

## Polyurethane–Attapulgite Porous Material: Preparation, Characterization, and Application for Dye Adsorption

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**ABSTRACT:** A series of polyurethane–attapulgite porous (HATT/PU) materials were prepared from polyether polyol (NJ-330), toluene diisocyanate (TDI), acid activated attapulgite (HATT), sodium bicarbonate as foaming agent, dibutylbis (lauroxy) tin (DBLT) as catalyst and silicon oil as stabilizer by foaming technique. The materials were characterized by FTIR, XRD and SEM. The polyurethane–attapulgite porous material as adsorbent was applied to malachite green (MG) dye wastewater treatment. Effects of attapulgite content, time, temperature, pH, and adsorbent dosage have been studied. The experimental results show that the maximum adsorption efficiency occurred at an attapulgite content of 6.0%, a time of 2.5 h, a temperature of 35°C, a pH >5 and a HATT/PU dosage of 40 mg/mL. Equilibrium isotherms for the adsorption of the dye have been measured experimentally. Results were analyzed by the Freundlich and Langmuir equation and the characteristics parameters for each adsorption isotherm were determined: Gibb's free energy ( $\Delta G^\circ$ ), change in enthalpy ( $\Delta H^\circ$ ) and change in entropy ( $\Delta S^\circ$ ) have been calculated. The results indicated that the adsorption process was spontaneously an endothermic reaction and kinetically proceeded according to the pseudo-second-order model. The experimental results suggest that the prepared polyurethane–attapulgite porous materials have potential application for the wastewater treatment containing MG dye. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1697–1706, 2013

**KEYWORDS:** dyes; pigments; polyurethanes; porous materials; adsorption; kinetics

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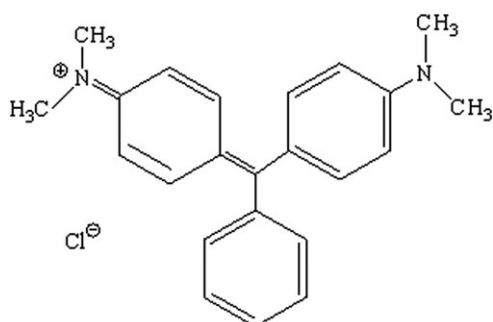
### INTRODUCTION

Dyes are synthetic organic compounds that are increasingly being produced and used as colorants in many industries worldwide, including textile, plastic, paper, etc.<sup>1,2</sup> Most of the dyes are toxic and carcinogenic compounds; they are also recalcitrant and thus stable in the receiving environment, posing a serious threat to human and environmental health.<sup>3</sup> Among these many types, cationic dyes, commonly known as basic dyes, are widely used in acrylic, nylon, silk, and wool dyeing.<sup>4</sup> Removal of dyes from water is very important because the water quality is greatly affected by color and even the presence of very small concentrations of dyes (less than 1 mg/L) in water is highly visible and is considered unpleasant.<sup>5</sup>

Malachite Green, 4-[(4-dimethylaminophenyl)-phenyl-methyl]-*N,N*-dimethyl-aniline is a cationic triphenylmethane dye with molecular formula  $C_{23}H_{25}ClN_2$  and molecular weight 364.92 (MG, Scheme 1). It is used in the aquaculture, commercial fish hatchery, and animal husbandry as an antifungal therapeutic agent, while for human it is used as antiseptic and fungicidal. However, its oral consumption is carcinogenic.<sup>6</sup> Scientific evidence indicated that MG and especially its reduced form, leuco-

malachite green (LMG) (a metabolite), might persist in edible aquatic organisms, consumption of these organisms leads to toxicity of human beings for extended periods of time.<sup>7</sup> Therefore, it is necessary to treat the effluent containing such dye before it released into aquatic environment. Many physicochemical methods have been attempted for treatment of effluent containing dyes,<sup>8</sup> such as coagulation,<sup>9,10</sup> precipitation,<sup>11</sup> and oxidation.<sup>12,13</sup> However, adsorption is found to be a convenient, economical and efficient to remove the dyes. Several adsorbents have been studied for the treatment of dye wastewater, such as activate carbon,<sup>14,15</sup> fly ash,<sup>16,17</sup> clay,<sup>18</sup> and silica gel.<sup>19</sup>

Attapulgite (ATT) is a hydrated magnesium aluminum silicate that exists in nature as a fibrous mineral.<sup>20</sup> It is a natural, cheap, adsorbent clay mineral with exchangeable cations and reactive –OH groups on its surface,<sup>21</sup> and its rough surface resulting in a relatively high surface area and high sorption capacities.<sup>22</sup> In addition, some isomorphous substitutions in the tetrahedral layer develop negatively charged sorption sites that can absorb cations through electrostatic attraction.<sup>23</sup> So, as a natural, cheap and large surface area, ATT is a very suitable adsorbent for the removal of cation dyes, like MG. Acid treatment



**Scheme 1.** The structure of Malachite Green (MG).

of ATT can increase its surface area and number of the active sites, and then optimize the adsorption capacity. However, the separation of ATT from aqueous solution is very difficult; the traditional methods are centrifugation and filtration,<sup>20</sup> while it is inconvenient and time-consuming. Therefore, finding an excellent carrier with good water resistance is very significant. Flexible foam polyurethane can be used as selective adsorbents for a number of substances from dilute aqueous solutions.<sup>24</sup> For its high porosity, light weight and large adsorption capacity, porous foam polyurethane has attracted considerable attention, so it can be a good carrier.

This study is devoted to MG's removal from the wastewater using adsorption technique. The study has been carried out under different variables, like temperature, pH, adsorbent dose, and adsorbent concentration and a convenient and economically viable process has been developed by involving a waste material-porous material as potential adsorbent. To the best of our knowledge, this is the first time that MG dye adsorption application of polyurethane-attapulgit porous material is reported.

