

## Preparation of Graphite Oxide/Polyurethane Foam Material and Its Removal Application of Malachite Green from Aqueous Solution

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**ABSTRACT:** Synthetic dyes are commonly used in textile, paper, leather, food, plastic and cosmetic industries. In this study, a series of novel graphite oxide/polyurethane (GO/PU) polymeric foam materials were prepared by foaming technique. The GO/PU was applied to remove malachite green (MG) from aqueous solution. When static adsorption experiment was carried out with a GO content of 3.0%, a GO/PU dosage of 40 mg/mL, a temperature of 50°C, and a time of 3 h, the highest adsorption efficiency can reach 99.7%. The kinetics, equilibrium and thermodynamics of MG adsorption onto GO/PU polymeric foam material were investigated. The results indicated that adsorption behavior was found to follow closely the pseudo-second order kinetics, equilibrium data were well fitted by Langmuir adsorption model and the adsorption process was spontaneous and endothermic. Prepared GO/PU foam material has potential application for the wastewater treatment containing MG dye. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40988.

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### INTRODUCTION

Many dyes are used widely in industrial products of up to date technology, for example, in various branches of the textile industry and the leather tanning industry, in production of paper, in food technology, in agricultural research, in light-harvesting arrays, and in hair colorings.<sup>1</sup> What's more, the growth of the worldwide textile industry in a period of time since then had seen a proportionately increase in taking advantage of such synthetic dyes, and this has brought about a rising pollution due to untreated dyestuff wastewater. Most commercial dyes are chemically stable and are difficult to be biodegraded in wastewater because the synthetic dyes have a complex molecular structure.<sup>2,3</sup>

Malachite green (MG) (Figure 1) is a cationic triphenylmethane dye, which is used in several industries such as cotton, food, paper, leather, pulp, textile, tannery, plastic, wool etc., for coloring their final products.<sup>4–6</sup> The effluents of these industries containing a huge amount of dyes, discharged into water bodies, cause severe damage to the environment. Owing to its carcinogenic properties, MG also has an adverse effect on the immune and reproductive systems. Recent studies suggest that MG and especially its reduced form, leucomalachite green (a metabolite), might be retained in aquatic organisms, such as fish muscle and fat, consumption of these organisms leading to toxicity of human beings for extended periods of time.<sup>7</sup> Therefore, the removal of toxic dye MG from effluents is necessary before it is

released into aquatic environment. Various attempts have been made for the removal of MG from the wastewater, including photo-degradation,<sup>8,9</sup> photocatalytic degradation<sup>10–12</sup> and adsorption.<sup>13,14</sup> Because of its ease of operation, simplicity of design, low cost, smaller amounts of harmful substances and insensitivity to toxic pollutants, adsorption has been considered as an attractive method to remove dye from aqueous solutions.

Graphite oxide (GO), quasi two-dimensional carbonaceous sheets, possesses a large number of hydrophilic oxygenated functional groups including hydroxyl, epoxy, carbonyl and carboxyl groups which are attached to carbons or at the edges of the layer.<sup>15</sup> These characteristic structures make GO interact strongly with organic molecules, via non-covalent forces, such as hydrogen bonding,  $\pi$ - $\pi$  stacking, van der Waals forces, and hydrophilic interactions which can dramatically improve their miscibility with polymer matrix. It has played a greater role in the application of solar cells, electronic devices, batteries, sensors, super capacitors, hydrogen storage,<sup>16–18</sup> and catalysis.<sup>19,20</sup> Moreover, its nanoscale structures also endow them some advantages such as rapid equilibrium rates, high adsorption capacity, and effectiveness over a broad pH range and readily disperse in aqueous medium to form a stable suspension. As a result, GO should have the capacity to adsorption dyes in wastewater. Bradder et al.<sup>21</sup> reported the removal of methylene blue and malachite green from aqueous solution by GO. They found that the amount of dyes adsorbed on the GO was much

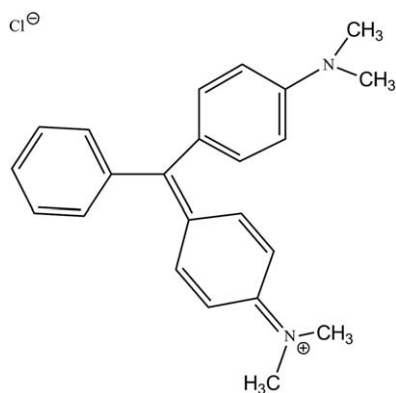


Figure 1. The structure of MG.

higher than that of graphite, and the adsorption capacity based on the Langmuir isotherm is much higher than activated carbon. However, the above carbonaceous GO adsorbents suffered from separation inconvenience. On account of the extremely easy separation, flexible foam PU polymers have been widely used in environmental remediation.<sup>22</sup> It was believed those polymeric foam materials, exhibiting high porosity, lightweight, large adsorption capacity and easy separation properties would have better performances in water purification.

The novelty of the current work is the preparation of new polymeric GO/PU material by foaming technique. The prepared material was used for the removal of the MG from aqueous solution. After preparation, the characterization with various techniques [scanning electron microscope (SEM), FTIR, thermogravimetric analysis (TGA) and DSC] was performed. The adsorption properties of the foam material towards MG were studied using equilibrium, kinetic and thermodynamics. As far as we know, MG dye adsorption application of GO/PU foam material rarely finds mention in reported literatures.

