

Fabrication of Graphene Oxide for Application in Removing Tetracycline Hydrochloride in Aqueous Solution

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Abstract

Recently, antibiotic pollution has been recognized as an aquatic environmental pollution, due to its potential adverse effects on ecosystems and human health. Therefore, it is necessary to have an effective and environmentally friendly method to remove antibiotic residues in the aquatic environment. In this study, Graphene oxide (GO) was synthesized for the treatment of antibiotic residues in the aquatic environment. The characteristics of GO material were analyzed by the X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Transmission electron microscopy (TEM, JEM-JEOL 2100) methods. The GO material was used for the adsorption of tetracycline hydrochloride (TCH) in an aqueous environment. The adsorption equilibration time is 30 min and an efficiency of approximately 88.57% with an initial TCH concentration of 20 mg/L. The factors that affect the adsorption process were investigated including the initial TCH concentration (10 to 40 mg/L), the GO dosage (0.1 to 0.5 g/L), and the pH solution (1 to 9). The adsorption process of TCH on GO material is consistent with the Freundlich isotherm model with a maximum adsorption capacity of 65.65 mg/g. The TCH adsorption process of GO material is exothermic.

Keywords: Adsorbent, GO, tetracycline, adsorption isotherm, kinetics.

1. Introduction

Currently, the problem of environmental pollution has been a painful problem, not only in Vietnam but also in countries around the world. Pollution occurs in most environments such as soil, water, air... Among them, water pollution is becoming more and more dangerous [1]. Water pollution is divided into two types: water pollution of natural origin and water pollution of artificial origin. Today, industrialization, modernization, and population growth have greatly affected the environment. Many organic pollutants are released into the environment without treatment, leading to water pollution that directly affects human health and the ecosystem [2, 3].

Currently, antibiotics are widely sold and used, not by regulations. Not only used in humans, antibiotics are also used in livestock [4]. Because of such popular and widespread use, it has led to an excess of antibiotics in the water environment. Therefore, there is a need for methods to remove antibiotic residues in the water environment. Currently, there are many treatment methods such as adsorption, advanced oxidation, biological methods, and electrochemical methods, etc [5, 6]. Among them,

the advanced oxidation method using solar energy has received the attention and research of major scientists at home and abroad. This is considered a promising and potential method because it takes advantage of sunlight - a free, abundant, and endless source of energy, the product of an environmentally friendly process.

Tetracycline is a broad-spectrum antibiotic widely used in both humans and animals. Many studies have shown that tetracycline antibiotic residues have been detected in surface water [5, 7]. Therefore, it is necessary to have an effective and environmentally friendly method to remove tetracycline antibiotic residues in aquatic environments. Hereto, many adsorbent materials have been synthesized and used to remove TCH in water environments. Ball-milled biochar was synthesized at different temperatures and used to adsorb TCH in an aqueous environment. The maximum adsorption capacity was 84.54 mg/g, but the adsorption process was carried out for a long time (0.5 - 168 h) [8]. A multi-walled carbon nanotube (MWCNT) loaded iron metal-organic framework (MIL-53(Fe)) composite was synthesized to adsorb TCH at pH equal to 7 with the maximum adsorption capacity of 180.68 mg/g [9]. However, the

MWCNT/MIL-53(Fe) synthesis process is complicated and the adsorption time is very long (24 h). Thus, materials that are easy to synthesize and have short processing times must be researched and developed.

For a long time, the application scope and potential of graphene have been discussed in many scientific conferences. This is a material with wide and very potential applications, especially in the field of water treatment, because of its two-dimensional layer structure, large surface area, pore volume, and presence of surface functional groups [10]. Wastewater can be treated through many different methods such as desalination, sedimentation, flotation, adsorption, and disinfection, etc. Certainly, the adsorption method always plays an important role and has many advantages compared to the other methods. This is an easy method to operate and relatively low cost.