## EXPERIMENTAL

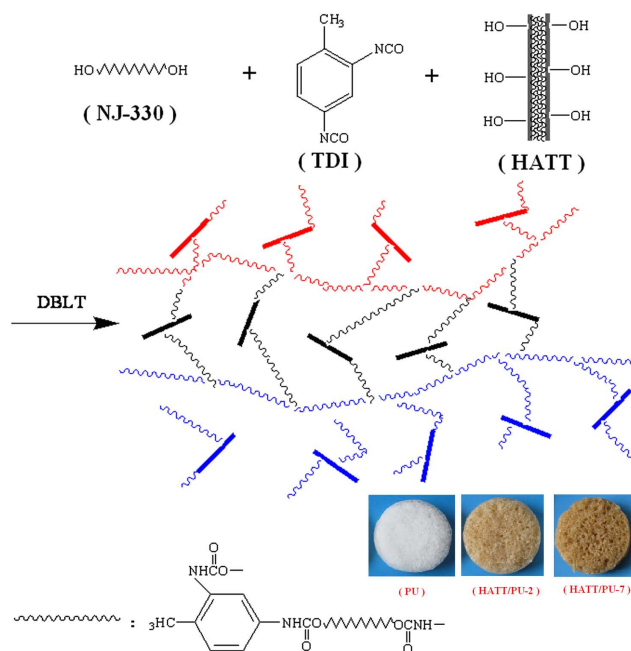
### Materials

Polyether polyol (NJ-330,  $M_n = 3000$  g/mol) was produced by Ningwu Chemical in Jurong, Jiangsu, China. Toluene diisocyanate (TDI) was supplied by Rongrong Chemical in Shanghai, China. Malachite Green, Attapulgit (ATT), sodium bicarbonate ( $\text{NaHCO}_3$ ), dibutylbis (lauryloxy) tin (DBLT), and silicone oil were obtained from Sinopharm Chemical Reagent in Shanghai, China.

### Preparation of Polyurethane-Attapulgit Porous Material (HATT/PU)

The attapulgit (ATT) was carried out by acid treatment and the process was as following steps. The attapulgit (10 g) was deposited in a hydrochloric acid solution (100 mL, 2 mol/L) in a flask, and stirred magnetically for 30 min at 30°C. Then, the solution was vibrated with the aid of ultrasonic instrument for 10 min at room temperature. After removing the supernatant, the residue was centrifuged and washed with distilled water several times until  $\text{pH} = 7$  and drying under vacuum at 105°C. After grinding, the acid activated attapulgit (HATT) solid was obtained and stored in desiccator.

The porous materials were prepared in three stages. First, calculated quantity of the polyether polyol (NJ-330), acid activated attapulgit (HATT), sodium bicarbonate as foaming agent,



**Scheme 2.** The synthetic route of the polyurethane-attapulgit porous material. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

dibutylbis (lauryloxy) tin (DBLT) as catalyst and silicone oil as stabilizer were stirred at the speed of 2500 rpm for 10 min. Then, calculated quantity of toluene diisocyanate (TDI) was added to the mixture, stirring for 20 s at the speed of 2500 rpm until the foam started to grow up. Last, the mixture was heated to 100°C for 2 h in the oven, where the material expanded. After foaming development, the blocks were demolded. The synthetic route of polyurethane-attapulgit porous material was shown in Scheme 2. Varying the proportion of HATT, a series of polyurethane-attapulgit porous materials were obtained with different HATT content of 1.0–10.0%.

The PU porous material was prepared using the same method described above except for the absence of HATT, the basic recipe was shown in Table I.

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

Sample	HATT (%)	NJ-330 (g)	TDI (g)	HATT (g)
PU	0	10	1.74	0
HATT/PU-1	0.85	10	1.74	0.1
HATT/PU-2	1.70	10	1.74	0.2
HATT/PU-3	2.56	10	1.74	0.3
HATT/PU-4	3.40	10	1.74	0.4
HATT/PU-5	4.26	10	1.74	0.5
HATT/PU-6	5.10	10	1.74	0.6
HATT/PU-7	5.96	10	1.74	0.7
HATT/PU-8	6.80	10	1.74	0.8
HATT/PU-9	7.67	10	1.74	0.9
HATT/PU-10	8.52	10	1.74	1.0

### Characterizations

FTIR spectra of the polyurethane and polyurethane–attapulgite porous material samples were recorded between 4000 and 500  $\text{cm}^{-1}$  with an FTIR spectrometer (AVATAR 360, Madison, Nicolet). A minimum of 32 scans was signal-averaged with a resolution of 2  $\text{cm}^{-1}$  in the 4000–500  $\text{cm}^{-1}$  ranges. The X-ray diffractograms of the samples were obtained using a Siemens D-5000 diffractometer with radiation Cu– $K\alpha$  ( $k = 15.4$  nm, 40 kV, and 30 mA) at 25°C. The relative intensity was registered in a dispersion range ( $2\theta$ ) of 5–80°. The fracture surface of the sample was investigated with a 15-kV accelerating voltage with a field emission scanning electron microscope (SEM) (S-4800, Hitachi, Tokyo, Japan).

### Dye Adsorption Application

Adsorption experiments were conducted to evaluate the optimal conditions for the malachite green dye adsorption. The procedure of MG adsorption application was briefly described as follows. The porous material was put into a certain volume wastewater solution containing MG. A specified time later, the porous material was taken out. The absorbance of the solution was measured spectrophotometrically at the  $\lambda_{\text{max}}$  617 nm. The adsorption efficiency ( $D$ ) of solution was calculated according to the following eq. (1):

$$D = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where  $A_0$  and  $A_t$  are the absorbance of the dye solution in the absence and in the presence of polyurethane–attapulgite porous material, respectively.

Concentrations of dye in solutions were determined through a calibration curve for the known MG concentration in the individual aqueous solution. The amount of adsorbed MG dye on polyurethane–attapulgite porous material (mg/g) was calculated according to the following eq. (2):

$$Q = \frac{(C_0 - C) \times V}{m} \quad (2)$$

where  $Q$  is the amount of adsorbed MG dye by the porous material (mg/g);  $C_0$  and  $C$  are the concentrations of the MG dye solution in the absence and in the presence of porous material, respectively (mg/L);  $V$  is the volume of the MG dye solution (L); and  $m$  is the dry weight of the porous material (g).