## EXPERIMENTAL

### Materials

Isophorone diisocyanate (IPDI, purity  $\geq 99.5\%$  and  $-\text{NCO}$  content  $\geq 37.5\%$ ) was supplied by Rongrong Chemical Co., in Shanghai, China. Polyether polyol (NJ-330,  $M = 3000$  g/mol) was obtained from Ningwu Chemical Co., in Jurong, Jiangsu, China. Graphite powder, concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), sodium nitrate ( $\text{NaNO}_3$ ), hydrogen peroxide solution ( $\text{H}_2\text{O}_2$ , 30%), MG, potassium permanganate ( $\text{KMnO}_4$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ) as a blowing agent, dibutyltin dilaurate (DBLT) as catalyst, and silicone oil ( $[\text{-Si}(\text{CH}_3)_2\text{O-}]_n$ ) as a foam stabilizer<sup>23</sup> were achieved from Sinopharm Chemical Reagent Co., in Shanghai, China.

### Synthesis of GO

GO was carried out through modified Hummers method.<sup>24</sup> Commercial graphite powder (1.0 g) and sodium nitrate (0.5 g) were stirred in concentrated sulfuric acid (23 mL,  $0^\circ\text{C}$ ). Afterwards, potassium permanganate (3.0 g) was gradually added to the suspension. The control of the add speed was to prevent the rapid rise in the temperature of the suspension (lower than  $20^\circ\text{C}$ ). The suspension was stirred for 1 h, and then maintained at  $35^\circ\text{C}$  for 2 h. Distilled water (46 mL) was slowly dropped

into the reaction bulb, keeping the temperature at  $98^\circ\text{C}$ . The diluted suspension was continued to stir for 30 min. After that it was further diluted with 140 mL of distilled water and then 10 mL of 30% hydrogen peroxide was added for the purpose of removing the residual  $\text{KMnO}_4$  and  $\text{MnO}_2$  to change the color into luminous yellow. The mixture was left for 1 or 2 h. Then, the suspension was separated by centrifuge and washed with 5% HCl aqueous solution of normal temperature and deionized water, respectively, until no sulfates were detected and the pH of the filtrate was 7. The sample of GO was dried under vacuum at  $60^\circ\text{C}$  to a constant weight, and then ground to an ideal particle size.

### Preparation of GO/PU Foam Material

GO/PU foam materials were prepared in three stages. (1) A calculated amount mixture of the polyether polyol (NJ-330), GO, sodium bicarbonate (1.0 g) as foaming agent, silicon oil (0.65 g) as stabilizer and DBLT (0.0876 g) as catalyst in the reaction, were stirred at the revolving speed of 2000 rpm for 5 min. (2) A certain amount of IPDI was added to the mixture, stirring for 20 s at the speed of 2000 rpm until the foam began to grow up. (3) The mixture was heated to  $100^\circ\text{C}$  and maintained 3 h in the oven, where the material expanded. After foaming development, the block was demolded. The synthetic route of GO/PU foam material is shown in Figure 2. Changing the content of GO, a series of GO/PU foam materials were obtained with different GO content of 1.0–8.0 wt %. The display of basic recipe is in Table I.

