

Adsorption behavior of crystal violet from aqueous solutions with chitosan–graphite oxide modified polyurethane as an adsorbent

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ABSTRACT: A series of chitosan (Ch)–graphite oxide (GO)-modified polyurethane foam (PUF) materials as adsorbents were synthesized by a foaming technique. The adsorbent was characterized through IR spectroscopy, scanning electron microscopy, and thermogravimetric analysis (TGA). Batch adsorption experiments of the cationic dye crystal violet (CV) were carried out as a function of the Ch–GO content (1.0–8.0 wt %), solution pH (2–10), dye concentration (100–300 mg/L), adsorbent dosage (10–60 mg/mL), and temperature (20–45°C). At a lower pH value, the surface of Ch–GO/PUF acquired positive charge by absorbing H^+ ions; this resulted in a decreasing adsorption of the cationic CV dye because of electrostatic repulsion. As the pH of the aqueous system increased, the numbers of negatively charged sites increased by absorbing OH^- ions, and a significantly high electrostatic attraction existed between the negatively charged surface of Ch–GO/PUF and the cationic dye (CV) molecules. This led to maximum dye adsorption. The kinetics, thermodynamics, and equilibrium of CV adsorption onto Ch–GO/PUF were investigated. The equilibrium data for CV adsorption fit the Langmuir equation, with a maximum adsorption capacity of 64.935 mg/g. The adsorption kinetics process followed the pseudo-second-order kinetics model. Thermodynamic parameters analysis revealed that the adsorption of CV from an aqueous solution by a Ch–GO modified PUF material was a spontaneous and endothermic process. We concluded that Ch–GO/PUF is a promising adsorbent for the removal of CV from aqueous solutions. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41828.

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INTRODUCTION

Environmental pollution caused by synthetic dyes is one of the most serious environmental problems.¹ The water polluted by synthetic dye molecules can cause damage to aquatic life because of their negative ecotoxicological effects and bioaccumulation in wildlife.² In addition, the color in bodies of water can also reduce the penetration of sunlight to the lower layers.³ Crystal violet (CV), a typical triphenyl methane dye, is widely applied in the textile industry. It has been used as antifungal and antimicrobial agents.⁴ CV is a mutagen, mitotic poison,⁵ and proven potent carcinogen,⁶ and is toxic to mammalian cells. Moreover, CV has been classified as a recalcitrant molecule because of its poor biodegradation and because it can last for a long time in a variety of environments. CV can cause painful sensitization to light, and it can also cause perpetual injury to the conjunctiva and cornea. Purple is easily visible to the naked eye even, at very low concentrations. Thus, it is necessary to remove such contaminants from industrial effluents to protect the environment and offer people a better quality of life.

The disposal of dyes into wastewater systems should draw great concern and should be used in the experiment and imminent

implementation. Until now, there have been many methods to use in the removal of dye, including biological treatment,⁷ electrolytic method,⁸ flocculation,⁹ adsorption,^{10,11} and oxidation.¹² Adsorption has been proven to be a more excellent way to treat industrial wastewater; it offers significant advantages, including a low cost, availability, profitability, ease of operation, and efficiency, in comparison with conventional methods, especially from economical and environmental points of view.¹³

Chitosan (Ch), which represents a family of polymers derived from chitin by deacetylation, is used as an adsorbent. Ch can remove dyes and heavy metals because of the presence of hydroxyl and amino groups and can serve as active sites.¹⁴ Because of its sensitivity to pH, Ch derivatives have been investigated to improve the performance of Ch as an adsorbent. Various substances have been used to form composites with Ch; these include activated clay,¹⁵ polyurethane,¹⁶ perlite,¹⁷ and so on. Graphite oxide (GO), a precursor in the synthesis of graphene layers, has been an adsorbent for removing cationic dyes.¹⁸ GO can be easily prepared by the oxidation of graphite with $KMnO_4$ and H_2SO_4 or $HClO_4$. In the process of synthesis, the strong oxidation makes GO have many oxygen-containing

functional groups; these include hydroxyl, carboxyl, and epoxy groups. As GO is a highly functionalized carbon with an expanded pore structure and various functional groups, it can be used as an adsorbent.¹⁹

Polyurethane foam (PUF) materials, prepared from polyol and isocyanate, are widely used in many applications. PUF has been chosen as an alternative material for the treatment of large quantities of contaminated water; this is due to its reduced cost, availability, and reutilization after dye desorption.²⁰ Moreover, PUFs contain a high surface area and porous structures; these enable them to act as matrix materials to fix various kinds of adsorbents, such as Ch,¹⁶ hydroxyapatite,²¹ and attapulgite,²² in the removal of dyes and heavy-metal ions from aqueous solution. In this study, Ch and GO were adopted to modify PUF materials to make them functional with carboxyl, amine, and hydroxyl groups. This study was devoted to the absorption of CV from wastewater with Ch-GO/polyurethane foam (Ch-GO/PUF) materials. The effects of various variables, such as the adsorbent dose, pH, temperature, and Ch-GO content, were studied to optimize the experimental conditions to obtain the best adsorption efficiency (*D*). To the best of our knowledge, this is the first time that the CV dye adsorption removal application of Ch-GO modified PUF materials is reported.

EXPERIMENTAL

Materials and Stock Solutions

Poly(ether polyol) (NJ-330, number-average molecular weight = 3000 g/mol) was produced by Ningwu Chemical Co., Ltd. (Jurong, Jiangsu, China). Toluene diisocyanate (TDI) was supplied by Rongrong Chemical Co., Ltd. (Shanghai, China). All of the other chemicals used in this study were of high purity and were analytical-reagent grade. The water used in the experiment was deionized water.