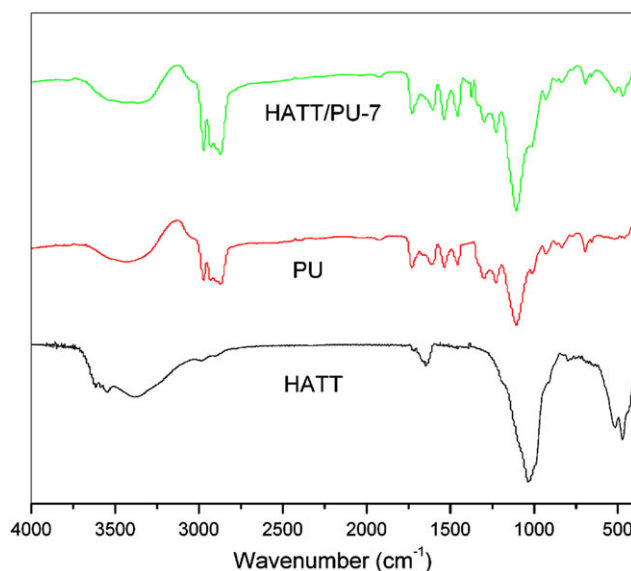
### Desorption and Regeneration

After the adsorption experiments, the MG-loaded samples were left in contact with 1.0 mol  $\text{L}^{-1}$  HCl for 30 min at room temperature. Then, take out the sorbent and dry. To determine the reusability of the HATT/PU materials, consecutive adsorption–desorption cycles were repeated four times under the same conditions.

## RESULTS AND DISCUSSION

### FTIR Characterization

The FTIR spectra of acid activated attapulgite (HATT), PU, and HATT/PU are shown in Figure 1. From the spectrum of HATT, the broad and strong peak between 3010 and 3740  $\text{cm}^{-1}$  is characteris-

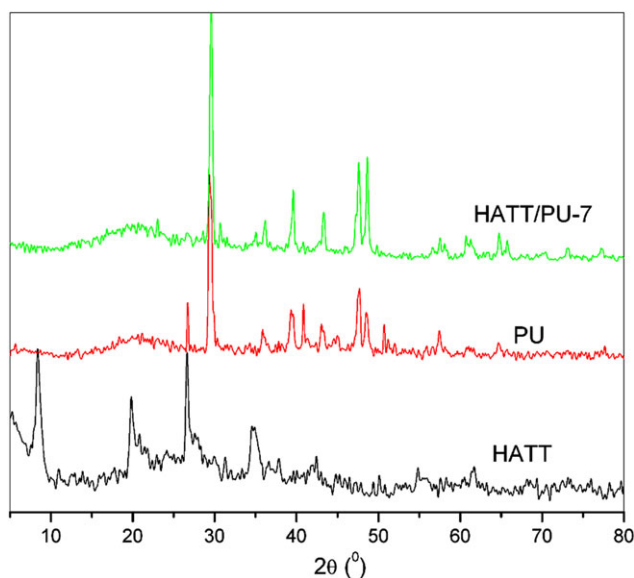


**Figure 1.** FTIR spectra of HATT, PU, and HATT/PU-7. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

tic of –OH stretching vibration. The –OH groups present in HATT can react with –NCO present in TDI and form hydrogen bonds with dye molecules. The peak at 1010  $\text{cm}^{-1}$  is assigned to the stretching vibration of Si–O–Si bonds and the peak at 470  $\text{cm}^{-1}$  is attributed to the bending vibration of Si–O–Si bonds, the peaks also exist in HATT/PU-7, which indicated that the HATT was grafted on the polyurethane molecule. The bond at 1654  $\text{cm}^{-1}$  is ascribed to the –OH bending mode of the adsorbed water molecules on the surface. From the spectra of PU and HATT/PU materials, the stretching vibrations of carbon-hydrogen bonds in –CH<sub>2</sub> and –CH<sub>3</sub> are observed at 3000–2800  $\text{cm}^{-1}$  range. Bending vibrations of methylene and methyl groups are also observed at 1378  $\text{cm}^{-1}$  and 1458  $\text{cm}^{-1}$ , respectively. The absorption at 1700–1720  $\text{cm}^{-1}$  is attributed to the ester stretching vibration peaks, indicating that the –OC(=O)– group exist. The disappearance of the peak at 2270  $\text{cm}^{-1}$ , which corresponded to –NCO group in FTIR spectra of PU and HATT/PU materials, proves the completed polymerization.

### X-Ray Diffraction Analysis

XRD is a powerful tool to study the crystallization behavior of polymer composites.<sup>25</sup> The XRD patterns of HATT, PU, and HATT/PU-7 materials are presented in Figure 2. The typical diffraction peaks of ATT is about 8.32°, it is due to the intrinsic axis structure of rod-like crystals. The disappearance in HATT/PU is due to the small amount of HATT in the polymer. The crystalline of PU elastomer is provided by the soft segments. As the hard segments have a higher polarity than soft segments, they interact with each other faster than soft segments, and thus, the part of the PUs structure due to the hard segments would be less crystalline than the one due to the soft segments, which are able to reorganize themselves until they reach a more stable disposition before interacting with each other, and hence, give a structure as crystalline as possible. The hard segment, when present at higher concentration, present diffraction peak