To promote the potential of graphene and solve the problem of antibiotic pollution in the water environment, GO was synthesized in this study. The characteristics of material are analyzed using many methods such as SEM, TEM, and XRD methods. The adsorption capacity of the GO was evaluated through the adsorption efficiency of tetracycline hydrochloric (TCH) in the aqueous environment. Several factors affecting adsorption performance were also studied including the adsorption time, the temperature, the pH of solution, concentration of the TCH, the adsorbent dosage.

2. Experiment

2.1. Materials

Graphite, sulfuric acid (H₂SO₄, 98%), sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂, 33%), sodium hydroxide (NaOH), and TCH (C₂₂H₂₄N₂O₈.HCl, 99%) were purchased from China and used directly without further refining. In addition, distilled water was used throughout the experiment.

2.2. Preparation of GO

The synthesis procedure is carried out as follows: 4 g of graphite and 4 g of NaNO₃ were placed in a beaker containing 200 mL of 98% H₂SO₄ and stirred well for 2 h. The reaction was maintained at 0 to 5 °C (the reaction beaker was placed in a basin containing a mixture of ice and salt). Then, 12 g of KMnO₄ was slowly added to the above mixture and the reaction was maintained at a temperature of less than 15 °C for 30 min. This mixture was stirred for another 48 h, at a temperature of 30 to 35 °C, to obtain a brown solution. 200 mL of distilled water was added to the above mixture (temperature increased rapidly to 98 °C, white smoke was released and the solution became light brown) and continued stirring for 30 min. To cool the

mixture, 400 mL of distilled water was added and stirred well. Then, 20 mL of H₂O₂ was added and stirred well. This mixture was allowed to settle overnight, then centrifuged and filtered 5 times, and dried at 80 °C for 72 h to obtain GO.

2.3. Characterization

The morphology of the GO material was observed through a scanning electron microscope (SEM JEOL series 7600F) with a landing voltage of 10.0 kV and TEM, JEM-JEOL 2100. XRD was used to analyze the characteristics of materials. The X-ray diffractometer was equipped with Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$) at 25 °C. The 2θ range was swept from 5 to 80° and the transmitter was set at 35 mA and 40 kV.

2.4. TCH Adsorption Process

To evaluate the TCH adsorption efficiency of the GO material, the experiment was arranged as follows: 0.05 g of the GO material was added to a beaker containing 100 mL of the TCH solution with an initial concentration of 20 mg/L and ultrasound to disperse the material evenly into the solution. This mixture was stirred evenly at a speed of 250 rpm. After a certain period of time (5 - 30 min), 5 mL of this mixture was taken and filtered through a filter and measured UV-Vis at 375 nm to determine the remaining TCH concentration. The equilibrium adsorption capacity and TCH removal percentage were calculated according to the following formula [11]:

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

$$R_e = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

where C_0 , C_t , and C_e are respectively the TCH concentration (mg/L) at the beginning ($t = 0$), after the time t , and the adsorption equilibrium time (min). m is the mass of the adsorbent (g), V is the volume of the solution (L). R_e is the TCH removal efficiency (%).

To determine the adsorption isotherm model, the experiment was performed similarly and only the TCH concentration was changed (10-40 mg/L). Similarly, the adsorption isotherm model was also determined by changing the temperature of the process (30 - 50 °C).

In addition, to study the pH_{pzc} value of the GO material, the procedure is as follows: Initially, 100 mL of TCH solution with a concentration of 20 mg/L was put into a 250 mL beaker. Then, this solution was adjusted to a pH value of 2 - 12 with HCl and NaOH solutions of 0.1 M concentration. After achieving the desired initial pH value, 0.05 g of GO material was added to the above solution and stirred at room temperature for 24 h. The final pH value was measured and plotted against the initial pH value. The intersection of the initial and final pH value lines is

determined as the pH_{pzc} value of the GO material.

3. Results and Discussion

3.1. Characterization of the Material

XRD method was used to study the crystalline nature and purity of the GO material and the result is presented in Fig. 1.