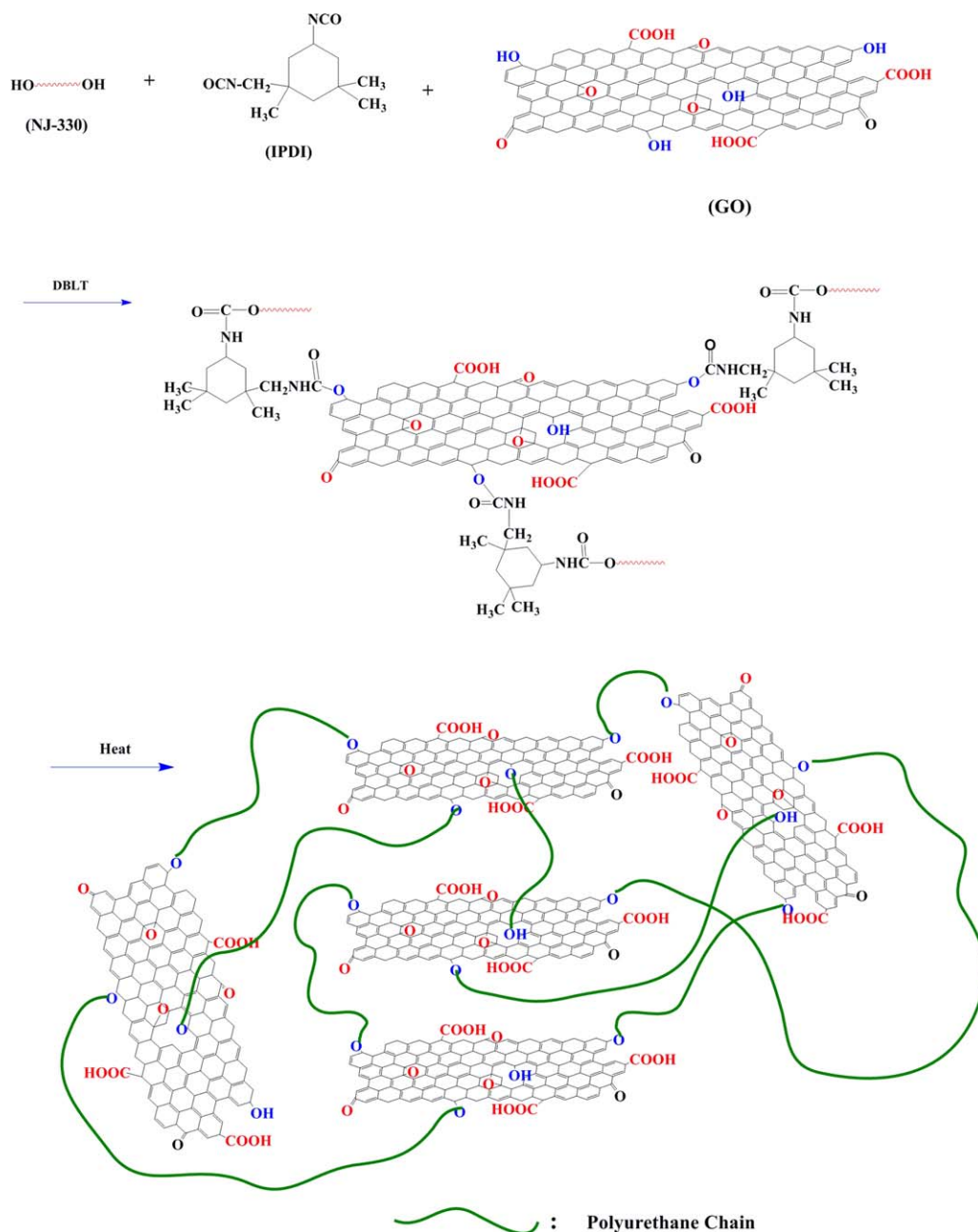
### Characterizations

FTIR spectroscopy was used to obtain information about GO/PU sample. FTIR spectra were recorded in the range  $4000\text{--}500$   $\text{cm}^{-1}$  with a Madison-Nicolet spectrometer (AVATAR 360). A minimum of 32 scans was signal-averaged with a resolution of  $2$   $\text{cm}^{-1}$  in above ranges. The fracture surface of the sample was investigated using a Hitachi S-4800 with an accelerating voltage of 15-kV with SEM. TGA and differential scanning calorimetry (DSC) were performed on a Netzsch (Germany) STA 449C instrument with an air flow of 50 mL/min. The programmed heating range was from room temperature to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere. The measurement was taken with 6–10 mg samples.

### Dye Adsorption Experiments

To evaluate the adsorption capability of the GO/PU, the MG dye was selected as the model dye. The process of MG adsorption application was briefly described as follows. The experiments were carried out by putting a certain weight of foam material into 10 mL of 100 mg/mL MG aqueous solution. At a specified time interval, the foam material was taken out. The solution was measured by UV-visible spectrophotometrically method at the  $\lambda_{\text{max}} = 618$  nm. The effects of experimental parameters such as the GO content, the dosage of foam material, contact time and temperature were studied to obtain the best adsorption conditions.

The amount of adsorbed MG dye on GO/PU foam material (mg/g) was calculated by the following eq. (1):



**Figure 2.** The synthetic route of GO/PU foam material. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$$Q_t = \frac{(C_o - C_t)}{W} V \quad (1)$$

where  $Q_t$  is the amount of adsorbed MG dye by the foam material (mg/g);  $C_o$  is the initial concentration of the MG dye solution and  $C_t$  is the concentration of the MG dye solution at time  $t$  (mg/L);  $W$  is the mass of foam material (g);  $V$  is the volume of the MG dye solution (L).

#### Desorption and Regeneration

After the adsorption experiments, samples which adsorbed the MG were left in the beaker with 1.0 mol/L HCl for 60 min at room temperature. Then, get out the sorbent and dry. To obtain

the reusability of the GO/PU materials, the cycles were repeated three times under the same adsorption conditions.

## RESULTS AND DISCUSSION

### FTIR Characterization

The FTIR spectra of GO, PU and GO/PU-3 are shown in Figure 3. As can be seen from the spectrum of GO, a strong and broad absorption peak is located at  $3410 \text{ cm}^{-1}$  which is assigned to the stretching vibrations of  $\text{-OH}$  groups. These  $\text{-OH}$  groups presented in GO can react with  $\text{-NCO}$  of IPDI and form hydrogen bonds with dye molecules. The  $\text{-OH}$  bending mode of the adsorbed water molecules on the surface can be observed