CV was chosen to prepare the model wastewater and was commercial quality (C₂₅H₃₀N₃Cl, weight-average molecular weight = 408, maximum absorption wavelength (λ_{max}) = 581 nm). The chemical structure of the CV dye is presented in Figure 1. An aqueous stock solution (2000 mg/L) was prepared by the dissolution of an accurately weighed quantity of

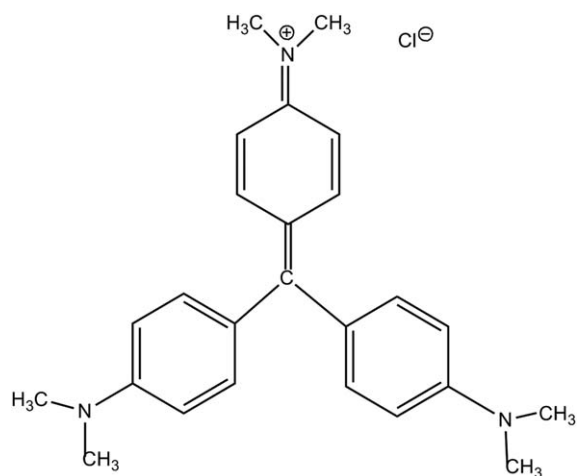


Figure 1. Structure of the CV dye.

CV in deionized water. The solution pH was adjusted by the addition of 0.1 M NaOH and 0.1 M HCl solutions.

Synthesis of Adsorbent (Ch-GO/PUF)

GO was synthesized by the oxidation of graphite with a modified Hummers method.²³ The Ch solution (2%, w/v) was prepared by the dissolution of 0.8 g of powder Ch into 40 mL of an acetic acid solution (2% v/v) under ultrasonic stirring for 90 min at 30°C. Then, 0.6 g of GO were added in the prepared solution, and the mixed system was continuously stirred for 2 h in a water bath at 50°C (GO/Ch = 3:4). The pH of the reaction system was adjusted to 9–10 with the microadditions of NaOH (0.2 mol/L), which were kept in the water bath for a further 80 min at 80°C. The products were washed with distilled water and ethanol in turn until the pH reached about 7. The sample of Ch-GO was dried in a vacuum oven at 60°C and then ground to an ideal particle size.²⁴

Ch-GO/PUF materials were prepared in three stages:

1. A calculated amount mixture of the polyether polyol (NJ-330, 10.0 g), Ch-GO, sodium bicarbonate (0.9 g) as a foaming agent, silicon oil (0.65 g) as a stabilizer, and dibutyltin dilaurate (T-12, 0.0876 g) as catalyst in the reaction were stirred at a revolving speed of 2000 rpm for 5 min.
2. A certain amount of TDI (1.74 g) was added to the mixture. The mixture was stirred for 20 s at a speed of 2000 rpm until the foam began to grow up.
3. The mixture was heated to 100°C and maintained for 3 h in the oven, where the material expanded. After foaming development, the block was demolded.

In this study, the Ch-GO/PUF materials with different Ch-GO contents of 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0 wt % were expressed as PUF, Ch-GO/PUF-1, Ch-GO/PUF-2, Ch-GO/PUF-3, Ch-GO/PUF-4, Ch-GO/PUF-5, Ch-GO/PUF-6, Ch-GO/PUF-7, and Ch-GO/PUF-8, respectively. The synthetic route of Ch-GO/PUF material is shown in Figure 2.

Characterizations

Fourier transform infrared (FTIR) spectra were recorded in the range 4000–500 cm⁻¹ with a Madison-Nicolet spectrometer (Avatar 360). A minimum of 32 scans was signal-averaged with a resolution of 2 cm⁻¹ in previous ranges. Scanning electron microscopy (SEM) was performed with Hitachi S-4800 SEM instrument with an accelerating voltage of 15 kV. TGA was performed on a Netzsch STA 449C instrument (Germany) with a gas flow of 50 mL/min. The programmed heating range was from room temperature to 1000°C at a heating rate of 10°C/min under a nitrogen atmosphere. The measurement was taken with 6–10-mg samples.

Batch Adsorption Experiments

Batch adsorption experiments were carried out to evaluate the effects of the content of Ch-GO, solution pH, adsorbent dose, and temperature. We carried out the experiments by putting a certain weight of foam material into 10 mL of 100 mg/mL CV aqueous solution. After equilibrium was reached, the foam material was taken out. The solution was measured by an ultraviolet-visible spectrophotometric method at a λ_{max} of 581 nm.

