# **REMOVAL OF RHODAMINE B DYE FROM AQUEOUS SOLUTION USING CHITOSAN – MAGNETITE COMPOSITE**

**Vu Quang Tung, Bui Minh Quy**\* *TNU - University of Sciences* 

ARTICLE INFO	ABSTRACT			
Received: 05/01/2022	Chitosan-magnetite composite (CS-MNPs) was made by an in-situ			
Revised: 19/4/2022	combined co-precipitation method. Material characteristics were investigated by X-ray, SEM, BET, and VSM methods. CS-MNPs has			
Published: 21/4/2022	a spherical shape with a diameter of around 20 nm and a surface area			
	of 119.43 m <sup>2</sup> /g. Magnetic characteristic of the CS-MNPs has a good			
KEYWORDS	saturation magnetization of 36.5 emu/g. Adsorption of Rhodamine B			
	— dye (RhB) was studied through parameters such as solution pH,			
Chitosan – magnetite	contact time, initial RhB concentration, and temperature. RhB			
Rhodamine B dye	adsorption kinetics onto CS-MNPs was described using a pseudo-			
Kinetic	second-order model. Adsorption isotherms were in agreement with			
Isotherm	Langmuir and Freundlich adsorption models. Maximum adsorption			
Isotherm	capacity decreased from 2/1.79 to 148.41 mg/g when temperature			
Thermodynamic	raised from 293 to 313K. Adsorption process is spontaneous, random			
	and endothermic.			

# LOẠI BỎ THUỐC NHUỘM RHODAMIN B RA KHỎI NƯỚC BẰNG VẬT LIỆU COMPOSIT CHITOSAN – MA NHÊ TIT

Vũ Quang Tùng, Bùi Minh Quý\*

Trường Đại học Khoa học - ĐH Thái Nguyên

THÔNG TIN BÀI BÁO	ΤΟΜ ΤΑΤ
Ngày nhận bài: 05/01/2022	Vật liệu composite chitosan - ma nhê tit (CS-MNPs) đã được tổng
Ngày hoàn thiện: 19/4/2022	hợp băng phương pháp in-situ kêt hợp đông kêt tủa. Các đặc trưng của vật liệu đã được nghiên cứu thông qua các phương pháp X-Ray,
Ngày đăng: 21/4/2022	SEM, BET và VSM. Vật liệu CS-MNPs đã tổng hợp có dạng hình cầu với đường kính khoảng 20 nm, diện tích bề mặt 119,43 m <sup>2</sup> /g. Vật
TỪ KHÓA	liệu có từ tính tốt với từ độ bão hòa là 36,5 emu/g. Khả năng loại bỏ thuốc nhuộm rhodamin B (RhB) đã được nghiện cứu thông qua
Chitosan - ma nhê tit	nghiên cứu ảnh hưởng của các tham số hấp phụ: pH dung dịch, thời
Rhodamin B	gian hấp phụ, nồng độ ban đầu của RhB và nhiệt độ hấp phụ. Động
Động học	học quá trình hập phụ RhB trên CS-MNPs tuân theo mô hình giả
Mô hình hấp phụ	Langmuir và Freundlich. Dung lượng hấp phụ cực đại giảm từ
Nhiệt động hấp phụ	271,79 đến 148,41 mg/g khi nhiệt độ tăng từ 293 đến 313K. Quá trình hấp phụ là quá trình tự xảy ra, diễn ra tự nhiên và thu nhiệt.

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<sup>\*</sup> Corresponding author. *Email: quybm@tnus.edu.vn* 

#### 1. Introduction

Nowadays, the problem of water pollutants such as heavy metals, pesticides, dyes, ... are being investigated by scientists. Rhodamine B dye (Figure 1) is widely used as a textile pigment that is frequently used. The toxicity of rhodamine B (RhB) is both acute and chronic. Vomiting and poisoning can be caused by mild rhodamine B toxicity. When rhodamine B accumulates in the body for a long time, it can lead to cancers [1]. As a result, RhB must be removed from water sources. Adsorption is one of the most commonly used methods because of its low cost, simplicity, high removal efficiency and easy reuse of adsorbents [2], [3].