**Table I.** The Basic Recipe of the Foam Material

Sample	GO (%)	NJ-330 (g)	IPDI (g)	GO (g)
PU	0	10	2.22	0
GO/PU-1	1	10	2.22	0.12
GO/PU-2	2	10	2.22	0.24
GO/PU-3	3	10	2.22	0.37
GO/PU-4	4	10	2.22	0.49
GO/PU-5	5	10	2.22	0.61
GO/PU-6	6	10	2.22	0.73
GO/PU-7	7	10	2.22	0.86
GO/PU-8	8	10	2.22	0.98
GO/PU-10	10	10	2.22	1.22
GO/PU-12	12	10	2.22	1.47

at the bond at  $1657\text{ cm}^{-1}$ . From the spectra of GO/PU and PU foam materials, the peaks at the range of  $3000\text{--}2800\text{ cm}^{-1}$  are the stretching vibrations of carbon–hydrogen bonds in  $-\text{CH}_2$  and  $-\text{CH}_3$ . Moreover, absorbance peaks at  $1220\text{ cm}^{-1}$  for phenolic groups ( $\text{C}-\text{OH}$ ),  $1385\text{ cm}^{-1}$  for carboxyl and  $1729\text{ cm}^{-1}$  for  $\text{C}=\text{O}$  are observed. In GO/PU material, the peaks also exist, indicating that the GO is grafted in the PU molecule. Peaks at  $1376$  and  $1458\text{ cm}^{-1}$ , may be bending vibrations of methylene and methyl groups, respectively. The absorption peaks of the ester stretching vibration exist at  $1700\text{--}1720\text{ cm}^{-1}$ , demonstrating the existence of  $-\text{OCON}-$  group. The peak at  $2270\text{ cm}^{-1}$  disappears, which corresponded to  $-\text{NCO}$  group in FTIR spectra of GO/PU and PU foam materials, proving the completed polymerization.

### SEM Analysis

SEM images of GO (a), pure PU foam material (b), and the prepared GO/PU foam material (c) are shown in Figure 4. As can be seen from Figure 4(a), the uneven wrinkled layer structure is observed. And from Figure 4(b), open and closes pores make up the internal structures, the latter accounting for the more share. A large quantity of air was generated by the structures formed during the foaming process, which leads to a rising passive insulation. However, due to the violent foaming reaction, some of them are likely to collapse. The edge struts are much thicker compared with the porous walls. The structure exhibits an anisotropic geometry. It can be seen from Figure 4(c) that there is no layered GO, which shows that the prepared GO dispersed well in PU. Moreover, the GO/PU foam material has more open pores and the pores are interconnected; and the average porous diameter of GO/PU foam material reaches about  $0.136\text{ mm}$ .

### TG-DSC Analysis

To examine thermal property of foam material, PU and GO/PU-3 were chosen to carry out DSC and TGA experiments with the heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen air on NETZSCH STA449C. The results are shown in Figure 5. As can be seen from Figure 5, the glass transition temperatures ( $T_g$ ) of PU and GO/PU-3 are  $131$  and  $166^\circ\text{C}$ , respectively. Meanwhile, it can be seen that the decomposition temperatures ( $T_d$ ) at 5% mass loss

of PU and GO/PU-3 are  $147.6$  and  $250.3^\circ\text{C}$ , respectively. The results show that GO/PU-3 foam material has better thermal property than PU.<sup>25</sup> According to the mechanism proposed by Duquesne,<sup>26</sup> the initial decomposition temperature is higher after adding GO and exhibits excellent heat resistance.

### Dye Adsorption Application

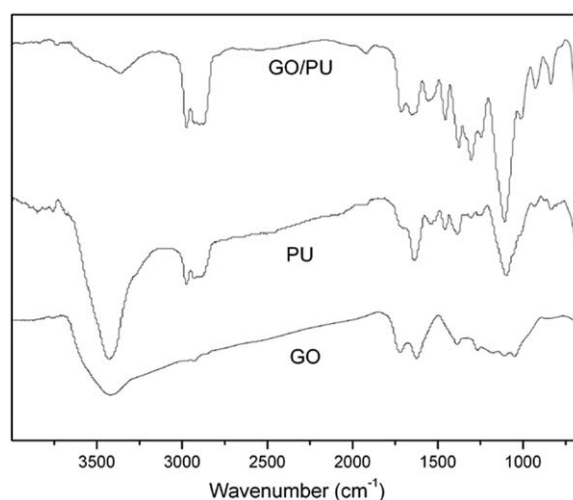
This study aims at establishing the best ideal conditions for the maximum extraction of MG by GO/PU foam and to characterize the adsorption process. In order to achieve this goal, the effects of GO content (a), dosage of foam material (b), temperature (c) and time (d) on the adsorption capacity of MG dye solution were investigated. The obtained results are shown in Figure 6.