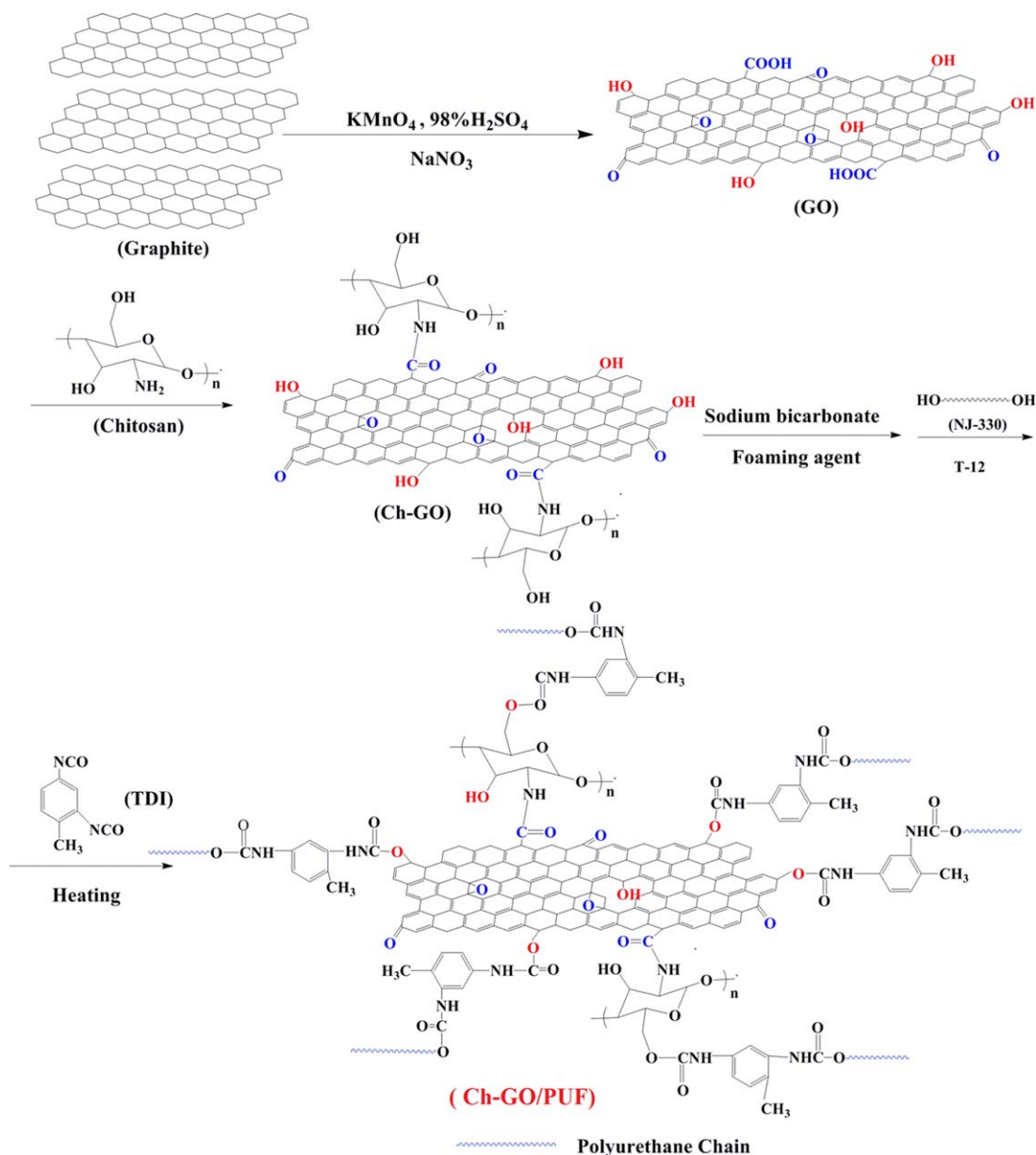


Figure 2. Synthetic route of the Ch-GO/PUF material. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The effect of the solution pH on the CV removal was studied over a range 2–10. We also conducted the experiments by changing the content of Ch-GO (1.0–8.0%), the amount of the adsorbents (10–60 mg/L), and the temperature (20–45°C). We studied the adsorption kinetics by analyzing the adsorptive uptake of the dye from the solution at different time intervals. For adsorption isotherms, the dye solutions of different concentrations were investigated with a known amount of adsorbent until the equilibrium was achieved. The amount of adsorbed CV and the adsorption capacity at equilibrium (q_e ; mg/g) was calculated according to eq. (1):

$$q_e = \frac{(C_o - C_e)}{W} V \quad (1)$$

The D of solution was calculated according to eq. (2):

$$D = \frac{C_o - C_t}{C_o} \times 100\% \quad (2)$$

where C_o and C_e are the initial liquid-phase concentrations of CV and that at equilibrium, respectively; V is the volume of the CV dye solution (L); W is the dry weight of the adsorbent (g); and C_t is the concentration of the CV dye solution at time t .

RESULTS AND DISCUSSION

FTIR Characterization

The FTIR spectra of Ch-GO, PUF, and Ch-GO/PUF-5 are shown in Figure 3. In the spectrum of the Ch-GO composite, the strong peak around 3400 cm^{-1} was due to the stretching vibrations of the O–H groups. These –OH groups present in GO reacted with –NCO of TDI and formed hydrogen bonds

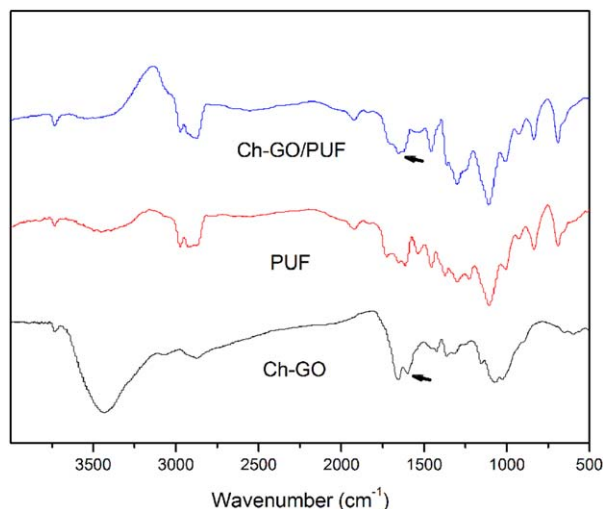


Figure 3. FTIR spectra of (a) Ch-GO, (b) PUF, and (c) Ch-GO/PUF-5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with the dye molecules. The characteristic band centered at 1610 cm^{-1} was attributed to the N—H bending of NH_2 represented in Ch. As shown in the spectra of PUF and Ch-GO/PUF-5, the peaks at the range $3000\text{--}2800\text{ cm}^{-1}$ were the stretching vibrations of carbon–hydrogen bonds in $-\text{CH}_2$ and $-\text{CH}_3$. The absorption peaks of the ester stretching vibration existed at $1700\text{--}1720\text{ cm}^{-1}$; this demonstrated the existence of the $-\text{OCON}-$

group. In the spectrum of Ch-GO/PUF-5, the intensity of the peaks at 1615 cm^{-1} (N—H) increased compared to PUF. This was attributed to the introduction of Ch-GO and indicated that the Ch-GO was grafted in the polyurethane molecule. The peak at 2270 cm^{-1} for the $-\text{NCO}$ group of TDI disappeared; this proved the completed polymerization of PUF and Ch-GO/PUF.

SEM

SEM is widely used to study the surface characteristics and morphological features of materials. In this study, SEM images of the GO, Ch-GO, Ch-GO/PUF-5, and CV-loaded Ch-GO/PUF-5 materials are shown in Figure 4. As shown in Figure 4(a), GO presented a sheetlike structure. After a combination with Ch, the sheetlike structure of GO was not changed (arrows), but a rougher surface was obtained, as shown in Figure 4(b). This indicated Ch was assembled on the surface of the GO layers.²³ Moreover, Ch was assembled on the surface of the GO layers, and the particle size of GO was about $1.5\text{ }\mu\text{m}$. As shown in Figure 4(c), there was no layered Ch-GO. This was because the $-\text{OH}$ groups present in Ch-GO reached the $-\text{NCO}$ groups of TDI and also the prepared Ch-GO uniformly dispersed in PU. Furthermore, open and closed pores made up the internal structures. The Ch-GO/PUF-5 material had more open pores. These open pores were observably interconnected, and this increased the surface area of the adsorbent. A lot of air was generated during the foaming process, and this resulted in passive insulation. However, some of them could possibly collapse because of violent foaming reaction. The porous walls were much thinner compared with the edge struts. As shown in