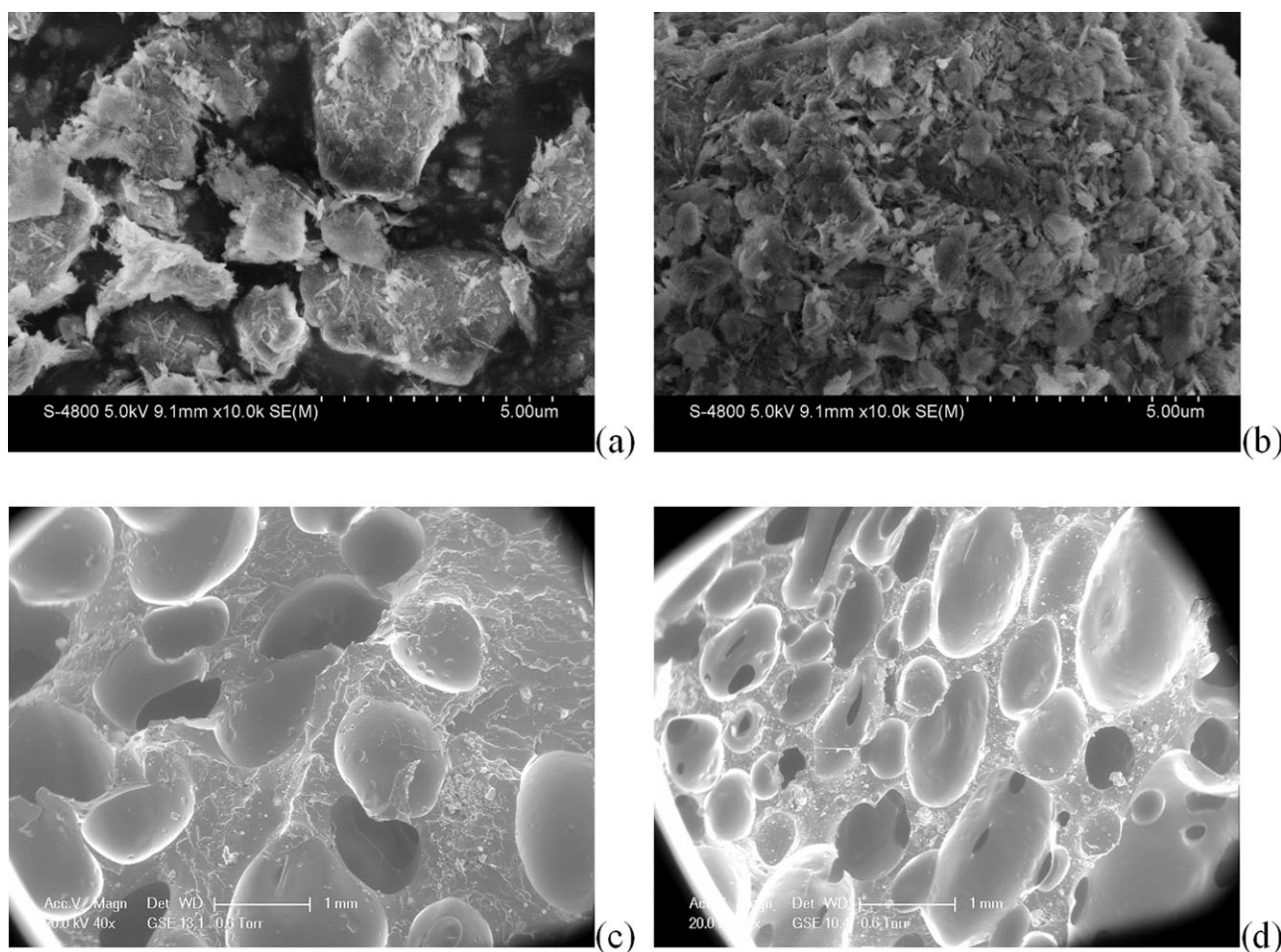


**Figure 2.** XRD patterns of HATT, PU, and HATT/PU-7. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

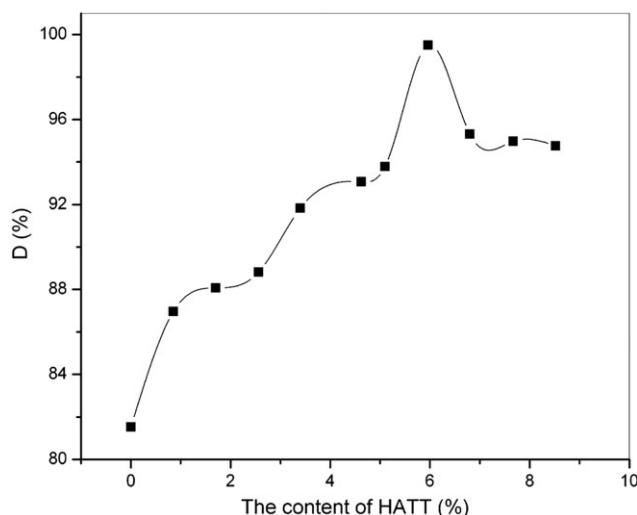
in a range of  $2\theta = 11.12$ .<sup>26</sup> It disappears in the PU and HATT/PU in this study, so that crystalline is due to the soft segment of PU and HATT. The pure PU shows a broad peak around  $18.2^\circ$ , which could be attributed to the amorphous phase in the polymer matrix mainly composed of soft segments.<sup>27</sup> The broadening peak and increased intensity in the case of HATT/PU, shows that the HATT is intercalated into the chain of polymer resulting in a well-ordered multilayer morphology built up with alternating polymer and inorganic.<sup>28</sup>

#### SEM Micrographs

The SEM photographs of raw attapulgite (ATT), acid activated attapulgite (HATT), pure PU, and the prepared HATT/PU are shown in Figure 3. From Figure 3(a), it is observed that ATT exhibits some fibrous structure. After acid treatment, the structure of the HATT (b) unchanged, some carbonate impurities have disappeared, leaving holes in the fibrous solid. Moreover, the HATT exhibits a much tighter and rougher surface. Compared with ATT, the size is smaller and the edge is smoother. From the SEM micrographs of PU (c) and HATT/PU (d), the internal structures comprises both open and closes porous, the latter accounting for the greater portion. The structures formed during the foaming process make large number of air, leading



**Figure 3.** SEM photographs of ATT (a), HATT (b), PU (c), and HATT/PU-7 (d).



**Figure 4.** Effect of HATT content on the adsorption efficiency of MG dye solution.

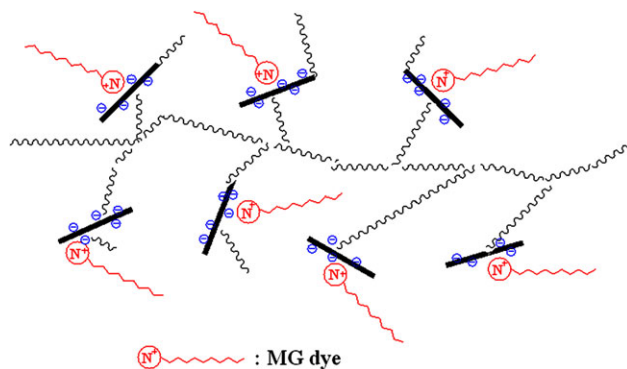
to an increased passive insulation, but some may collapse due to the violent foaming reaction. The porous walls are thin, but the edge struts are much thicker. The structure exhibits an anisotropic geometry.<sup>29</sup> Moreover, the HATT/PU shows ordered permutation than the pure PU, the average porous diameter of HATT/PU is about 0.7 mm. The facts indicate that the HATT can increase the surface area of materials, which is benefit for the adsorption of dye molecules.

#### Dye Adsorption Application

The main goal of this work was to establish optimal experimental conditions for the maximum adsorption of MG by the porous materials and to characterize the adsorption process. The experiments were carried out by spectrophotometry at the maximum absorption wavelength of MG. The effect of various parameters on the performance of the method was investigated and the adsorption efficiency (*D*) was calculated according to section 2.4.