### Effect of the GO Content on the Adsorption Capacity of MG

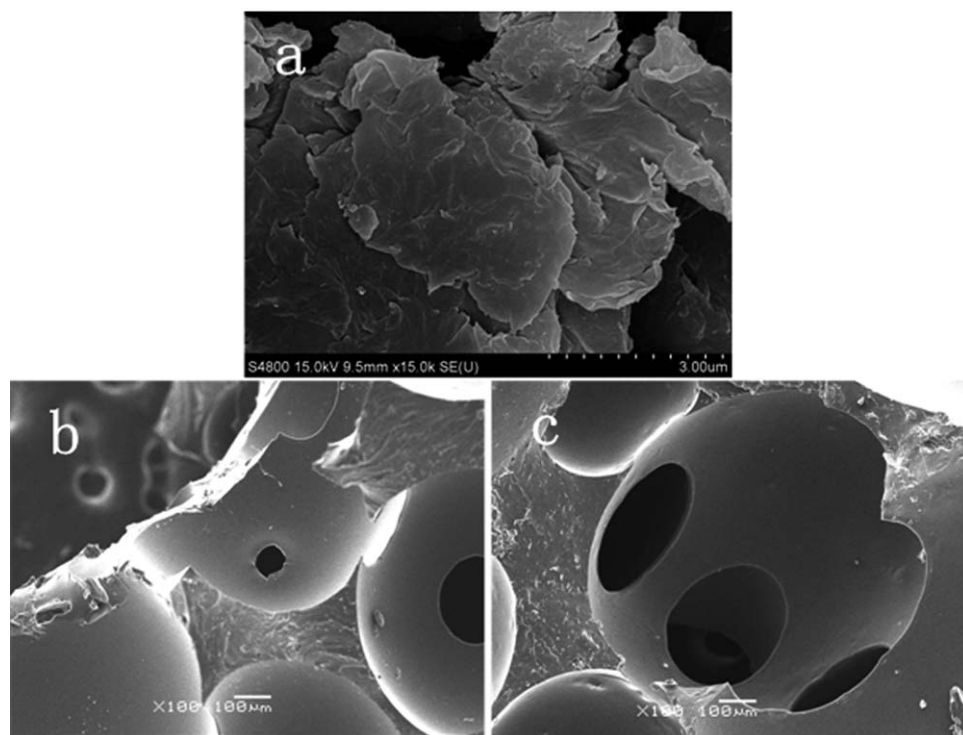
**Dye Solution.** Fixed a dosage of  $50\text{ mg/mL}$  foam material, a time of  $15\text{ h}$  and a temperature of  $28^\circ\text{C}$ , a series of GO/PU foam materials containing different GO content were prepared. The effects of GO content on the adsorption capacity of MG dye solution are shown in Figure 6(a). As can be seen from Figure 6(a), the adsorption capacities of all GO/PU foam materials are bigger than that of pure PU foam material. Besides, the adsorption capacity of GO is about  $2.16\text{ mg/g}$ , which is lower than those of most GO/PU adsorbents. This is mainly because the foam material has a larger surface area, and GO has quasi two-dimensional carbonaceous sheets. In addition, there are permanent negative charges on the surface of GO, which enable to enhance the adsorptive properties of GO/PU materials to form ionic-pair with the cationic dye. With the content of GO increasing, the adsorption capacity increases. The relatively higher adsorption capacity ( $2.44\text{ mg/g}$ ) is reached when the mass proportion of GO is  $3.0\text{ wt } \%$ . Furthermore, the adsorption efficiency of MG dye solution increases little with the content of GO further increasing to  $12\text{ wt } \%$ . Thus, the foam material GO/PU-3 (the mass content of GO of  $3.0\text{ wt } \%$ ) was chosen for further experiments.

### Effect of the Dosage of Foam Material on the Adsorption Capacity of MG Dye Solution.

Fixed a time of  $10\text{ h}$  and a temperature of  $28^\circ\text{C}$ , MG dye adsorption onto GO/PU-3 was