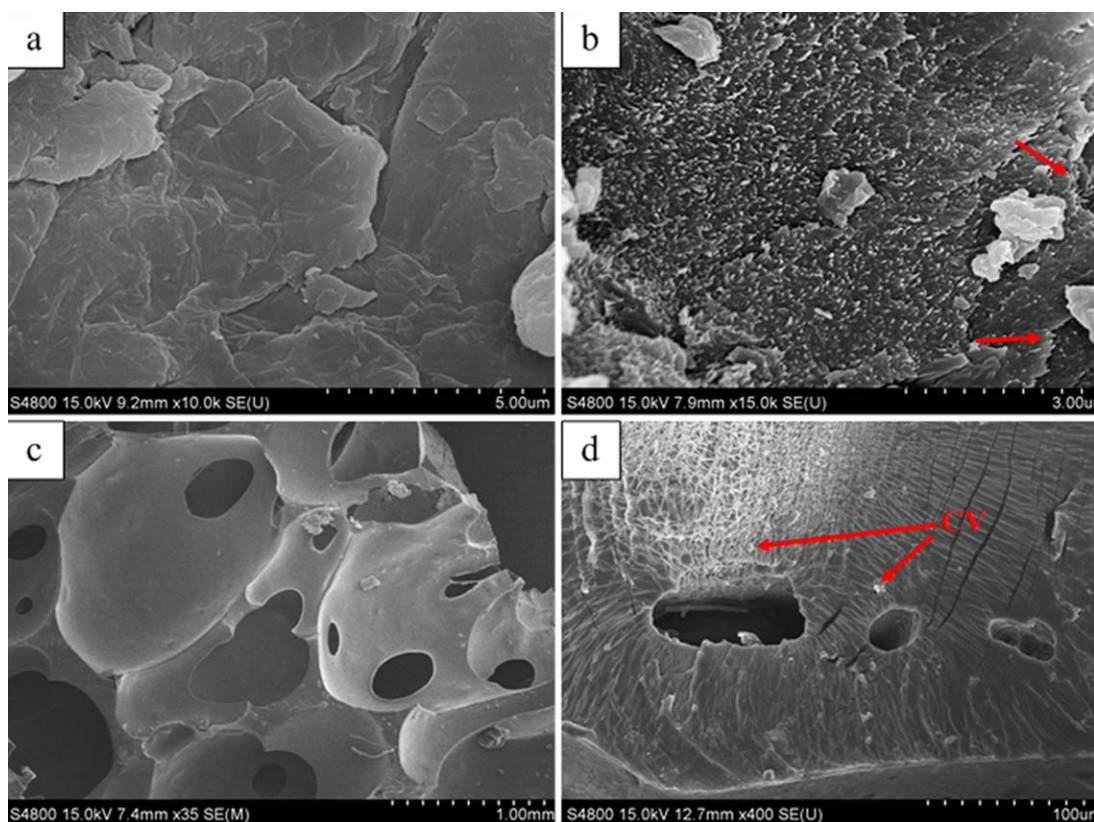


Figure 4. SEM images of (a) GO, (b) Ch-GO, (c) Ch-GO/PUF-5, and (d) CV-loaded Ch-GO/PUF-5 materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4(d), the shiny part, which is not shown in Figure 4(c), was the adsorbed CV dye (arrows) on the foam material, and the surface was folded. The CV dye was attached to the folded surface with a high density. The results show that the change in the textural properties of Ch-GO/PUF-5 after CV adsorption was due to the accumulation of dye onto the adsorbent surface; this indicated that an adsorption phenomena occurred.

TGA

To examine the thermal activities of foam material, PUF and Ch-GO/PUF-5 were chosen to carry out TGA experiments on a Netzsch STA449C instrument under nitrogen at a heating rate of 10°C/min. Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of the PUF and GO/PUF-5 foam materials are shown in Figure 5. As shown in Figure 5(a), the initial decomposition temperature of the PUF material at 2.83% was 180.91°C. However, the initial decomposition temperature of the Ch-GO/PUF-5 material at 4.44% was 196.8°C. The results show that Ch-GO/PUF-5 had better thermal properties than the PUF material; this indicated that the addition of Ch-GO increased the heat resistance of the foam material. This was consistent with the mechanism proposed by Duquesne.²⁵

Effect of the Content of Ch-GO on *D*

The effect of the content of Ch-GO on *D* of CV by Ch-GO/PUF was obtained at a fixed volume of 10 mL of the 100 mg/

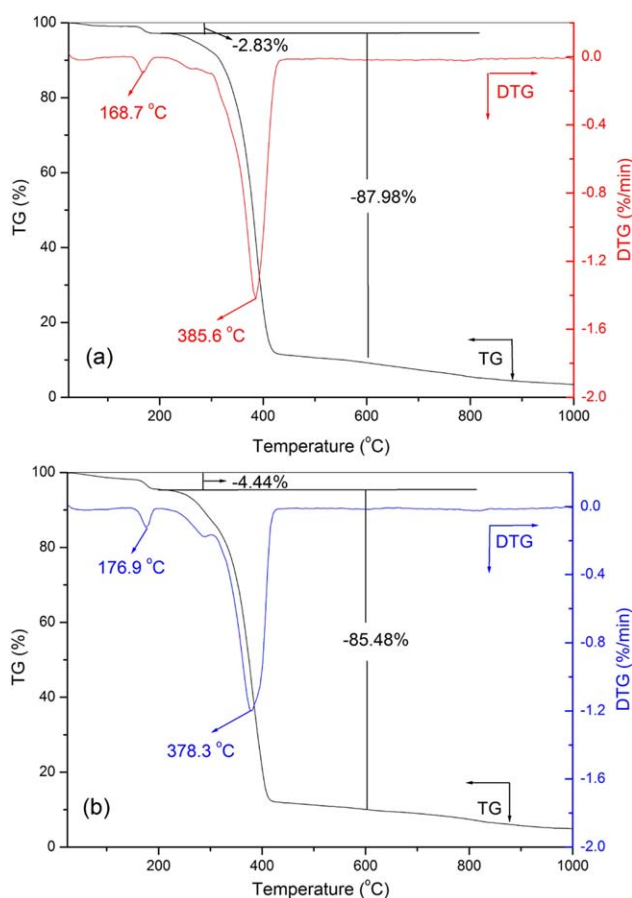


Figure 5. TG and DTG curves of the (a) PUF and (b) GO/PUF-5 foam materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