Chitosan-magnetite composite (CS-MNPs) is a material made from chitosan and Fe<sub>3</sub>O<sub>4</sub> that has excellent biological and magnetic properties. CS-MNPs have a wide range of applications in biomedicine and adsorption [2]-[6]. However, there hasn't been much research related to the usage of CS-MNPs in adsorption field in Vietnam. Due to its magnetism, the usage of CS-MNPs as adsorbents will offer advantages in terms of recovery and reuse [7], [8]. Process of removing RhB from aqueous was mentioned in this work by investigating influential parameters in the adsorption process. Kinetics, isotherms, and thermodynamics of the adsorption process were also studied.



Figure 1. Structure of Rhodamine B dye

# 2. Experiment

# 2.1. Chemicals

All chemicals used for synthesis were analytical grade and ordered from Sigma Aldrich and Xilong company with purity 98.0 - 99.9%, including iron (III) chloride hexahydrate (FeCl<sub>3.6</sub>H<sub>2</sub>O), iron (II) sulfate heptahydrate (FeSO<sub>4.7</sub>H<sub>2</sub>O), sodium hydroxide (NaOH), chitosan (CS), and rhodamine B (RhB).

# 2.2. Synthesis of CS - MNPs composite

MNPs were synthesized using a co-precipitation method with a  $Fe^{3+}$ :  $Fe^{2+}$  molar ratio of 1:2. In-situ engineering was used to create the composite. During the preparation of  $Fe^{3+}$  and  $Fe^{2+}$  solutions, chitosan was also added. The amount of  $Fe^{2+}$  and  $Fe^{3+}$  solutions was calculated so that the mass ratio of CS and MNPs formed was 5:5. The synthesis lasted 50 minutes at 80°C, pH of 13. The synthesized material was washed in distilled water and dried for 24 hours at 70°C. CS-MNPs were easily separated by magnets.

## 2.3. Analysis methods

Morphology of CS-MNPs were determined by *Scanning Electron Microscopy (SEM) on* FE-SEM Hitachi S-4800 (Japan). Crystalline phase analysis was carried out on an X-ray diffractometer – D2-Phase Bruker (Germany) with radiant Cu K $\alpha$  ( $\lambda$  = 1,5406 Å). *Magnetic properties of materials at room temperature were measured by a vibrating sample magnetometer* (VSM). Surface area of the material was determined according to Brunauer–Emmett–Teller method (BET).

# 2.4. Adsorption experiments

The adsorption of RhB onto CS-MNPs was used to study removal of RhB from aqueous. pH of solution (2–10), contact time (5–180 minutes), initial concentration of RhB ( $C_0 = 5-150$ 

mg/L), and temperature (293–303–313 K) were used to study effect on adsorption process. Volume of RhB solution was 50 mL. pH of solution was changed using HCl and NaOH solutions. The remaining components were kept constant when studying influence of one factor.

Concentrations of RhB before and after adsorption were determined by standard curve method on UV-Vis U2900 Hitachi (Japan) at maximum absorption wavelength  $\lambda_{max} = 554$  nm.

Adsorption capacity of RhB at equilibrium time and at time t was determined according to equations (1) and (2), respectively. RhB removal efficiency was determined according to equation (3).

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (\text{mg/g}) \tag{1}$$

$$q_t = \frac{(C_0 - C_t).V}{M} \quad (\text{mg/g}) \tag{2}$$

$$RE = \frac{(C_0 - C_t)}{C_0} .100 \quad (\%)$$
(3)

In which:  $C_0$ ,  $C_e$ ,  $C_t$  are concentration of RhB at initial time, equiblium and time t (mg/L);  $q_e$  and  $q_t$  are capacity adsorption at equibrilium and time t (mg/g); V is volume of RhB solution (V = 0.05 L), M is mass of CS-MNPs (M = 0.02 g). RE is removal efficiency of adsorption process (%).

