA/DM treatment with samples of different pH values. pH of the solution played an important role in the adsorption process and much affected the adsorption. Figure 5 showed that the highest removal efficiency was 99.4% at pH = 1.04. When the pH was higher, the adsorption capacity and the adsorption rate of RO122 decreased. This was explained in the following: at the low pH, the amino groups of CS were protonated and interacted with RO122 ions by electrostatic attraction, so that RO122 adsorbed onto the surface of the material and removed from the solution. At high pH, the amino groups of CS were not favorable for the adsorption of RO122. Thus, an optimum pH of about 1.0 was chosen for the further experiments.
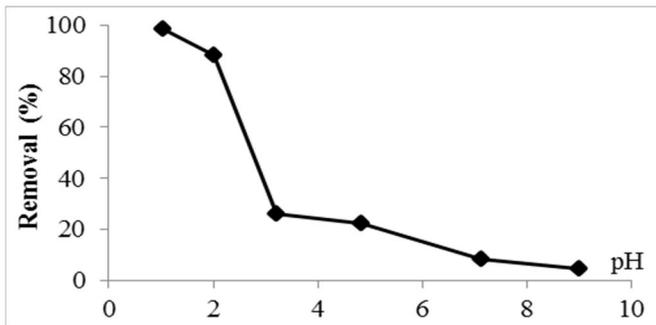

Figure 5. Effect of pH on the RO122 removal

3.2.5. The adsorption isotherms

The adsorption isotherms were studied by varying the initial concentration of RO122 with fixed dose of CS-GLA/DM. To investigate the sorption isotherms, two models, Langmuir and Freundlich isotherm equations were applied. The Langmuir isotherm equation in a linear form can be expressed as [8]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}.K_L} + \frac{C_e}{q_{max}}$$

Where:

C_e (mg/L) is the equilibrium liquid phase concentration of RO122 (mg/L); q_e (mg/g) is the amount of RO122 adsorbed per unit weight of CS-GLA/DM at equilibrium; q_{max} (mg/g) is the maximum amount of RO122 (per unit weight of CS-GLA/DM) capable of forming complete monolayer coverage on the surface at the high equilibrium concentration; K_L is the Langmuir constant.

The Freundlich isotherm equation in a linear form is [9]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

Where:

K_F (mg/L) is the predicted indicator of adsorption capacity and 1/n of the adsorption intensity. A linear form of the Freundlich equation yields the constants K_F and 1/n.

Base on experiments, the isotherm equation in the form of the Langmuir and Freundlich were represented in Figure 6 and Table 2.
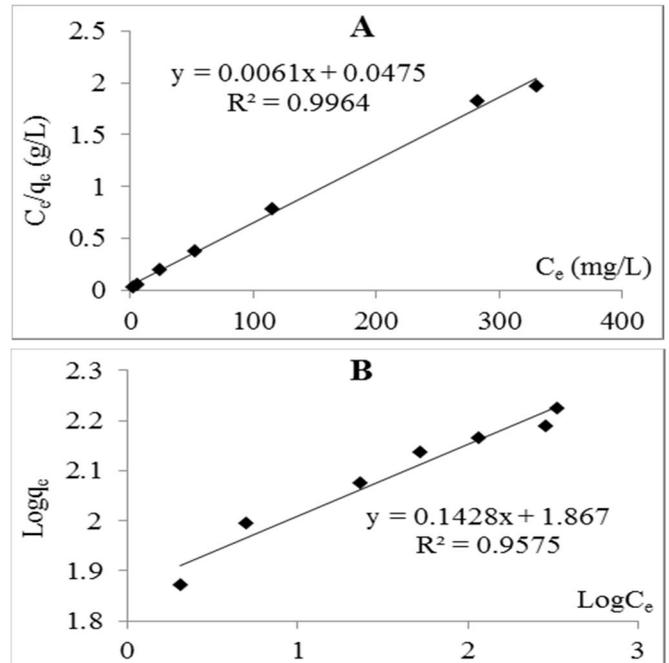

Figure 6. Adsorption isotherm linear for the adsorption of RO122 by CS-GLA/DM

(A) The Langmuir isotherm and (B) The Freundlich isotherm

Table 2. The parameters corresponding to the two isothermal models

Isotherm models	Langmuir			Freundlich		
Parameters	K_L (l/mg)	q_{max} (mg/g)	R^2	K_F l/mg)	N	R^2
Value	0.13	163.9	0.996	73.6	7.0	0.958

Table 2 showed the correlation coefficient R^2 for the Langmuir and the Freundlich isothermal model were 0.996 and 0.958, respectively. Therefore, the equilibrium data were found to be fitted well to the Langmuir isotherm and the maximum adsorption capacity was determined to be 163.9mg/g.

3.2.6. Adsorption kinetics model

Two kinetic models which were used to investigate the kinetics of RO122 adsorption by the CS-GLA/DM were Lagergren pseudo-first-order and Ho pseudo-second-order equations.

Lagergren pseudo-first-order equation [10]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1.t}{2.303}$$

Ho pseudo-second-order equation [10]:

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{t}{q_e}$$

Where:

q_e and q_t (mg/g) are the adsorption capacity of RO122 at equilibrium and at time t.

k_1 (min^{-1}), k_2 (g.mg^{-1}.min^{-1}) are the pseudo-first-order and pseudo-second-order rate constants.