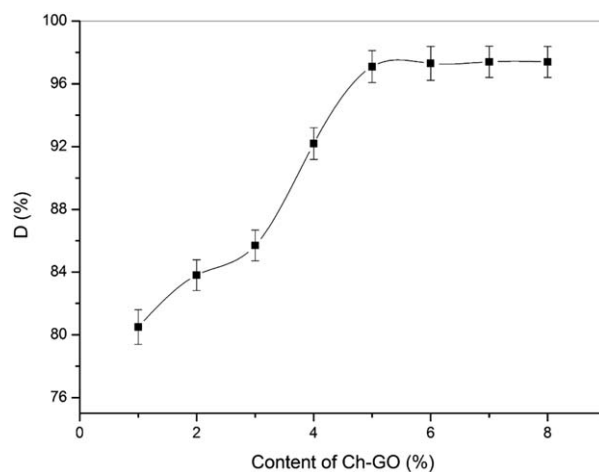


Figure 6. Effect of the Ch-GO content on the adsorption efficiency of the CV dye solution.

mL CV aqueous solution, a Ch-GO/PUF dosage of 50 mg/mL, a pH of 8.0, and a temperature of 30°C. The results are shown in Figure 6. As shown in Figure 6, *D* of CV increased with increasing content of Ch-GO. The adsorption efficiencies of all of the Ch-GO/PUF materials were greater than 80%. This was mainly because Ch-GO could adsorb dyes by chemical bonding interactions, whereas Ch-GO/PUF provided a macroporous network structure and a large surface area. A relatively higher *D* (97.1%) was reached when the mass proportion of Ch-GO was 5.0%. Furthermore, the *D* value of the CV dye solution increased little when the content of Ch-GO increased further to 8.0%. Under the same adsorption conditions, the adsorption efficiencies of Ch (0.0143 g) and GO (0.0107 g) on the CV dye were 10.4 and 23.8%, respectively; these values were much lower than that of Ch-GO/PUF-5. Hence, the optimal content of Ch-GO 5% (Ch-GO/PUF-5) was selected for further study.

Effect of pH on *D*

It is well known that the pH value of the solution is an important monitoring parameter governing an adsorption process. Figure 7 shows the effect of the solution pH for the adsorption

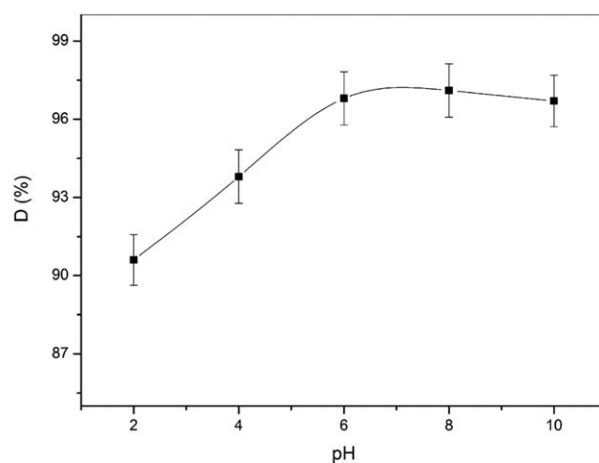
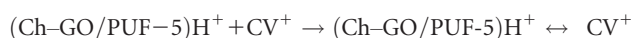


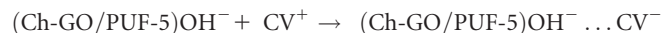
Figure 7. Effect of the solution pH on the adsorption efficiency of the CV dye solution.

of the CV dye on Ch-GO/PUF-5 at a fixed volume of 10 mL of 100 mg/mL CV aqueous solution, a Ch-GO/PUF-5 dosage of 50 mg/mL, and a temperature of 30°C. The range of the solution pH was adjusted between 2 and 10. As shown in Figure 7, it is possible to note that when the pH values increased from 2.0 to 8.0, an increase in the CV adsorption efficiency occurred (90.6–97.1%). This behavior could be explained by the fact that CV is a basic dye and has a pK_a of 0.8.²⁶ Because of its very low pK_a value, CV was completely ionized at almost all pHs and existed as a cationic species. At a lower pH value, the H^+ ion concentration in the aqueous system increased, and the surface of Ch-GO/PUF-5 acquired a positive charge by the absorption of H^+ ions. The positively charged surface sites on Ch-GO/PUF-5 did not favor the adsorption of cationic CV dye because of the electrostatic repulsion and caused a decrease in the dye adsorption. As the pH of the aqueous system increased, the numbers of negatively charged sites increased through the absorption of OH^- ions. As the Ch-GO/PUF-5 surface became negatively charged at high pH, a significantly high electrostatic attraction existed between the negatively charged surface of Ch-GO/PUF-5 and the cationic dye molecules; this led to maximum dye adsorption. The following reactions were expected to occur at the solid/liquid interface:²⁷

Electrostatic repulsion in acidic medium: $Ch-GO/PUF-5 + H^+ \rightarrow (Ch-GO/PUF-5)H^+$



Electrostatic interaction in basic medium: $Ch-GO/PUF-5 + OH^- \rightarrow (Ch-GO/PUF-5)OH^-$



With a further increase in the pH (8.0–10.0), no significant change in the CV dye adsorption efficiency was observed. On the basis of the aforementioned reasons, the initial pH of 8.0 was selected as the more adequate value for the other adsorption experiments.

Effect of the Dosage of Foam Material on the Adsorption Efficiency

The adsorbent dose is an important parameter that strongly influences the adsorption process by affecting the adsorption capacity of the adsorbent. The effect of the adsorbent dosage on the adsorption efficiency of the CV dye solution at a fixed volume of 10 mL of a 100 mg/mL CV aqueous solution, a pH of 8.0, and a temperature of 30°C is shown in Figure 8. We found that the CV adsorption efficiency increased from 69.9 to 97.1% as the Ch-GO/PUF-5 dosage increased from 10 to 50 mg/mL. The increase in the efficiency of the CV dye adsorption with the adsorbent dose was attributed to an increase in the adsorbent surface area; this augmented the number of adsorption sites available for adsorption, as already reported.¹ Above 50 mg/mL, the CV adsorption efficiency was constant. On the basis of these results, we found that 50 mg/mL was an adequate adsorbent dosage for the adsorption CV from the aqueous solutions, and so, this concentration was used for subsequent experiments.