#### 3. Results and discussion

# 3.1. Characterization of CS-MNPs



**Figure 2.** The XRD of CS, MNPs and CS-MNPs (a), SEM images of CS-MNPs (b), Nitrogen adsorption – desorption isotherms of CS-MNPs (c), Magnetization curves of MNPs and CS-MNPs (d)

XRD results (Figure 2a) showed that 2-theta =  $29.97^{\circ}$ ,  $35.45^{\circ}$ ,  $43.24^{\circ}$ ,  $53.49^{\circ}$ ,  $57.15^{\circ}$ ,  $62.81^{\circ}$  corresponded to lattice faces [hlk] = (220), (311), (400), (422), (511) and (440) of spinel structure of Fe<sub>3</sub>O<sub>4</sub> [7], [9]. Furthermore, a diffraction peak at 2-theta location corresponded to  $11.15^{\circ}$  shown on the plot, demonstrated the presence of CS in composite [6], [10]. Spinel structure of Fe<sub>3</sub>O<sub>4</sub> was unchanged when combined with chitosan. This demonstrated that composite materials composed of CS and MNPs successfully made. Average crystal sizes of MNPs and CS-MNPs were calculated with the Debye-Scherrer formula (Equation 4) [10]. Average crystal sizes of

MNPs and CS-MNPs were 8.70 nm and 5.95 nm, respectively. Composites' average crystal size is less than that of individual MNPs. This can be explained by the fact that CS played as a surfactant when forming NMPs crystals while synthesizing materials [5].

$$D = \frac{K.\lambda}{\beta.\cos\theta} \tag{4}$$

D is the average crystallite size (nm), K is the Scherrer constant (K = 0.9),  $\lambda$  is the wavelength of the X-ray source ( $\lambda$  = 0,15406),  $\beta$  is the full width at half-maximum (FWHM) of the main peak diffraction (radians),  $\theta$  is the peak position (radians).

CS-MNPs has a uniform spherical shape with a diameter of around 20 nm, as shown in SEM image (Figure 2b). Surface area of CS-MNPs was 119.43 m<sup>2</sup>/g using the N<sub>2</sub> adsorption isotherms (Figure 2c). This was higher than the previous study (88.7 m<sup>2</sup>/g) [9]. Saturation magnetization of CS-MNPs was 36.5 emu/g, lower than that of individual MNPs (63.5 emu/g) (Figure 2d). Because of the absence of non-magnetic chitosan in CS-MNPs, saturation magnetization value of CS-MNPs was lower than that of MNPs (42.5%). However, this value of material was larger than that result reported by Li Gui yin *et al.* (21.5 emu/g) [4].

# 3.2. Effect of adsorption factors on the RhB dye removal efficiency



**Figure 3.** Effect of adsorption factors on the RhB dye removal efficiency: pH (a), contact time (b), initial concentration of RhB and temperature (c)

Figure 3 showed effect of several factors (pH, contact time, initial concentration of RhB, temperature) on adsorption of RhB in aqueous onto CS-MNPs. At pH of 6 - 8, results (Figure 3a) showed that CS-MNPs has high effectiveness in removing RhB. It might be explained that: RhB has a pKa value of 3.7. RhB exists as RhB<sup>+</sup> when pH is less than 3.7. RhB existed in zwitterionic form (RhB<sup>±</sup>) when pH was greater than 3.7 [3]. CS-MNPs, on the other hand, has 6.7 points of zero charge. Surface of CM-MNPs was positively charged when pH was less than 6.7, while surface of CS-MNPs was negatively charged when pH was greater than 6.7. As a result of the charge competition on surface of CS-MNPs and RhB at pH 2, adsorption efficiency decreased. Adsorption was attributed to charged interaction of RhB and CS-MNPs surface at pH > 3.7, which increased removal effectiveness. On the other hand, RhB removal effectiveness at pH 6, which is close to the natural pH of water, was nearly equivalent to that at pH 7 and 8, so pH 6 was chosen for further research.

RhB removal efficiency (Figure 3b) was quite stable from 50 to 180 minutes. As a result, 60 minutes was chosen as adsorption equilibration time. RhB removal efficiency decreased as the initial concentration of RhB and adsorption temperature raised (Figure 3c).