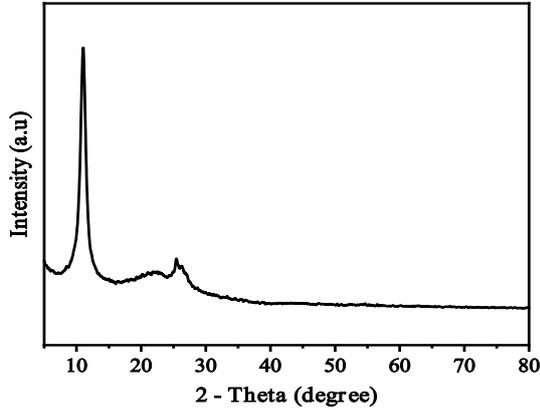


Fig. 1. XRD pattern of the GO material.

The diffraction peak at $2\theta = 11.07^\circ$ can be assigned to the structure of the GO, this result is consistent with the previous publication on the GO [12]. The diffraction peak at $2\theta = 25.36^\circ$ characterizes graphite [12]. Based on the peak intensity, it can be seen that the characteristics of graphite are almost gone and are replaced by the characteristics of the GO. This proves that oxygen-containing functional groups (-OH, -COOH...) were formed during the oxidation of the graphite and leached into the space between the graphite layers, increasing the distance between the GO layers to 0.78 nm. This distance is calculated according to the Bragg equation:

$$2d\sin\theta = n\lambda \quad (3)$$

where d is the distance between planes in the parallel plane family, n is the reflection beam, λ is the X-ray wavelength ($\lambda = 0.15406$ nm), and θ is the Bragg angle.

The crystallite size of the GO material can be calculated according to the Scherrer formula [2]:

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (4)$$

where K is a constant that depends on the crystal shape (usually $K = 0.9$), λ is the X-ray wavelength (0.15406 nm), θ is the Bragg diffraction angle, and β is the line broadening of the sample corresponding to half maximum intensity in radians (FWHM).

From there, the average crystallite size of the GO material was calculated as 3.73 nm.

Fig. 2 shows the surface of the GO material as a thin and wrinkled carpet. The randomly arranged thin GO sheets form a disordered solid as shown in Fig. 2a.

The wavy GO material surface is randomly arranged, with a peeling phenomenon as shown in Fig. 2a. The observed GO material has a distinct layered structure with a flat surface, the graphene sheets were also shown through folds (Fig. 2b). As observed from the TEM image (Fig. 3), it can be seen that the GO material has about 3 - 5 layers stacked on top of each other.

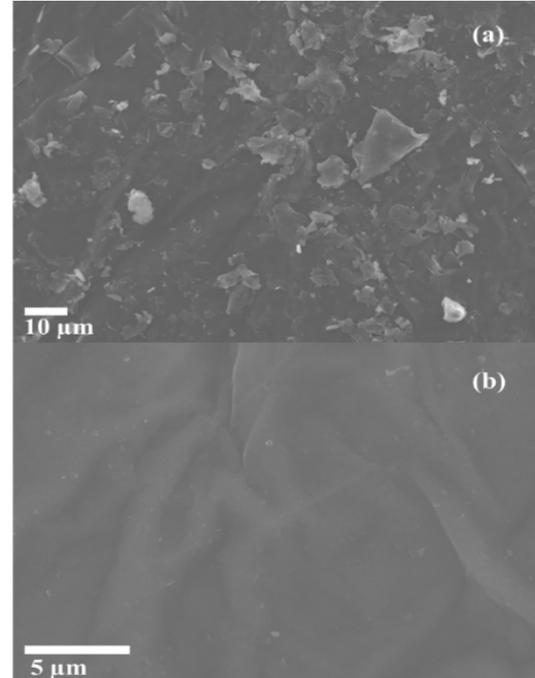


Fig. 2. SEM images of the GO materials.