Effect of the Temperature on the Adsorption Efficiency

The adsorption temperature has a significant effect in wastewater treatment systems. The effect of the temperature on the

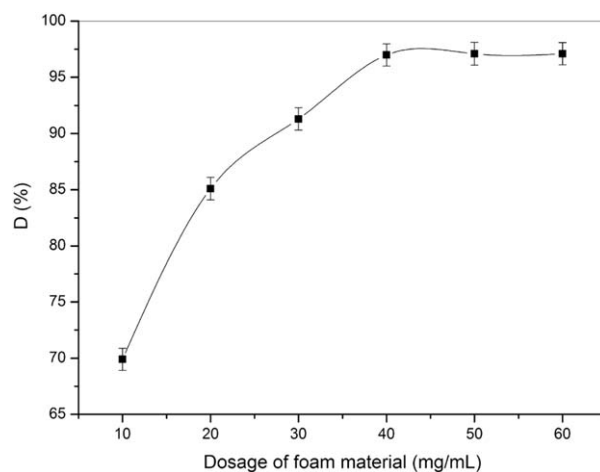


Figure 8. Effect of the adsorbent dosage on the adsorption efficiency of the CV dye solution.

adsorption efficiency of CV dye solution at a fixed volume of 10 mL of a 100 mg/mL CV aqueous solution, a pH of 8.0, and a Ch-GO/PUF-5 dosage of 50 mg/mL is shown in Figure 9. As shown in Figure 9, we observed that the CV adsorption efficiency increased from 80.3 to 99.2% as the temperature increased from 20 to 35°C; this indicated that the adsorption was controlled by an endothermic reaction. We found that a higher temperature facilitated the adsorption of CV onto Ch-GO/PUF-5. This may have been a result of the increase in the mobility of the dye molecule with increasing temperature. Furthermore, an increasing temperature produced a swelling effect within the internal structure of Ch-GO/PUF-5; this enabled the dye molecule to penetrate further. When the temperature was 35, 40, or 50°C, the adsorption efficiency was 99.2, 99.2, or 99.3%, respectively. We found that no significant change in the CV dye adsorption efficiency was observed. So, an adsorption temperature of 35°C was chosen in this study.

Adsorption Kinetics

Adsorption kinetic are necessary for investigating adsorption because they can predict the rate in the process where a

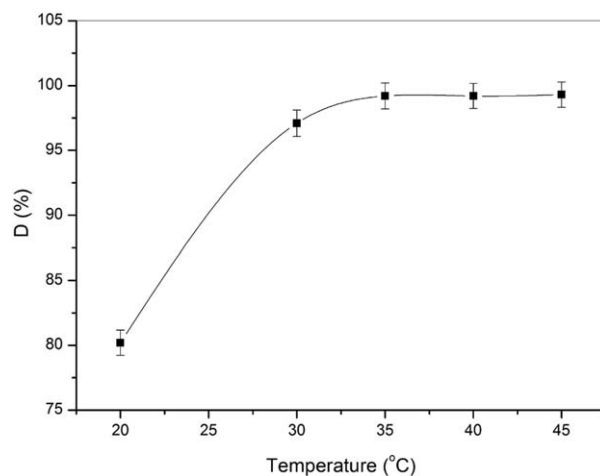


Figure 9. Effect of the temperature on the adsorption efficiency of the CV dye solution.

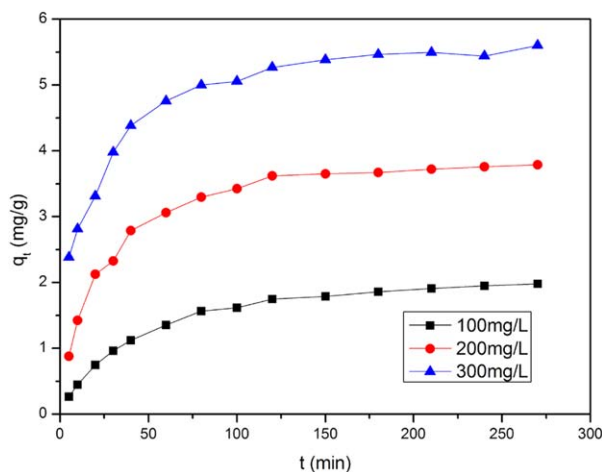


Figure 10. Effect of the contact time on the q_e values of different concentrations of CV on Ch-GO/PUF-5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pollutant is removed from aqueous solutions and provide valuable information for understanding the mechanism of adsorption reactions.²⁸ Figure 10 represents the adsorption capacity versus the contact time for various initial concentrations (100, 200, and 300 mg/L) of the CV dye. As shown in Figure 10, a fast adsorption capacity was obtained during the first 100 min of contact between the two phases, and the equilibrium was attained in about 180 min. The adsorption capacity was higher in the beginning because of the large surface area of the adsorbents available for the adsorption of the dye. An increase in the initial dye concentration led to an increase in the adsorption capacity of the CV dye on Ch-GO/PUF-5 because of the increase in the driving force of the concentration gradient. q_e increased from 1.9794 to 5.5442 mg/g with an increase in the initial dye concentration from 100 to 300 mg/L.