#### Effect of the HATT Content on the Adsorption Efficiency of MG Dye Solution

Figure 4 shows the effect of the HATT content on the adsorption efficiency of MG dye solution on the fixed the porous material HATT/PU dosage of 50 mg/mL, time of 2.5 h and temperature of 35°C. In this experiment, the adsorption efficiency of HATT is about 85.58%. As can be seen from Figure 4, the all HATT/PU materials have bigger adsorption efficiencies than the pure PU and HATT, suggesting that the prepared porous material was more favorable for the adsorption of MG. This is mainly because the attapulgite is a three dimensional layered structure and has fibrous morphology. On the other hand, it also has permanent negative charges on its surface, which enable the ionic-pair formed with the cationic dye to enhance the adsorptive properties of HATT/PU materials. The adsorption mechanism of MG onto HATT/PU is shown in Figure 5. Furthermore, acid treatment makes it possible to increase specific surface, to create and modify the pores and produce changes in the nature and number of the active sites.<sup>30</sup> It is also observed that the adsorption efficiency increase with the content of

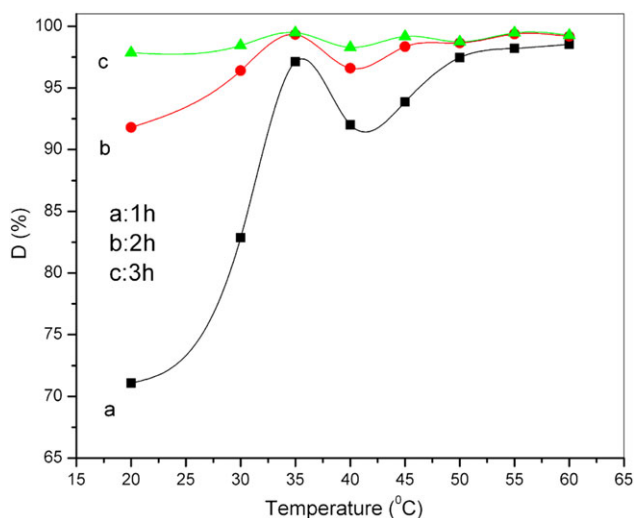


**Figure 5.** Adsorption mechanism of MG onto HATT/PU-7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

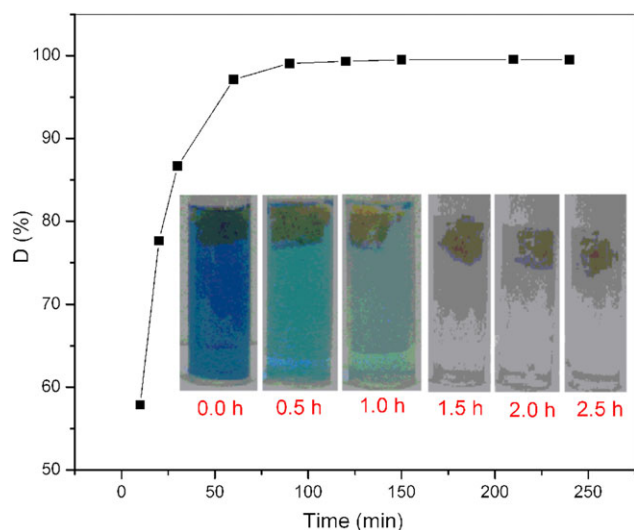
HATT. When the mass proportion of HATT is 6.0%, the highest MG adsorption efficiency is obtained and the value is 99.51%. The adsorption efficiency decrease when the content of HATT increases. This is mainly due to the higher amount of HATT, the more crosslink points, which increase the cross linking density of absorbent and reduces the absorbency of the composite.<sup>31</sup> Hence, the porous material HATT/PU-7 (the mass content of HATT of 6.0%) was chosen for further experiments.

#### Effect of the Temperature on the Adsorption Efficiency of MG Dye Solution

Temperature has a significant effect on the adsorption efficiency of dye solution. Figure 6 shows the effect of the temperature on the adsorption efficiency of MG dye solution at a fixed the HATT/PU-7 dosage of 50 mg mL<sup>-1</sup>. From Figure 6, it is observed that with increase in temperature up to 35°C, the dye adsorption efficiency increases, and then decreases by further increase in temperature which indicates that dye adsorption efficiency is strongly dependent on the temperature of system. However, when the temperature further increases, the adsorption efficiency changes little. Moreover, increasing the contact



**Figure 6.** Effect of the temperature on the adsorption efficiency of MG dye solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 7.** Effect of the time on the adsorption efficiency of MG dye solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

time, the adsorption efficiency all attained a high value. In this experiment, the temperature of 35°C was chosen for the further study of MG adsorption.

#### Effect of Contact Time on the Adsorption Efficiency of MG Dye Solution

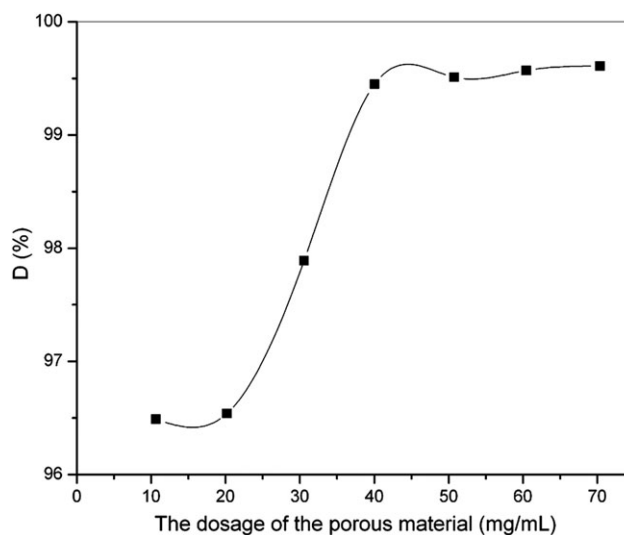
The effect of the contact time on the adsorption efficiency of MG dye solution at 35°C is shown in Figure 7. At the initial adsorption stage, the adsorption efficiency increases very quickly with time prolonging, then it increases slowly. And it is nearly unchangeable when time is more than 2.5 h. The rapid adsorption may be due to the adsorption sites are void and the fast interactions between dye and the surface of the material, and then reach adsorption equilibrium. The experimental result indicates that 2.5 h is sufficient to reach adsorption equilibrium for the MG dye. Therefore, 2.5 h was selected as the optimum contact time for the further study.