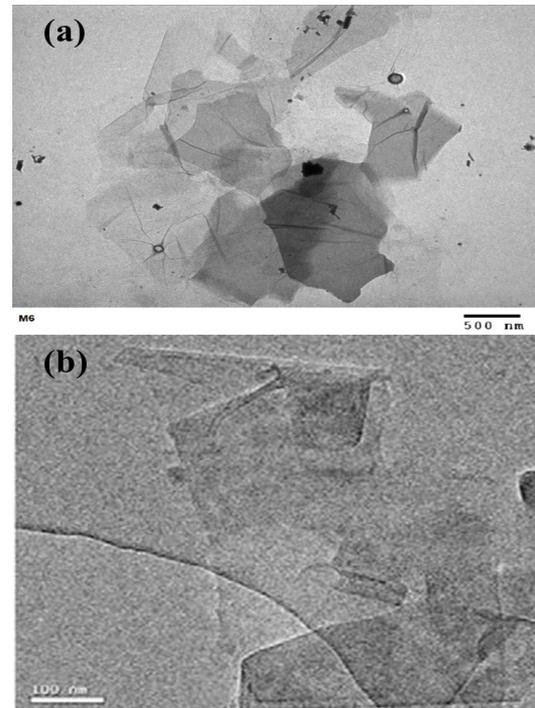


Fig. 3. TEM images of the GO materials.

3.2. Investigation of the Adsorption Equilibrium Time of the GO Material

Adsorption equilibrium time is an important factor that is always studied in adsorption processes. In this study, the experiment was conducted with $[TCH] = 20 \text{ mg/L}$, $[GO] = 0.5 \text{ g/L}$, and survey time from 0 to 60 min. Fig. 4 describes the TCH adsorption equilibrium time of the GO material. The results showed that after 5 min, the GO material had adsorbed 87.07% of 20 mg/L TCH solution. After 30 min, the efficiency increased to 88.57%. From 30 to 60 min, the adsorption efficiency is almost constant. This can be confirmed that the adsorption equilibrium has been established. Thus, 30 min was chosen as the adsorption equilibrium time point and applied for the subsequent studies.

3.3. Factors Affecting the TCH Adsorption Capacity of the GO Material

3.3.1. Effect of the GO material dosage

To study the effect of the GO dosage on the TCH adsorption performance, the experiment was studied at conditions including $[TCH] = 20 \text{ mg/L}$, room temperature ($25 \text{ }^\circ\text{C}$), $[GO] = 0.1 \text{ to } 0.5 \text{ g/L}$. The results of this study are presented in Fig. 5.

It can be seen that when the GO dosage increases from 0.1 to 0.5 g/L, the adsorption efficiency increases significantly from 33.07 to 88.57%. This can be explained as follows: when the GO dosage increases, the available active sites of the GO material increase the adsorption efficiency. However, as the GO dosage increases, the q_e value decreases. With the GO dosage of 0.1 g/L, the highest q_e value is 121.87 mg/g and the efficiency is only 33.07%. But when the GO dosage increased to 0.5 g/L, the efficiency increased to 88.57% and the q_e value decreased, reaching only 35.43 mg/g. Thus, to optimize TCH adsorption efficiency, the GO dosage of 0.5 g/L is the most suitable. On the contrary, a concentration of 0.1 g/L is the most suitable in terms of adsorption capacity. As shown in Fig. 4, it can be determined that the GO dosage of 0.167 g/L is the best condition to optimize both the TCH adsorption efficiency and adsorption capacity. In this study, the GO dosage selected for use in subsequent studies is 0.5 g/L.

3.3.2. Effect of the initial concentration of the TCH solution

The results in Fig. 6 show that the TCH adsorption of the GO material decreased as the initial concentration of the TCH solution increased.

With an initial TCH concentration of 10 mg/L, the adsorption efficiency reached 96.91% after 30 min. When the initial TCH concentration gradually increases from 10 to 40 mg/L, the adsorption efficiency gradually decreases from 96.91 to 82.07%.

This can be explained as follows: when the initial TCH concentration increases, the density of the TCH molecules in the solution increases, and they compete for available active sites on the surface of the GO material leading to the effective adsorption capacity.