The adsorption kinetics describe the adsorption efficiency of an adsorbent with the contact time; this is one of the significant features that represent the adsorption procedure. In this study, one adsorption kinetics model of pseudo-second-order equations was investigated. The rate equation for the pseudo-second-order model is given by eq. (3):

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

where k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), whose value was obtained from the plots of t/q_t versus

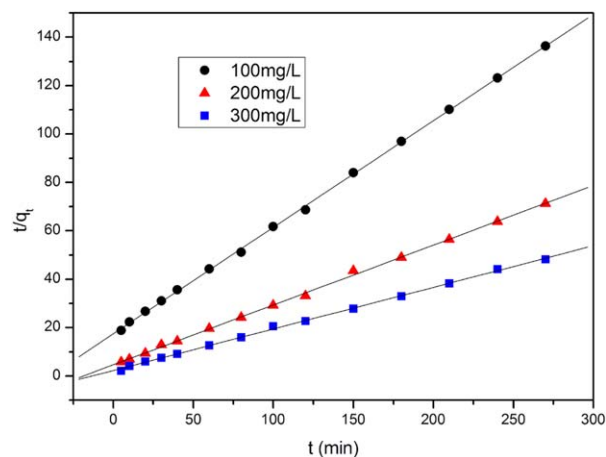


Figure 11. Linear fit of the pseudo-second-order equation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

t , and q_e (mg/g) and q_t (mg/g) are the adsorption capacities at equilibrium and at time t (min), respectively. The initial rate of adsorption (h) is

$$h = k_2 q_e^2 \quad (4)$$

The plots of the pseudo-second-order model, which can determine k_2 and h , are shown in Figure 11, and the basic values are listed in Table I. As shown in Figure 11, an increase in the initial CV concentration led to an increase in the adsorption capacity. The fitted pseudo-second-order curve fit well in the whole process of adsorption and predicted q_e accurately. When we examined the values of the coefficient of determination (R^2), we observed the values of R^2 at different concentrations were all above 0.99. We assumed that the adsorption efficiency was controlled by a chemical process. As the initial CV concentration was varied from 100 to 300 mg/L, the value of h increased from 0.05562 to 0.40778 ($\text{mg g}^{-1} \text{min}^{-1}$). The pseudo-second-order kinetic model indicated that these chemisorptions systems involved vacancy forces through the sharing or exchange of electrons between the sorbent and solute.²⁹ The process optimization modeling suggested optimum values of different independent process variables as follows: initial dye concentration = 300 mg/L, temperature = 35°C, initial solution pH = 8, and adsorbent dose = 50 mg/mL. This allowed us to achieve a maximum adsorption (5.9038 mg/g) of the CV dye. The corresponding experimental value of the dye adsorption under the optimum condition of the variables was determined as 5.5442 mg/g; this was very close to the optimized value.

Table I. Kinetic Parameters for CV Dye Adsorption onto the Ch-GO/PUF-5 Foam Material

C_o (mg/L)	$q_{e, \text{exp}}$ (mg/g)	h (mg g/min)	Pseudo-second-order equation:		
			$Q_{e, \text{cal}}$ (mg/g)	k_2 ($\text{g mg}^{-1}/\text{min}$)	R^2
100	1.9794	0.05562	2.28	0.0107	0.9996
200	3.8342	0.2246	4.0938	0.0134	0.9992
300	5.5442	0.4078	5.9038	0.0117	0.9989

$q_{e, \text{exp}}$, $q_{e, \text{experiment}}$; $Q_{e, \text{cal}}$; $Q_{e, \text{calculation}}$.

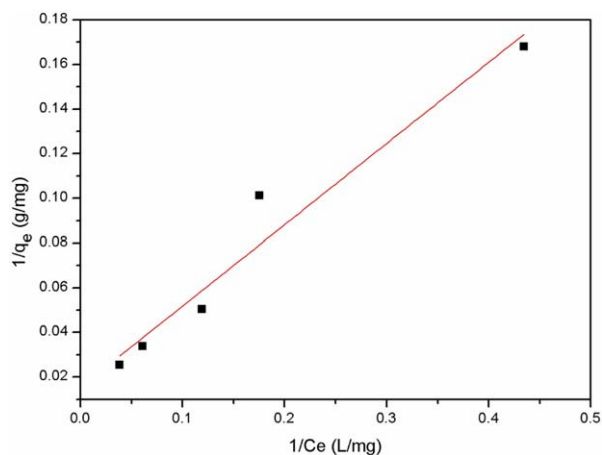


Figure 12. Langmuir isotherm plot for the CV adsorption by the Ch-GO/PUF-5 material. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Adsorption Isotherm Study

To study the adsorption performance of the Ch-GO/PUF-5 material, the Langmuir and Freundlich isotherm adsorption models were used to analyze the experimental data. The Langmuir isotherm assumed that adsorption occurred at specific homogeneous sites, whereas the Freundlich isotherm was based on the assumption of a heterogeneous surface with a nonuniform distribution of heat of sorption over the surface. We conducted the isotherm study of CV at different concentrations by keeping the temperature fixed at 35°C. The Langmuir and Freundlich adsorption models can be expressed by eqs. (5) and (6), respectively:

$$\frac{1}{q_e} = \frac{1}{C_e K_L q_m} + \frac{1}{q_m} \quad (5)$$

$$\ln q_e = \frac{\ln C_e}{n} + \ln K_f \quad (6)$$

where q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), and K_f and n are Freundlich constants characteristic of the system that indicated the

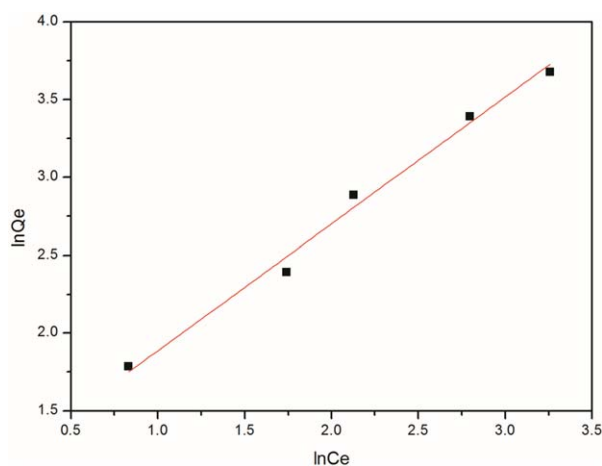


Figure 13. Freundlich isotherm plot for the CV adsorption by the Ch-GO/PUF-5 material. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Adsorption Isotherms Parameters for CV Dye Adsorption onto the Ch-GO/PUF-5 Foam Material

Langmuir equation				Freundlich equation		
q_m (mg/g)	K_L (L/mg)	R_L	R^2	K_f (mg/g)	$1/n$	R^2
64.935	0.0423	0.190	0.942	2.919	0.81547	0.958

adsorption capacity and adsorption intensity, respectively. In addition, the essential characteristics of the Langmuir isotherm could be expressed in terms of either a dimensionless constant separation factor or by an equilibrium parameter (R_L) as in eq. (7):

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

where C_0 is the highest dye concentration (mg/L). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