#### 3.3. Adsorption kinetics

Experimental data were fitted to pseudo-first- and second-order, Temkin, intra-particlediffusion models to investigate the adsorption kinetics (Figure 4). The pseudo-first- and secondorder, Temkin, intra-particle-diffusion nonlinear equations were given by equations 5, 6, 7, and 8, respectively [7], [8], [11], [12].

$$q_t = q_e (1 - e^{-K_1 t})$$
(5)

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \tag{6}$$

$$q_t = \frac{1}{B}\ln(AB) + \frac{1}{A}\ln t \tag{7}$$

$$q_t = K_{in} t^{0.5} + C (8)$$

Where:  $K_1(1/min)$  is the adsorption rate constant of this model.  $K_2$  (g/mg.min) is the secondorder adsorption rate constant.  $K_{in}$  is the diffusion rate constant (mg.min<sup>0.5</sup>/g); C is constant. A (mg/g.min) is the initial rate of adsorption rate and B (g/mg) is the Elovich constant.



Figure 4. The fitting curves of RhB adsorption kinetic models onto CS-MNPs

Figure 5. The fitting curves of Langmuir, Freundlich and Temkin models for RhB onto CS-MNPs at different temperatures

The regression coefficient  $R^2$  according to the pseudo-second-order model is higher than the remaining  $R^2$  values and closes to 1 ( $R^2 = 0.97$ ), as in Table 1. On the other hand, the adsorption capacity according to pseudo-second-order ( $q_e$ ) is likewise near to the experimentally found maximum adsorption capacity ( $q_{exp}$ ). As a result, the pseudo-second-order model fits the RhB adsorption kinetics onto CS-MNPs. This was also in agreement with other previous researches on RhB adsorption kinetics onto adsorbents [7], [8], [11]-[13].

Pseudo-first-order	Pseudo-second-order	Elovich	Intra-particle-diffusion				
$R^2 = 0.85$	$R^2 = 0.97$	$R^2 = 0.92$	$R^2 = 0.75$				
$K_1 = 0.12$	$K_2 = 0.43.10^{-2}$	A = 108.96	$K_{in} = 1.61$				
(1/min)	(g/mg.min)	(mg/g.min)	$(mg.min^{0.5}/g)$				
$q_e = 42.15 \ (mg/g)$	$q_e = 45.13 \text{ (mg/g)}$	B = 0.18 (g/mg)	C = 25.93				
$q_{exp} = 44.25 \text{ (mg/g)}$							

**Table 1.** The parameters of RhB adsorption isotherm onto CS-MNPs

#### 3.4. Adsorption isotherm

RhB adsorption onto CS-MNPs was investigated with Langmuir, Freundlich, and Temkin isotherm adsorption models (Figure 5). The Langmuir, Freundlich, Temkin equations are given by equations (9), (10), (11), respectively [7], [8], [11], [12], [14].

$$q_e = \frac{Q_{\max} K_L C_e}{(1 + K_L C_e)} \tag{9}$$

$$q_e = K_F \exp(C_e^{1/n}) \tag{10}$$

$$q_e = \frac{RT}{b_r} \ln(K_T C_e) \tag{11}$$

where  $C_e$  and  $q_e$  are concentration of RhB (mg/L) and capacity adsorption (mg/g) at equilibrium.  $Q_{max}$  is the maximum adsorption capacity of monolayer (mg/g).  $K_L$  is Langmuir constant (L/mg).  $K_F$  (mg<sup>1-(1/n)</sup> L<sup>1/n</sup>/g) and n are Freundlich isotherm constant and adsorption intensity, respectively. Adsorption process's favorability is dependent on the value of 1/n. Favourable adsorption is defined as a value of 1/n between 0 and 1 [15].

 $K_T$  (L/mg) is Temkin isotherm constant,  $b_T$  (J/mol) is Temkin isotherm constant related to adsorption heat. R (8.314 J/mol. K) is the gas constant. T (K) is the absolute temperature.

 $R_1$  is a Langmuir parameter that is calculated using equation (12). The value of  $R_1$  is connected to the adsorption process' feasibility or favorability. Following is the relationship between Rl and adsorption favorability: A  $R_1$  value between 0 and 1 indicates favourable adsorption,  $R_1 > 1$  denotes unfavourable adsorption, and  $R_1 = 0$  and  $R_1 = 1$  denote reversible and linear adsorption, respectively [8], [12].

$$R_{l} = \frac{1}{(1 + K_{L}C_{0})} \tag{12}$$

Regression coefficients ( $R^2$ ) for Langmuir and Freundlich models at investigated temperatures are high and near to 1 ( $R^2 = 0.98$  and 0.99), as shown in Table 2. That demonstrated that adsorption of RhB onto CS-MNPs follows both Langmuir and Freundlich models.  $R_1$  and 1/n values also indicated that RhB adsorption process onto CS-MNPs was favourable.