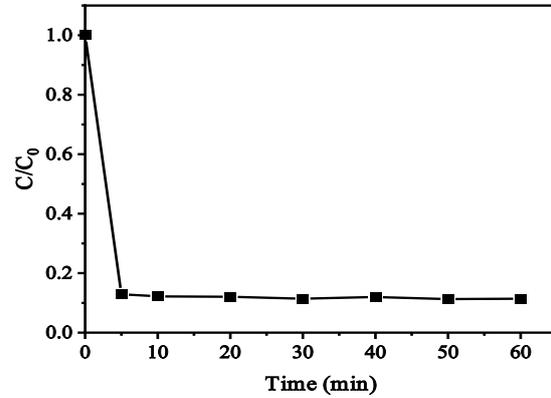


Fig. 4. Investigation of the adsorption equilibrium time of the GO material.

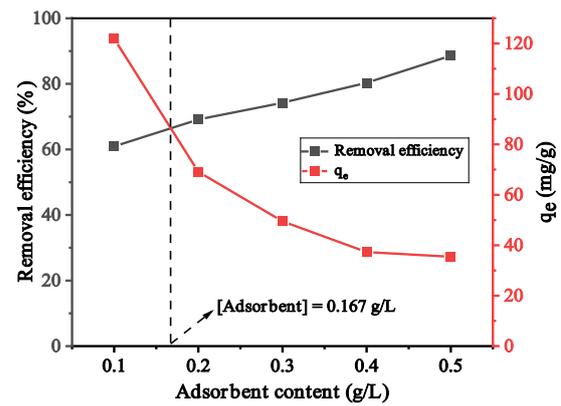


Fig. 5. Effect of the GO dosage.

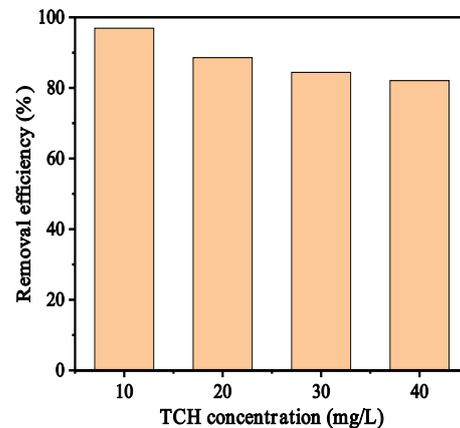


Fig. 6. Effect of the initial concentration of the TCH solution.

3.3.3. Effect of the pH of the initial TCH solution

pH is always an important factor in wastewater treatment, especially the adsorption process. To study the effect of the pH of the initial TCH solution on the adsorption capacity of the GO material, pH was studied in the range from 1 to 9, [TCH] = 20 mg/L, [GO] = 0.5 g /L, at room temperature (25 °C). The results of this study are shown in Fig. 7.

At pH equal to 1, the low adsorption efficiency reached 33.07% after 30 min. When pH increases to 3, the adsorption efficiency increases to 66.57%. At pH equal to 5 and 9, the adsorption efficiency is almost equal (~88%). The highest adsorption efficiency (89.98%) was at a pH equal to 7. Thus, the favorable pH condition for the TCH adsorption of the GO material is pH equal to 7.

The TCH has three pK_a values leading to it can exist in three different forms depending on the pH of the solution. When pH is below 4, the TCH exists as a cation (TCH_3^+), due to protonation of the dimethyl-ammonium group. At the pH between 3.5 and 7.5, the TCH exists as a zwitterion (TCH_2^0), due to the loss of a proton from the phenolic diketone group. At pH above 7.5, the TCH exists as an anion (TCH^- or TC^{2-}) due to proton loss from the tri-carbonyl system and the phenolic di-ketone radical [12]. In addition, the surface charge properties of the adsorbent also depend on the pH.