#### Effect of the Dosage of Porous Material on the Adsorption Efficiency of MG Dye Solution

The amount of adsorbent reflects the adsorption capacity of an adsorbent. MG dye adsorption onto HATT/PU-7 was studied by changing the amount of adsorbent at a fixed time of 2.5 h and a temperature of 35°C. The obtained result is shown in Figure 8. It can be seen that the increasing dosage resulted in an increase in the adsorption efficiency. This could be attributed to the more adsorbent, the more available active sites and the higher surface area of adsorbent. The MG adsorption efficiency reaches a high value when the dosage is 40 mg mL<sup>-1</sup>. Therefore, considering the cost and efficiency of wastewater treatment, 40 mg mL<sup>-1</sup> was selected as the optimum dosage in the experience.

#### Effect of pH on the Adsorption Efficiency of MG Dye Solution

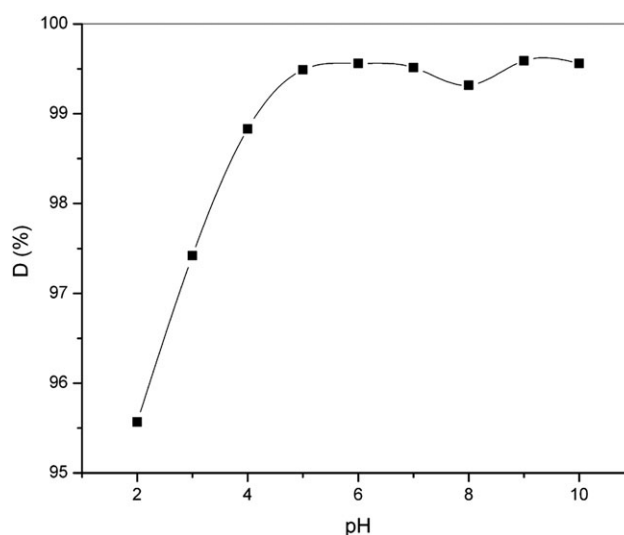
Other important factor in adsorption studies is the effect of pH of the solution. It can influence the protonation of the functional groups on the adsorbents as well as the solution chemis-



**Figure 8.** Effect of the dosage of porous material on the adsorption efficiency of MG dye solution.

try (for example, hydrolysis, complexation, and redox reaction).<sup>32</sup> Consequently, the effect of pH on MG dye adsorption was studied within the pH range of 2–10. The results are shown in Figure 9. It can be seen that the adsorption efficiency increased sharply with the increase of the pH ranging from 2.0 to 5.0. Then, the adsorption efficiency is maintained at about the same level. The possible reason of these results can be ascribed to following. ATT has permanent negative charges on its surface, at lower pH, more hydrogen ions competed with MG molecules for the adsorption sites. Continue increasing the pH, the cations decreased, the competition was weakly.

In conclusion, the optimum conditions of wastewater treatment containing MG dye were: a HATT content of 6.0%, a time of 2.5 h, a temperature of 35°C and an adsorbent dosage of 40 mg mL<sup>-1</sup>, pH > 5.0. At the optimum condition, the porous



**Figure 9.** Effect of the pH on the adsorption efficiency of MG dye solution.

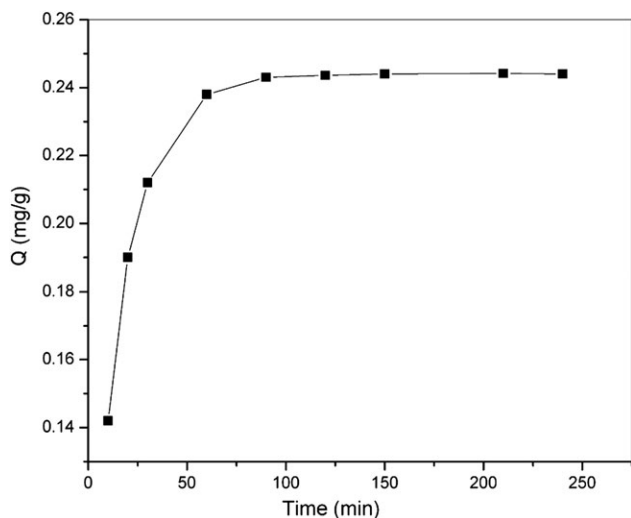


Figure 10. Adsorption kinetic curve of the HATT/PU-7 towards MG dye.

material had the highest adsorption efficiency and the value was 99.51%. The obtained result indicated that the polyurethane–attapulgite porous material could be used as the candidate materials of MG dye wastewater treatment.

#### Evaluation of Adsorption Kinetics

Figure 10 shows the adsorption kinetics curve of MG dyes onto HATT/PU material at the optimal conditions. As it can be seen from Figure 10, the adsorption efficiency is very high during the first hour of the process. After that, the adsorption equilibrium is reached within 2.5 h.

Adsorption is a physical and chemical process that involves mass transfer of a solute from liquid phase to the adsorbent surface. Kinetic study provided important information about the mechanism of dye adsorption onto HATT/PU material, which was necessary to depict the adsorption rate of adsorbent and control the residual time of the whole adsorption process. Two of the most widely used kinetic models, the pseudo-first-order adsorption and the pseudo-second-order adsorption and the intraparticle diffusion model were used to test dynamical experimental data. The pseudo-second-order kinetic equation is widely used to express the kinetic adsorption process because it always provides a more appropriate description. The second-order kinetic model is expressed as:

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

where  $k_2$  (g/(mg·min)) is the rate constant of second-order adsorption. Plotting  $t/Q$  against  $t$  gives a straight line with slope and intercept equal to  $(1/Q_e)$  and  $1/(k_2 Q_e^2)$ , respectively. It is described in Figure 11. The fitting parameters and theory data calculated by the nonlinear equations are listed in Table II.

As shown in Table II, the value of correlation coefficient ( $R^2$ ) for the pseudo-second-order rate equations was 0.9998. So, it is likely to predict the behavior over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate-controlling step. Meanwhile, the  $Q_{cal}$  value calculated from the pseudo-second-order model is more consistent with the experi-

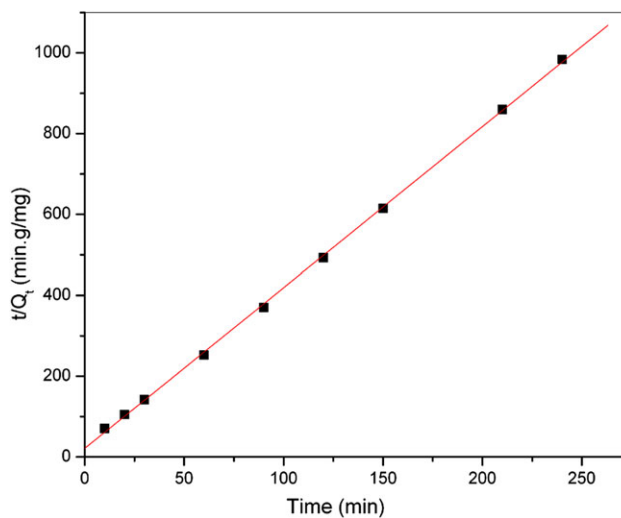


Figure 11. Linear fit of pseudo-second order equation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mental  $Q_e$  values. The obtained results indicated that the adsorption was well represented by a pseudo-second-order kinetic model. The pseudo-second-order adsorption mechanism dominates the adsorption process, and the adsorption rate of MG onto HATT/PU is probably controlled by the chemical process.