Figure 12 shows the plot of $1/q_e$ against $1/C_e$ for the testing of the Langmuir isotherm. Similarly, the Freundlich isotherm was tested by the plotting of $\ln q_e$ versus $\ln C_e$ as shown in Figure 13. The constant values calculated from the linearity of the two isotherms are listed in Table II. As shown in Table II, two R^2 values (0.942 vs 0.958) were very close. However, the slope $1/n$, which ranged between 0 and 1, is a measure of the adsorption intensity or surface heterogeneity and became more heterogeneous as its value got closer to zero.²⁸ A value for $1/n$ below 1 indicates a normal Langmuir isotherm, whereas a value of $1/n$ of above 1 is indicative of cooperative adsorption. The value of R_L was found to be 0.190, and it confirmed that the Ch-GO/PUF-5 was favorable for the adsorption of CV dye under the conditions used in this study. The equilibrium data for CV adsorption fit the Langmuir equation, with a maximum monolayer adsorption capacity of 64.935 mg/g; this was bigger than

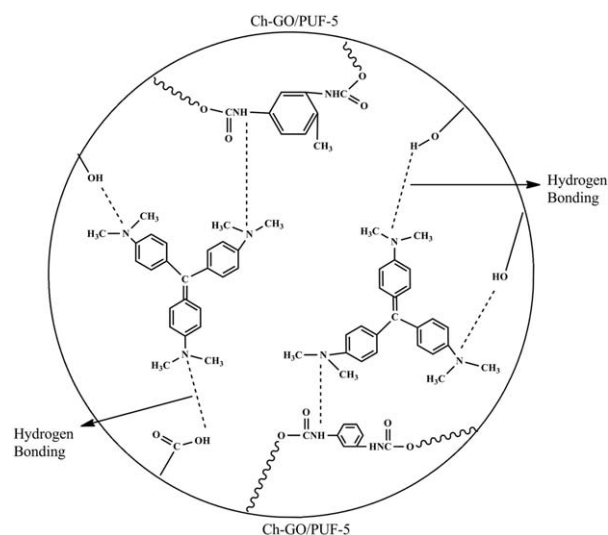


Figure 14. Proposed mechanism for the adsorption of CV onto the Ch-GO/PUF-5 material.

Table III. Thermodynamic Parameters for the Adsorption of the CV Dye

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(mol·K))
293	-3.45	71.77	256.74
303	-6.02		
308	-7.31		
313	-8.59		
318	-9.87		

$q_m = 9.112$ mg/g of the PUF material. This indicated that the addition of Ch-GO into PUF was successful.

There are many factors that may influence adsorption behavior; these include the dye structure and size, adsorbent surface properties, hydrogen bonding, van der Waal's forces, and electrostatic force. CV is a cationic dye having amine groups in its structure. The complexation between CV and Ch-GO/PUF-5 can take place through the strong and weak forces. Weak interactions occur because of van der Waal's forces, whereas strong interactions occur because of hydrogen-bonding interactions between the nitrogen-containing amine groups of CV and the Ch-GO/PUF-5 surface.²⁷ A proposed mechanism for the adsorption of CV onto the Ch-GO/PUF-5 material is shown in Figure 14.

Adsorption Thermodynamics

The thermodynamic parameters, including changes in the free energy (ΔG ; kJ/mol), enthalpy (ΔH ; kJ/mol), and entropy (ΔS ; J mol⁻¹·K⁻¹), were calculated by the reaction process and can be calculated by the following equations:

$$\Delta G^\circ = -RT \ln K_p \quad (8)$$

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

where K_p is the equilibrium constant at time T , R is the universal gas constant [8.314 J (mol/K)], T is the absolute temperature

Table IV. Comparison with Other Adsorbents for the Adsorption Behavior of CV from the Aqueous Solution

Sorbent	Temperature (°C)	Maximum sorption capacity (mg/g)	Reference
MWCNTs/Mn _{0.8} Zn _{0.2} Fe ₂ O ₄	40	5.23	30
AgNP-soil nanocomposite	37	1.918	31
Turkish coffee residue	30	25.0	32
Coir pith	27	24.75	33
Jackfruit leaf powder	40	37.43	34
NaOH-modified rice husk	30	41.035	35
ASRM	25	60.5	36
Ch-GO/PUF	35	64.935	This study

ASRM, acid-activated sintering process red mud; AgNP, silver nanoparticles; MWCNTs, multi-walled carbon nanotubes.

(K), ΔG° is standard Gibbs free energy change (KJ /mol), ΔS° is entropy change (J/(mol·K)), and ΔH° is enthalpy change (KJ /mol).

A linear fitting with the equation $\ln K_p = -8632.96/T + 30.8808$ ($R^2 = 0.86$) was obtained in this experiment. The values of ΔS° and ΔH° were calculated from the intercept and slope, respectively. The values are listed in Table III. The negative values of ΔG° certified the feasibility and spontaneous nature of the adsorption process. The listed data show that the free energy decreased with increasing temperature. Hence, the phenomenon indicated a higher adsorption at a higher temperature. The positive values of ΔS° demonstrated increased randomness at the solid/liquid interface.

Comparison with Other Adsorbents for the Adsorption Behavior of CV from Aqueous Solution

Comparisons of the adsorption efficiency (q_m) of other adsorbents for the adsorption behavior of CV from aqueous solution are given in Table IV.³⁰⁻³⁶ From the results, we observed that the adsorption efficiency and time were preferable and superior to those in the literature. This showed the perfect removal activity of the foam material and satisfactory performance for the removal of CV.

CONCLUSIONS

Ch-GO-modified PUF material was used as an effective adsorbent for the removal of CV from wastewater. The obtained results show that the optimal conditions were a Ch-GO content of 5%, a pH of 8, a Ch-GO/PUF dosage of 50 mg/mL, and a temperature of 35°C. Kinetic studies suggested that the adsorption process followed pseudo-second-order kinetics; this indicated the main adsorption mechanism of chemical adsorption. The better R^2 showed that the system could be conveniently modeled by the Freundlich model. A negative ΔG° at ambient temperature and a positive ΔH° showed that the adsorption process was spontaneous and endothermic. The obtained results indicate that the prepared adsorbent has potential application for the treatment of polluted water containing CV dye.

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