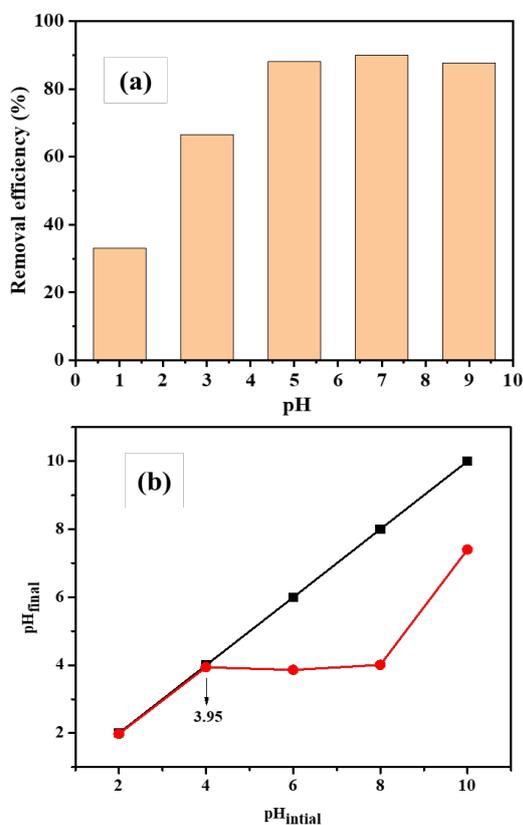


Fig. 7. Effect of the pH of the initial TCH solution.

The pH_{pzc} value of the GO material was studied and reached 3.95 as shown in Fig. 7b. This shows that when pH is below 3.95, the adsorbent surface is positively charged, and pH above 3.95, the adsorbent surface is negatively charged. Therefore, in strongly acidic environments (pH equal 1 and 3), the adsorbent surface will poorly adsorb TCH_3^+ cations, similarly, in basic environments (pH equal 9), the adsorption efficiency decreases due to repulsion electrostatic between the negatively charged surface of the GO and the TCH. On the other hand, in a neutral environment (pH equal 7), the adsorption efficiency is the best, approximately 90%, this can be explained by the electrostatic repulsion force not being too large between the negatively charged surface of the GO and TCH_2^0 should not hinder the adsorption capacity of the material.

3.4. Adsorption Kinetics

First-order and second-order equations were used to study the kinetics of the TCH adsorption of the GO material.

The first-order equation [11]:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (5)$$

The second-order equation [11]:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where q_t and q_e are the adsorption capacity at time t and at the equilibrium time (mg/g). k_1 and k_2 are the rate constants of the (5) and (6) equations, respectively.

Table 1. Kinetic parameters of the TCH adsorption process of the GO material.

	$q_{e, \text{exp}}$ (mg/g)	35.43
	$q_{e, \text{cal}}$ (mg/g)	7.260
First-order	k_1 (min^{-1})	0.211
	R^2	0.408
	$q_{e, \text{cal}}$ (mg/g)	35.714
Second-order	k_2 (g/mg.min)	0.028
	R^2	0.999

Fig. 8 shows the first-order and second-order kinetic equations of the TCH adsorption process of the GO material. The kinetic parameters are listed in Table 1.

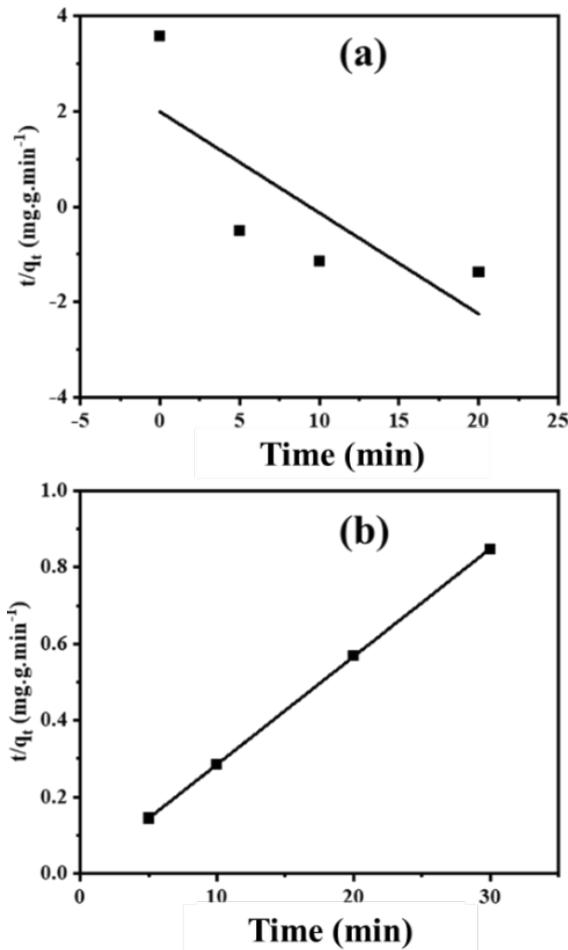


Fig. 8. The (a) first-order and (b) second-order kinetic equations of the TCH adsorption of the GO material.