#### Evaluation of Adsorption Isotherm

The adsorption of MG by HATT/PU material was carried out at different initial concentrations and the optimum conditions. The obtained result is shown in Figure 12. It is observed that the amount of dye adsorbed increases with the initial concentrations increase. Analysis of equilibrium data is important for evaluating adsorption properties of HATT/PU adsorbent. Two important isotherm equations, namely Langmuir and Freundlich isotherms, have been selected for the study of adsorption. The Langmuir model assumes that adsorption takes place at uniform energy sites on the surface of the adsorbent.

The linearized Langmuir isotherm equation can be expressed as follows:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e} \quad (4)$$

where  $C_e$  is the equilibrium concentration of dyes in solution ( $\text{mg L}^{-1}$ ),  $Q_e$  is the adsorbed value of dye at equilibrium concentration ( $\text{mg g}^{-1}$ ),  $Q_m$  is the maximum adsorption capacity ( $\text{mg g}^{-1}$ ), and  $b$  is the Langmuir binding constant which is related to the energy of adsorption ( $\text{L mg}^{-1}$ ). Plotting  $1/Q_e$  against  $1/C_e$  gives a straight line with slope and intercept equal

Table II. Kinetic Parameters for MG Dye Adsorption onto Porous Material

$Q_e$ (mg/g)	Pseudo-second-order equation		
	$K_2$ (g/(mg·min))	$Q_{cal}$ (mg/g)	$R^2$
0.244	0.767	0.251	0.9998

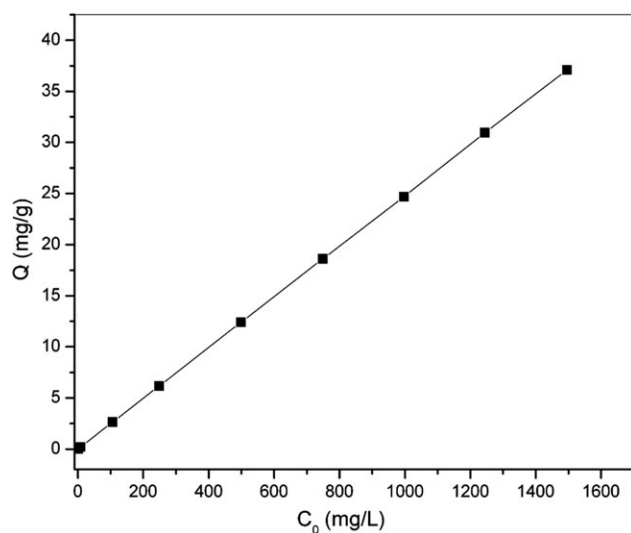


Figure 12. Effect of the initial MG concentration.

to  $1/(bQ_m)$  and  $1/Q_m$ . It is described in Figure 13. According to the equation, the maximum adsorption capacity of MG on HATT/PU was  $47.985 \text{ mg g}^{-1}$ .

Freundlich isotherm is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented by:

$$\log Q_e = \log K_f + \frac{\log C_e}{n} \quad (5)$$

where  $K_f$  and  $n$  are the Freundlich constants characteristics of the system, respectively, indicating the adsorption capacity and the adsorption intensity. If the value of  $1/n$  is lower than 1, it indicates a normal Freundlich isotherm, otherwise, it is indicative of cooperative adsorption. It is described in Figure 14.

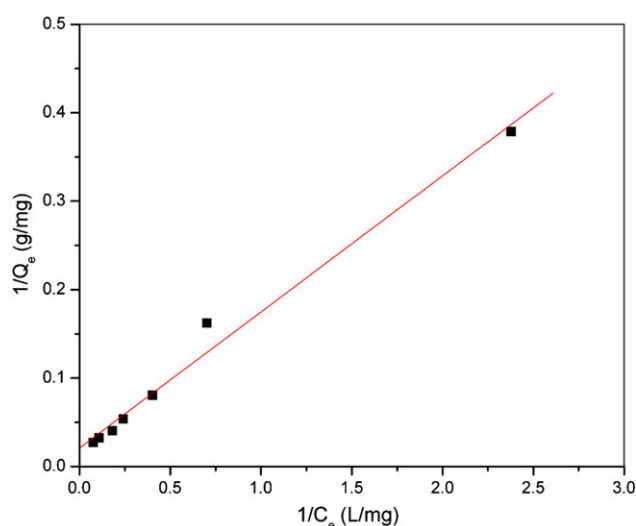


Figure 13. The Langmuir isotherm plots for MG adsorption by HATT/PU-7 material. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

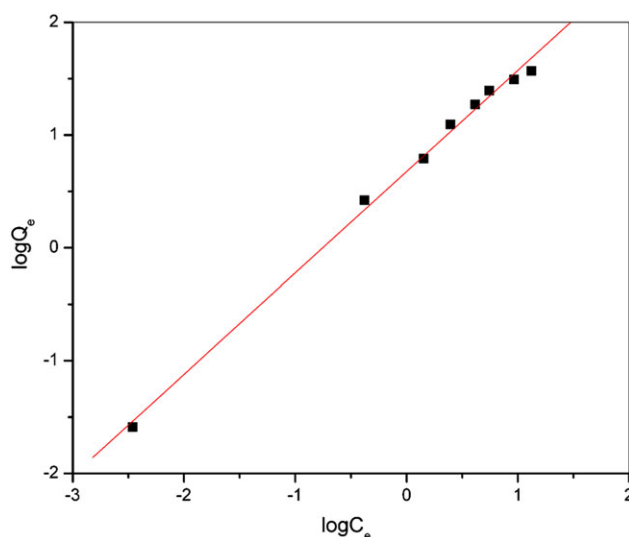


Figure 14. The Freundlich isotherm plots for MG adsorption by HATT/PU-7 material. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The fitted parameters and the theory data obtained by nonlinear equations are listed in Table III. It can be seen, that the Freundlich isotherm shows a better fit to experimental data in comparison with the Langmuir isotherm for MG adsorption. By calculating, the Freundlich constant  $1/n$  is smaller than 1, indicating that the Freundlich equation can satisfactorily describe the adsorption isotherms.