**Figure 3.** FTIR spectra of GO, PU and GO/PU-3.



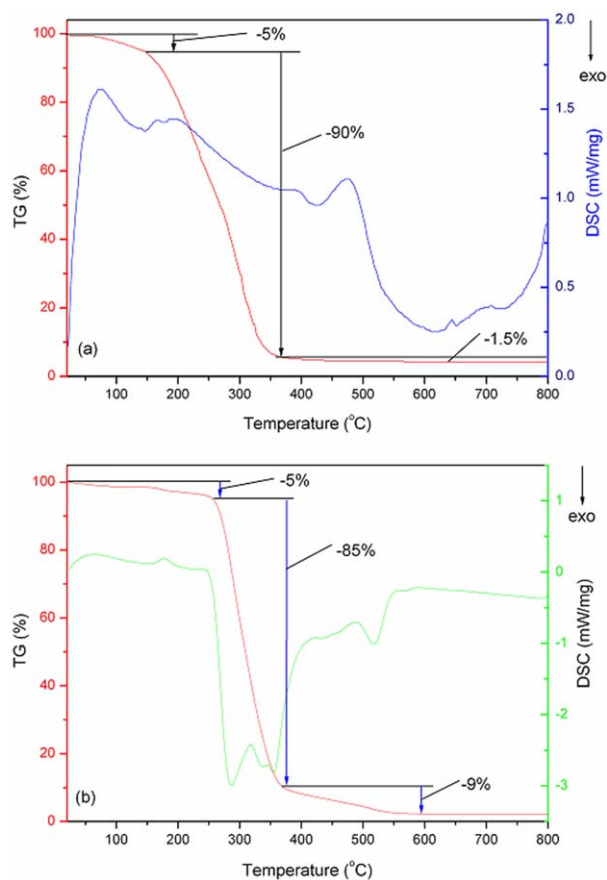


**Figure 4.** SEM images of GO (a), PU (b) and GO/PU-3 (c).

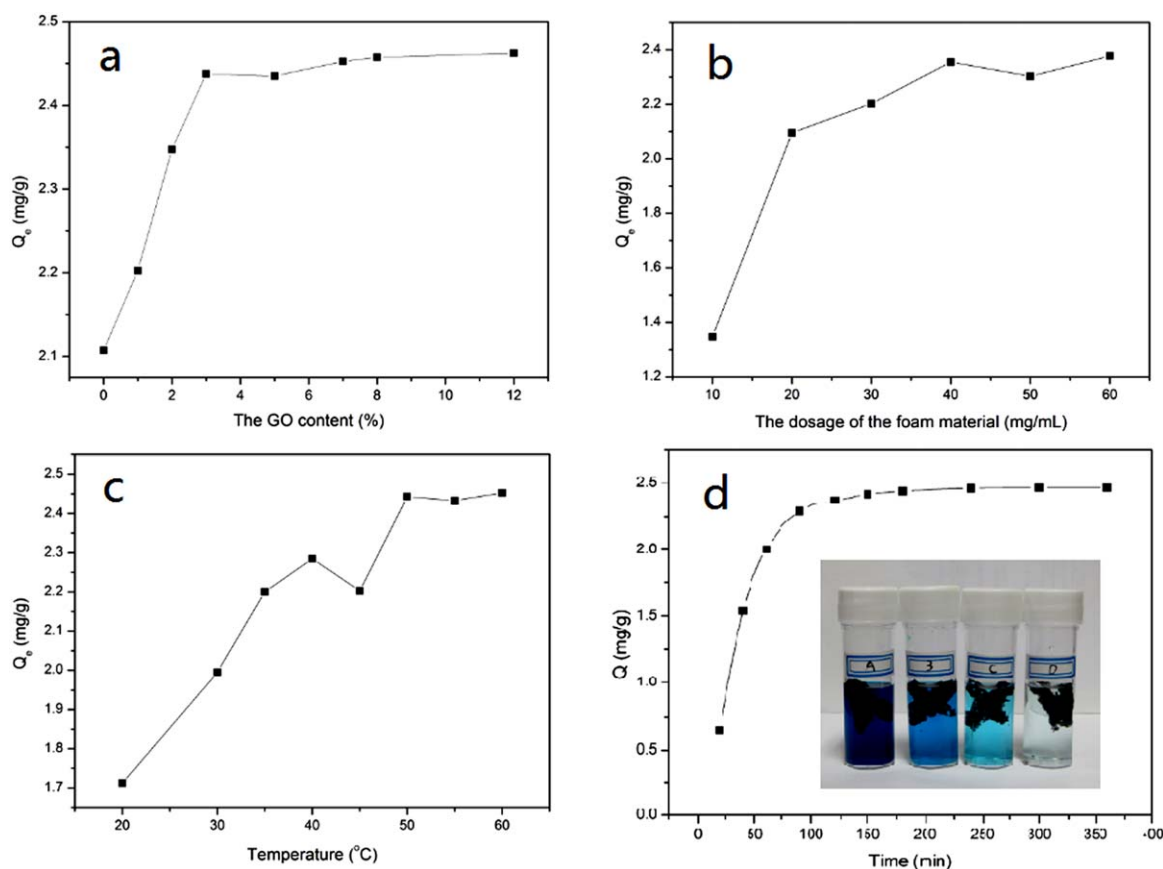
studied by changing the amount of adsorbent and the results are shown in Figure 6(b). From Figure 6(b), it shows that the increasing dosage resulted in an increase of the adsorption capacity. The more adsorption capacity is attributed to the higher surface area of adsorbent and the more GO which can provide oxygen-containing functional groups, including hydroxyls and carboxylic groups, to adsorb MG via hydrogen bonding.<sup>27–29</sup> As shown in Figure 6(b), the MG adsorption capacity exhibits a high value at the dosage of 40 mg/mL. With more dosage of foam material, adsorption shows an unchanged trend, which can be ascribed to the slower mass transfer between adsorbate and the solid. Therefore, 40 mg/mL was determined to be the optimum dosage in this experiment.

**Effect of the Temperature on the Adsorption Capacity of MG Dye Solution.** The adsorption temperature has a significant effect in wastewater treatment systems. The effect of temperature on the adsorption capacity of MG dye solution at a fixed dosage of 40 mg/mL and a time of 15 h is shown in Figure 6(c). It can be seen that when the temperature increases to 50°C, the adsorption capacity of dye improves. For this reason, the procedure is endothermic, showing that there may be several interactions between the dye and the GO/PU-3, such as Van der Waals forces, ion–dipole interactions, and even chemical bonding.<sup>30</sup> At last, the adsorption capacity changes little. In this study, 50°C was chosen for the best temperature.

**Effect of Contact Time on the Adsorption Capacity of MG Dye Solution.** In this study, Figure 6(d) shows the effect of the contact time on the adsorption of MG onto adsorbent at a fixed dosage of 40 mg/mL and a temperature of 50°C. As can be seen from Figure 6(d), the adsorption capacity increases rapidly with



**Figure 5.** DSC and TGA curves of the PU (a) and GO/PU-3 (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** The effects of GO content (a), dosage of foam material (b), temperature (c) and time (d) on the adsorption capacity of MG dye solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

time prolonging at initial adsorption stage; then it increases slowly and finally reaches the equilibrium. The changes of color also can be seen from Figure 6(d) (A is the initial time, B is the time of 60 min, C is the time of 90 min and D is at the equilibrium). The initial stage indicates the rapid attachment of MG molecules to the external surface of the GO/PU because the adsorption sites of the GO/PU are void. The second stage is mainly because of the diffusion of solute molecules into pores of the adsorbent or other surface reactions.<sup>30</sup> When the time is more than 3 h, the final equilibrium stage is reached. MG diffusion is very slow because of its lower remained concentration. The experimental result implies that reaching adsorption equilibrium is within 3 h. As a result, 3 h was selected as the optimum contact time.