It can be seen that the regression coefficient (R^2) of the first-order and second-order equations were 0.408 and 0.999, respectively. The R^2 value of the second-order equation was approximately equal to 1. The q_e value (35.714 mg/g) calculated by the quadratic equation is close to the q_e value (35.43 mg/g) calculated from the experiment. These indicate that the second-order kinetic model is more suitable for the TCH adsorption process of the GO material.

3.5. Adsorption Isotherm

The results of determining the equilibrium concentration (C_e) of the TCH adsorption on the GO material are shown in Table 2. Based on the Langmuir and Freundlich adsorption isotherm model, the relationship between q_e and C_e was built and the results are presented in Fig. 9.

Fig. 9 shows that the Freundlich isotherm model has a higher regression coefficient (R^2 equal 0.963) than the Langmuir model (R^2 equal 0.904). Therefore, the TCH adsorption process of the GO follows the Freundlich isotherm model.

Table 2. Adsorption isotherm parameters of the GO material.

C_o (mg/L)	C_e (mg/L)	q_e (mg/g)	m (g)	V (L)
10	0.309	19.382	0.05	0.1
20	2.286	35.428	0.05	0.1
30	4.793	50.414	0.05	0.1
40	7.173	65.654	0.05	0.1

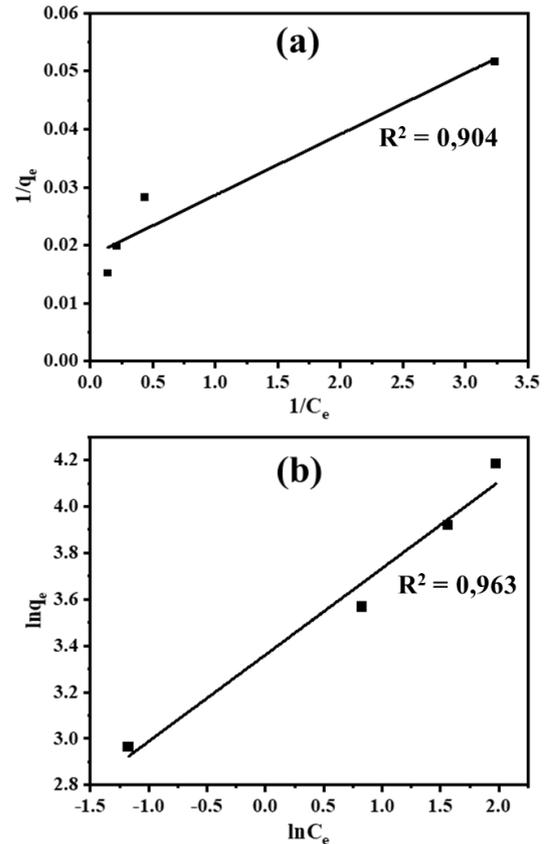


Fig. 9. (a) Langmuir and (b) Freundlich isotherm adsorption curves.

3.6. Thermodynamics of Adsorption

The TCH adsorption process was conducted at temperatures of 30, 40, and 50 °C to study the thermodynamic properties of the process. Thermodynamic parameters such as standard free energy (ΔG°), standard entropy (ΔS°), and standard enthalpy (ΔH°) are calculated according to the following equations [11]:

$$\Delta G^\circ = -RT \ln k_c \quad (7)$$

$$k_c = \frac{q_e}{C_e} \quad (8)$$

$$\ln k_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

where R is the gas constant (8.314 J.mol⁻¹.K⁻¹), and T is the absolute temperature (K). C_e (mg/L), and

q_e (mg/g), are the equilibrium concentration and equilibrium adsorption amount, respectively. k_c is the equilibrium constant.