#### Thermodynamic Parameters

The effect of temperature on the adsorption isotherm was investigated under isothermal conditions in the temperature range of  $20\text{--}60^\circ\text{C}$ . Thermodynamic parameters are calculated using the following thermodynamic functions:

$$\Delta G^0 = -RT \ln K_p \quad (6)$$

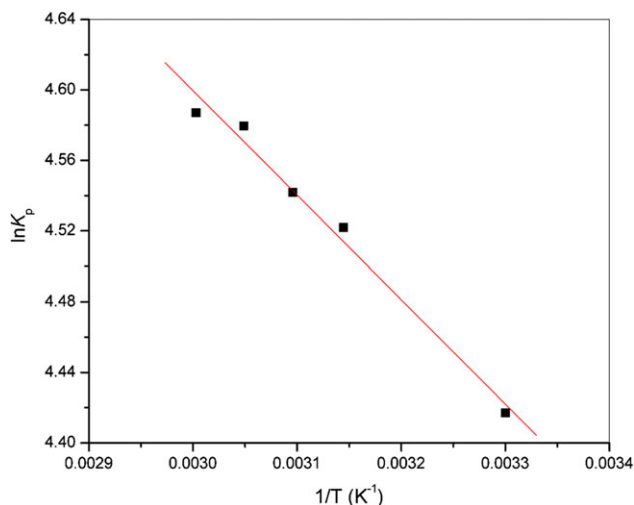
$$\ln K_p = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (7)$$

where  $K_p$  is the thermodynamic equilibrium constant, i.e., the ratio of the equilibrium concentration of MG on HATT/PU to that in solution.  $\Delta G^0$  ( $\text{KJ mol}^{-1}$ ),  $\Delta H^0$  ( $\text{KJ mol}^{-1}$ ), and  $\Delta S^0$  ( $\text{J}/(\text{mol}\cdot\text{K})$ ) are change in free energy, change in enthalpy and change in entropy, respectively.  $T$  is the absolute temperature in Kelvin, and  $R$  is the universal gas constant ( $8.314 \text{ J}/(\text{mol}\cdot\text{K})$ ). Plotting  $\ln K_p$  against  $1/T$  gives a straight line with slope and intercept equal to  $-\Delta H^0/R$  and  $\Delta S^0/R$ , respectively. A linear fit with an equation of  $\ln K_p = -592.08/T + 6.38$  ( $r = 0.9924$ ) was

Table III. Adsorption Isotherms Parameters for MG Dye Adsorption onto HATT/PU Materials

Langmuir equation			Freundlich equation		
$Q_m$ (mg/g)	$b$ (L/mg)	$R^2$	$K_f$ (mg/g)	$n$	$R^2$
47.985	0.1354	0.9932	4.73	1.11	0.9973





**Figure 15.** van't Hoff plot for the adsorption of MG by HATT/PU-7 material. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

obtained in this experiment and the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  calculated from Figure 15 are  $4.92 \text{ kJ mol}^{-1}$  and  $53.04 \text{ J/(mol}\cdot\text{K)}$ .

The calculated thermodynamic parameters are listed in Table IV. Negative values of  $\Delta G^\circ$  establish the feasibility of adsorption process. Further, the decrease in the values of  $\Delta G^\circ$  with the increase of the temperature indicates the spontaneity of the process at higher temperatures. The endothermic nature was also confirmed from the positive values of enthalpy change ( $\Delta H^\circ$ ), while good affinity of MG towards the adsorbent materials is revealed by the positive value of  $\Delta S^\circ$ .

#### Desorption Studies

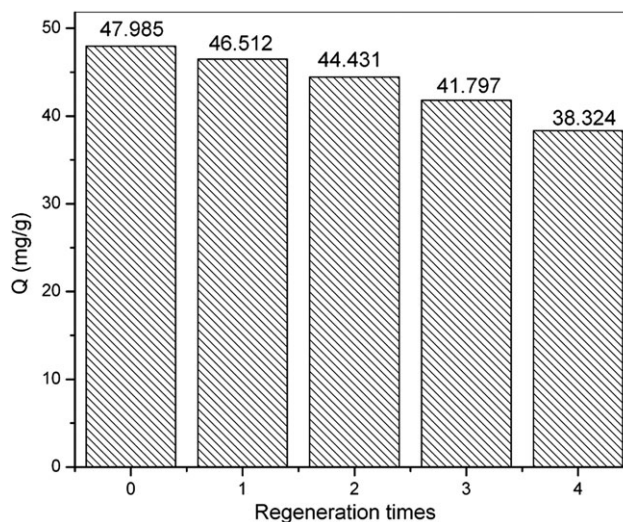
Figure 16 presents the adsorption capacity from 47.985 to 38.324 ( $\text{mg g}^{-1}$ ) when the process was repeated four times. The obtained results could prove that the prepared HATT/PU adsorbent was stable for azo adsorption. It also showed that a higher level of adsorption capacity corresponded to four cycles of desorption–adsorption.

#### CONCLUSIONS

In this study, adsorption process for the removal of MG dye from aqueous solutions has been carried out using polyurethane–attapulgite porous material (HATT/PU). The obtained results showed that the optimal conditions were: a HATT content of 6.0%, a time of 2.5 h, a temperature of  $35^\circ\text{C}$ , a  $\text{pH} > 5$ , and a HATT/PU dosage of  $40 \text{ mg mL}^{-1}$ . At the optimum con-

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

T (K)	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
303	-11.15	4.92	53.04
318	-11.95		
323	-12.21		
328	-12.48		
333	-12.74		



**Figure 16.** Reuse of the prepared adsorbent.

ditions, the porous material had the highest adsorption efficiency and the value was 99.51%. Kinetic studies indicated that the adsorption reaction follows the pseudo-second order kinetics, suggesting the main adsorption mechanism of chemical adsorption. Thermodynamic parameters obtained indicated that the adsorption process is spontaneous and endothermic. The obtained results indicated that the prepared polyurethane–attapulgite porous material has potential application for the wastewater treatment containing MG dye.

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