### Adsorption Kinetics

Adsorption kinetic study is necessary to determine the uptake rate of foam material and control the residual time of the whole adsorption process. Adsorption kinetics can also provide important information about the mechanism of dye adsorption at the solid-phase interface.<sup>31</sup> The adsorption kinetics curve of MG dyes onto GO/PU foam material at the optimal conditions is the same as Figure 6(d).

The pseudo-second-order kinetic equation is widely used to express the kinetic adsorption process because it always provides

a more appropriate description. It can be modeled using eq. (2):

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (2)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant. The theory data and the calculated fitting parameters by the nonlinear equations are listed in Table II.

As can be seen from Table II, the experimental data of adsorption of MG were well fitted to the pseudo-second-order model as shown by the  $R^2 = 0.9986$  value. Therefore, it indicates that the whole range behavior is in agreement with an adsorption mechanism being the rate-controlling step. Meanwhile, the experimental  $Q_e$  value is more consistent with the  $Q_{\text{cal}}$  value calculated from the pseudo-second-order model. The obtained results indicate that the adsorption is well represented by pseudo-second-order kinetic model. The adsorption process was dominated by pseudo-second-order adsorption mechanism. It is

**Table II.** Kinetic Parameters for MG Dye Adsorption onto Foam Material

$Q_e$ (mg/g)	Pseudo-second-order equation		
	$K_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$Q_{\text{cal}}$ (mg/g)	$R^2$
2.49	0.02957	2.58	0.9992

**Table III.** Adsorption Isotherms Parameters for MG Dye Adsorption onto GO/PU Foam Material

Langmuir equation			Freundlich equation		
$Q_m$ (mg/g)	$b$ (L/mg)	$R^2$	$K_f$ (mg/g)	$n$	$R^2$
68.823	0.2241	0.9959	15.084	2.00	0.9919

assumed that the adsorption rate is controlled by the chemical process.

### Adsorption Isotherm

The adsorption of MG by GO/PU material was carried out at the optimum conditions and at the different initial concentrations. Two important isotherm equations, namely Langmuir and Freundlich isotherms, have been applied to the experimental results. When the initial concentrations increase, the amount of dye adsorbed increases. It is important to analyze the equilibrium data to evaluate adsorption properties of GO/PU adsorbent. The Langmuir takes the basic assumption that adsorption takes place at uniform energy sites within the adsorbent and the capacity of the adsorbent is finite. The linearized Langmuir isotherm equation can be expressed as follows:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e} \quad (3)$$

where  $C_e$  is the concentration of dyes in solution at equilibrium (mg/L),  $Q_e$  is the equilibrium adsorption capacity (mg/g),  $Q_m$  is the maximum adsorption capacity (mg/g), and  $b$  is the Langmuir affinity constant (L/mg). According to the equation, the maximum adsorption capacity of MG on GO/PU foam material is 68.823 mg/g.

While the Freundlich isotherm is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface. The equation is commonly represented by:

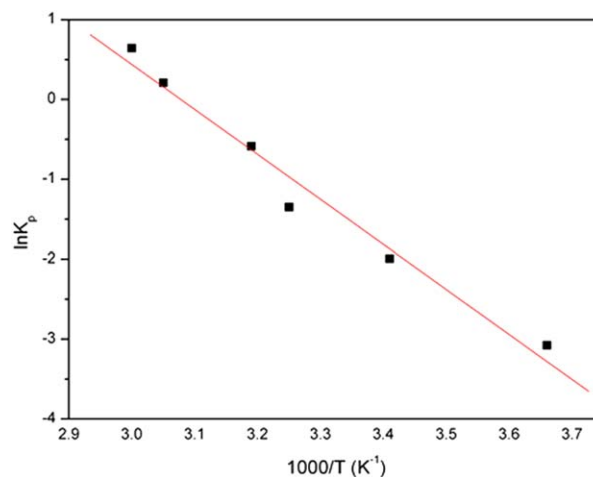
$$\log Q_e = \frac{1}{n} \log C_e + \log K_f \quad (4)$$

where  $K_f$  and  $n$  are the Freundlich constants characteristics of the system, respectively, indicating the adsorption capacity and the adsorption intensity.

Table III lists all calculated theory data and fitted parameters. As shown in Table III, the value of  $1/n$  was found to be less than 1 indicating that the adsorption is favorable. The Langmuir isotherm ( $R^2 = 0.9959$ ) matches experimental data better

**Table IV.** Thermodynamic Parameters for the Adsorption of MG Dye

$T$ (K)	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ ( $J^{-1} \text{mol} K^{-1}$ )
308	-8.157	46.79	178.40
313	-9.049		
318	-9.941		
323	-10.833		
328	-11.725		