Thermodynamic parameters are presented in Table 3. Graphs and Van't Hoff diagrams are shown in Fig. 10.

Table 3. Thermodynamic parameters of the TCH adsorption of the GO material.

T (K)	$\ln k_c$	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol.K)
303	3.425	-8.628		
313	3.093	-8.048	-26.177	-57.920
323	2.726	-7.320		

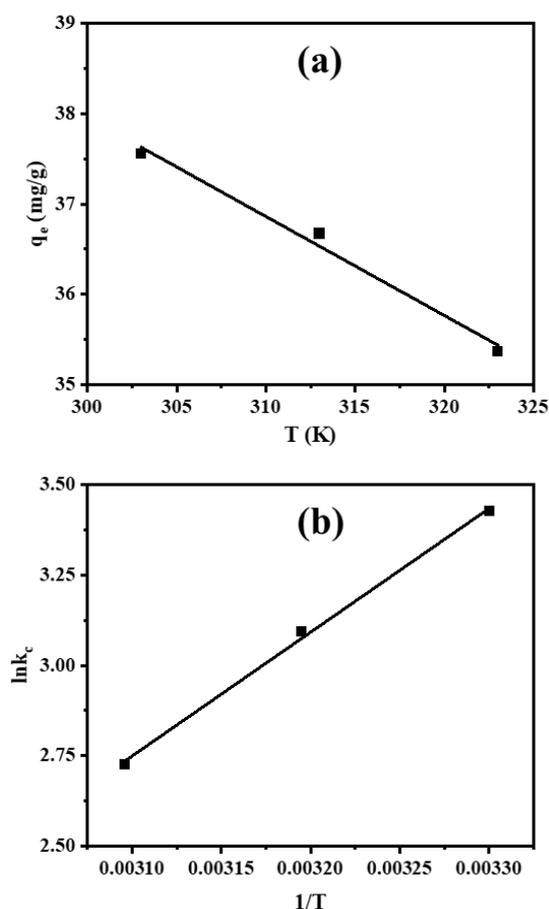


Fig. 10. (a) Effect of temperature on the adsorption capacity of the TCH on the GO material and (b) Van't Hoff diagram.

At different temperatures, the ΔG° value has negative values, which proves that the TCH adsorption process of the GO material is spontaneous. As the temperature increases, the ΔG° value increases, which shows that at low temperatures the TCH adsorption process of the GO material occurs more smoothly and effectively. With increasing temperature, the TCH

molecules move from the solid phase to the liquid phase due to their increasing mobility. Therefore, the amount of the TCH antibiotic adsorbed will decrease. The negative ΔH° value (-26.177 kJ.mol⁻¹) shows that the TCH adsorption process of the GO material is exothermic and the negative ΔS° value (-57.920 J.mol⁻¹.K⁻¹) indicates the degrees of freedom of the particles in the system.

4. Conclusion

The GO material was successfully synthesized by a simple method, capable of adsorbing the TCH in the aqueous environment in a short time. Research results show that the TCH adsorption capacity of the GO material is quite high, reaching an efficiency of approximately 88.57% with an initial TCH concentration of 20 mg/L with an adsorption time of 30 min. The appropriate factors affecting the TCH adsorption process of the GO material are the initial concentration of the TCH of 20 mg/L, pH equal 7.0, and the GO dosage of 0.5 g/L. The TCH adsorption process of the GO material follows the second-order kinetic equation and follows the Freundlich adsorption isotherm model with a maximum adsorption capacity of q_{max} equal 65.65 mg/g. The TCH adsorption process of the GO material is exothermic. This process takes place smoothly and effectively at low temperatures. This result opens up prospects for applying the GO materials in the field of wastewater treatment.

Acknowledgments

This study was funded by the Ministry of Education and Training of Vietnam, under grant number CT2022.04.BKA.01. Nguyen Thu Huong was funded by the Master, PhD Scholarship Programme of Vingroup Innovation Foundation (VINIF), code VINIF.2023.ThS.061.

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