 $K_L$  values increased as temperature increased (T = 293, 303, 313 K), while the maximum adsorption capacities calculated with Langmuir model decreased ( $Q_{max} = 271.79$ , 196.95, 148.41 mg/g). That indicated that when temperature raised, adsorption rate increased while adsorption efficiency reduced.

Temperature (K) —	Langmuir isotherm					
	Q <sub>max</sub> (mg/g)	K <sub>L</sub> .10 <sup>-2</sup> (L/mg)	RL	$\mathbb{R}^2$		
293	271.79	3.47	0.97 - 0.66	0.98		
303	196.95	4.61	0.96 - 0.59	0.98		
313	148.41	5.79	0.95 - 0.54	0.98		
		Freundlich isoth	erm			
Temperature (K)	n	K <sub>F</sub>	1/n	<b>R</b> <sup>2</sup>		
-		$(mg^{1-(1/n)}L^{1/n}/g)$				
293	1.92	22.08	0.52	0.99		
303	2.22	22.85	0.45	0.98		
313	2.51	11.23	0.40	0.98		
Temperature (K) —	Temkin isotherm					
	<b>b</b> т ( <i>J/mol</i> )	K <sub>T</sub> (L/mg)	<b>R</b> <sup>2</sup>			
293	54.32	0.68	0.91			
303	66.80	0.72	0.96			
313	84.49	0.81	0.98			

Table 2. The parametre of adsorption model at different temperatures

#### 3.5. Adsorption thermodynamic

To study thermodynamic adsorption, values of standard free energy ( $\Delta G^0$ ), standard enthalpy ( $\Delta H^0$ ) and standard entropy ( $\Delta S^0$ ) were determined with the equations 13 and 14:

$$\Delta G^{0} = -RT \ln K_{C} \tag{13}$$

$$\Delta G^{0} = \Delta H^{0} - T \Delta S^{0} \tag{14}$$

in which, equilibrium constant  $K_C$  could be calculated using several coefficients such as Langmuir isotherm constant ( $K_L$ ), Freundlich isotherm constant ( $K_F$ ) and distribution coefficient ( $K_d$ ). In this study,  $K_C$  was determined from Langmuir isotherm constant. Because  $K_C$  must be dimensionless,  $K_L$  value must be multiplied by  $10^6$  to obtain the density of pure water (mg/L). Plot of  $\Delta G^0$  versus T was used to calculate  $\Delta H^0$  and  $\Delta S^0$  [16].

Values  $\Delta G^0$  were negative when calculated using equation (13). RhB adsorption onto CS-MNPs was shown to be a spontaneous process. Standard enthalpy and entropy values were 19.50 kJ and 115.23 J/mol.K, respectively (Figure 6). This result also coincided with RhB adsorption thermodynamic onto previously studied materials such as L-Ser capped Fe<sub>3</sub>O<sub>4</sub> NPs, and MIL-53-Fe MOF/Magnetic Magnetite/Biochar Composites [8], [11].



**Figure 6.** *Effect of the standard free energy to temperature* 

#### 4. Conclusion

CS-MNPs composite material has been successfully synthesized by in-situ combined with coprecipitation method. The material has a spherical shape with a diameter of roughly 20 nm and a surface area of 119.43 m<sup>2</sup>/g. Magnetic characteristic of material is good. At a pH of 6, CS-MNPs adsorbs RhB dye well, with a contact time of 60 minutes. When initial concentration of RhB and adsorption temperature increase, efficiency of RhB removal decrease. The pseudo-second-order model can be used to explain RhB adsorption process onto CS-MNPs. Langmuir and Freundlich adsorption models apply to RhB isotherm adsorption. Adsorption temperatures are 293K, 303K, and 313K, maximum adsorption capacity are 271.79, 196.95, and 148.41 mg/g, respectively. RhB dye adsorption onto CS-MNPs is endothermic, spontaneous, and random.

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