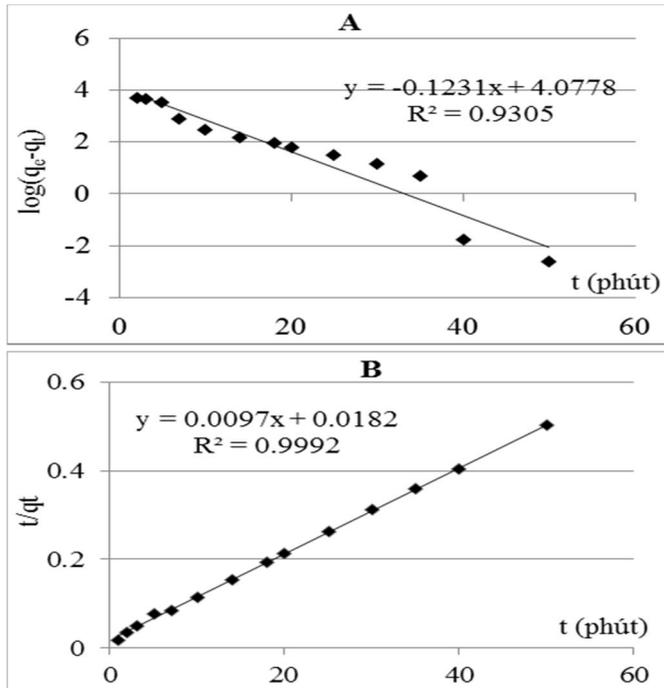The results were shown in Figure 7 and Table 3.

Figure 7. First-order order kinetic plot (A) and second-order kinetic plot (B) for the sorption of RO122 on CS-GLA/DM

Table 3 showed that the correlation coefficient (R^2) values obtained for the pseudo-second-order kinetics ($R^2 = 0.999$) was higher than that of pseudo-first-order kinetics ($R^2 = 0.931$). Therefore, it can be concluded that the RO122 adsorption process on the CS-GLA/DM was consistent with the pseudo-second-order kinetics model. In addition, by comparing the adsorption capacity at equilibrium (q_e) according to the models with the experimental values, the adsorption capacity obtained from pseudo-second-order model was closer to the experimental values $q_{e\,exp}$ ($q_{e2} = 99.3$mg/g $\approx q_{eexp} = 99.4$mg/g).

Table 3. The parameters corresponding to the two adsorption kinetics models of RO122 adsorption on CS-GLA/DM

C_o (mg/L)	$q_{e,\,exp}$ (mg/g)	Pseudo first order		Pseudo second order	
		$q_{e1,calculate}$ (mg/g)	R^2	$q_{e2,calculate}$ (mg/g)	R^2
400	99.4	59.0	0.931	99.3	0.999

4. CONCLUSIONS

In this study, CS-GLA/DM was prepared, characterized and used for the adsorption of RO122. The optimized values of contact time, pH and adsorbent dosage were found to be 50 mins; pH of 1.0; 0.2g, respectively. Langmuir equation fitted well the adsorption isotherm data and the maximum adsorption capacity for RO122 was 163.9mg/g. The pseudo second-order kinetics model agreed very well with the dynamic behavior of RO122 adsorption. It can be concluded that CS-GLA/DM may be used as a promising new adsorbent for RO122 removal from aqueous solutions.

REFERENCES

[1]. Willmott N., Guthrie J., Nelson G., 1998. *The biotechnology approach to colour removal from textile effluent*. Journal of the Society of Dyers and Colourists, 114(2), 38-41.

[2]. Vanitha K., Jibrail K., Sie Y. L., 2018. *Efficiency of various recent wastewater dye removal methods: A review*. Journal of Environmental Chemical Engineering, 6(4), 4676-4697.

[3]. Şahbaz D. A., Acikgoz C., 2017. *Cross-linked chitosan/marble powder composites for the adsorption of Dimozol Blue*. Water Science & Technology, 76(9-10), 2776-2784.

[4]. Jayakumar, R., Reis, R. L., Mano, J. F., 2006. *Chemistry and applications of phosphorylated chitin and chitosan*. e- Polymer, 6(1), 447-62.

[5]. Rinaudo, M ., 2006. *Chitin and chitosan: properties and applications*. Prog polym Sci., 31(7), 603-32.

[6]. Zhang, G., Xue, H., Tang, X., Peng, F., Kang C., 2011. *Adsorption of anionic dyes onto chitosan-modified diatomite*. Chemical research in Chinese universities, 27(6), 1035-1040.

[7]. Elden Galal Mors, H., 2010. *Diatomite: Its Characterization, Modifications and Applications*. Asian Journal of Materials Science 2 (3), 121-136.

[8]. Langmuir I., 1918. *The adsorption of gases on plane surface of glass, mica and platinum*. Journal of the American Chemical Society, 40(9), 1361-1403.

[9]. Freundlich, H. M. F., 1906. *Adsorption solution*. Zeitschrift fur Physikalische Chemie, 57, 384-470.

[10]. Ho, Y.S., Mckay, G., 1998. *A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents*. Process Safety and Environmental Protection, 76(4), 332-340.

THÔNG TIN TÁC GIẢ

Lê Thị Thi Hạ[1], Lại Thị Hoan[2], Nguyễn Thị Cúc[3], Nguyễn Thúy Hà[3], Hồ Phương Hiền[3]

[1]Trường Đại học Giao thông vận tải, Phân hiệu tại Thành phố Hồ Chí Minh

[2]Khoa Khoa học cơ bản, Trường Đại học Giao thông vận tải

[3]Khoa Hóa học, Trường Đại học Sư phạm Hà Nội