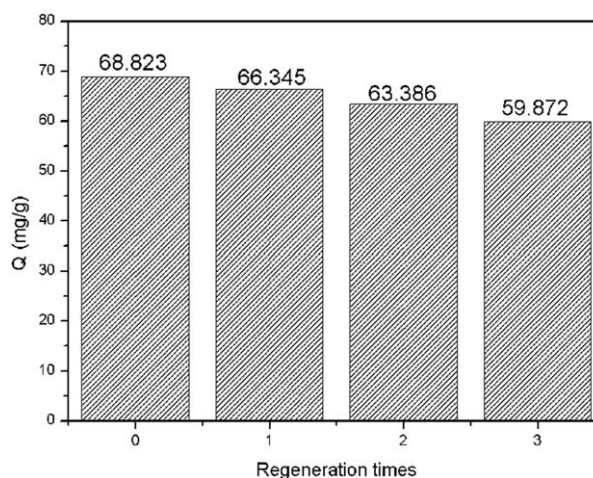


**Figure 7.** Van't Hoff plot for the adsorption of MG by GO/PU-3 material. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

in comparison with the Freundlich isotherm ( $R^2 = 0.9919$ ) for the adsorption of MG. The fact that Langmuir isotherm fits the experimental data quite well suggests the monolayer coverage of MG onto GO/PU surface. The high MG adsorption capacity of the GO/PU adsorbent can be well interpreted in terms of effective exposure of active GO adsorption sites. GO species were first grafted on PU via the reaction of hydroxyl groups with isocyanate groups of IPDI. Then, GO was evenly distributed in the PU, resulting in more adsorption sites than those in pure PU. Consequently, more active GO sites were accessible to MG adsorption.

### Thermodynamic Study

Under isothermal conditions in the temperature range of 20–60°C, the effect of temperature on the adsorption isotherm was investigated. The free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes are the thermodynamic parameters associated with the adsorption reaction. All these are calculated using eqs. (5) and (6) and the results are listed in Table IV.



**Figure 8.** The effect of recycle times of GO/PU-3 on the adsorption efficiency.

**Table V.** Comparison of Langmuir Adsorption Capacities of the Other Reported Different Adsorbents for the Removal of MG

Adsorbent	Adsorption capacity (mg/g)	References
Activated carbons commercial grade (ACC)	8.27	33
Arundo donax root carbon (ADRC)	9.10	34
Coconut coir activated carbon (CCAC)	29.92	35
Palm flower activated carbon (PFAC)	48.48	36
Organoclay (OC)	51.81	30
PU-attapulgite material (HATT/PU)	47.99	13
GO/PU-3	68.82	This study

$$\Delta G^{\circ} = -RT \ln K_p \quad (5)$$

$$\ln K_p = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (6)$$

where  $\Delta G^{\circ}$  is standard Gibbs free energy change (KJ/mol);  $K_p$  is the equilibrium constant at time  $T$ ;  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature (K).

The values of  $\Delta S^{\circ}$  and  $\Delta H^{\circ}$  are obtained from the interception and slope by respectively plotting  $\ln K_p$  against  $1/T$ . A linear fitting with an equation of  $\ln K_p = -5628.43/T + 21.45736$  ( $R^2 = 0.995$ ) is obtained in this experiment and the values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  calculated from Figure 7 are  $46.79 \text{ kJ/mol}$  and  $178.40 \text{ J mol}^{-1} \text{ K}^{-1}$ . Free energy changes ( $\Delta G^{\circ}$ ) were all negative, demonstrating that the studied adsorption was a spontaneous process. Further, the decrease in the values of  $\Delta G^{\circ}$  with the temperature increasing indicates the spontaneity of the process at higher temperatures. The endothermic nature is also confirmed by the positive values of enthalpy change ( $\Delta H^{\circ}$ ), while increased disorder at the solid-solution interface during the adsorption of MG is revealed by the positive value of  $\Delta S^{\circ}$ .<sup>32</sup>

#### Desorption Studies

When the process was repeated three times, the results were shown in Figure 8. As can be seen from Figure 8, the adsorption capacity changes from 68.823 to 59.872 (mg/g). The obtained results indicate that the prepared GO/PU foam materials have the ability of cycle and are stable for MG dye. Corresponding to three cycles of desorption-adsorption, the GO/PU-3 foam still has a higher level of adsorption capacity.

#### Comparison with Other Reported Different Adsorbents for Removal of MG

Some of other adsorbents with their respective Langmuir capacities for the removal of MG dye from aqueous solutions are given in Table V. As can be seen from Table V, the adsorption capacity of this work (68.823 mg/g) is higher than those of the reported results,<sup>33–36</sup> which indicates that the prepared GO/PU foam material is an ideal adsorbent and can be applied to adsorb MG dye from the untreated wastewater.

## CONCLUSION

In this work, a novel GO/PU foam material was developed. Adsorption process for the removal of MG dye has been carried out using GO/PU as adsorbents. The obtained results showed that the optimal conditions were: a GO content of 3.0%, a GO/PU dosage of 40 mg/mL, a temperature of 50°C, and a time of 3 h. At the optimum conditions, the capacity of foam material is 68.823 mg/g. Kinetic studies indicated that the adsorption reaction was found to follow closely the pseudo-second order kinetics, indicating the chemical adsorption mechanism. The obtained thermodynamic parameters suggest that the entire adsorption process is endothermic and spontaneous. From above results, it comes to a conclusion that the prepared GO/PU foam material can be applied to adsorb MG dye from the untreated wastewater.

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