

# Poly(ethylene imine)-modified graphene oxide with improved colloidal stability and its adsorption of methyl orange

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## ABSTRACT

Graphene oxide (GO) was chemically modified with poly(ethylene imine) (PEI) to improve its colloidal stability and was investigated as a potential adsorbent for the removal of methyl orange (MO). The synthesis of PEI-GO was verified with a Fourier transform infrared spectrometer and thermogravimetric analysis. A series of adsorption experiments were carried out to investigate the adsorption capacity of PEI-GO. Adsorption kinetics and thermodynamics studies were performed, and the thermodynamic parameters were calculated. The results showed that PEI could improve the colloidal stability of GO in aqueous solution, and the obtained PEI-GO showed a macroscopically homogeneous dispersion after more than three months. After standing for 90 days, the Brunauer–Emmett–Teller specific surface area of GO decreased from 353 to 214  $\text{m}^2 \cdot \text{g}^{-1}$ , while that of PEI-GO remained almost unchanged (from 432 to 413  $\text{m}^2 \cdot \text{g}^{-1}$ ). The PEI-GO exhibited significantly faster kinetic and higher adsorption capacity for MO than GO. Moreover, PEI-GO had a good adsorption capacity in the acidic range, and the highest adsorption of MO occurred at  $\text{pH} = 6.0$ . The adsorption of MO on PEI-GO was an endothermic, spontaneous and physisorption process.

**Key words** | adsorption kinetics, adsorption thermodynamics, graphene oxide, methyl orange, poly(ethylene imine)

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## INTRODUCTION

Organic dyes, such as methylene blue and methyl orange (MO), are used in printing and dyeing industries. The presence of organic contaminant in waste water has a large environmental and public health impact, because the complex aromatic structures make part of dyes more stable and more difficult to be removed from the effluents discharged into water bodies (Rafatullah *et al.* 2010). There are several methods established to remove dyes, including physical and chemical processes. Adsorption has proven to be an effective and attractive process for the treatment of dye-bearing waste water (Rao *et al.* 2007). The adsorption characteristics of dyes on various adsorbents have been extensively investigated for many purposes involving separation and purification (Bhatnagara & Minocha 2006).

Carbon materials, such as active carbon and carbon nanotubes, are a class of significant and widely-used engineering adsorbent. Carbon nanotubes, for example, of an

extremely small size, uniform pore distribution and large specific surface area, show excellent potential for the adsorption of dyes and metal ions (Ahmadzadeh Tofighy & Mohammadi 2011; Ghaedi *et al.* 2011). Recently, graphene oxide (GO), a new member of the carbon family, has exhibited great potential as an attractive adsorbent in the treatment of waste water (Wang *et al.* 2013). GO is a two-dimensional nanomaterial with a large plane. Through  $\pi$ - $\pi$  stacking interaction, GO can load aromatic compounds with a high loading ratio. The literature has reported GO as being adsorbent (Wang *et al.* 2013), but its unstable colloidal property makes GO sedimentate easily during long-term storage or practical application. Improving the colloidal stability of the GO sheet is therefore an essential step in achieving a variety of potential applications for GO and its derivatives. In order to achieve this goal, physical (Ma *et al.* 2012) or chemical (Sui *et al.* 2012) modifications

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have been used. For instance, Sui (Sui *et al.* 2012) reported an easy method for the fabrication of three-dimensional (3D) porous material via the coulombic interaction between a GO sheet and poly(ethylene imine) (PEI), and the as-prepared 3D porous material showed an excellent adsorption capacity for acidic dye. However, the coulombic interaction between GO and PEI is not stable and easy to disaggregate.

Compared with physical modification, chemical modification is more likely to make GO stable during long-term storage or practical application. In this paper, PEI, a cationic polymer, was used to chemically modify GO, which was expected to improve the colloidal stability of GO in aqueous solution. The obtained PEI-modified GO (PEI-GO) was evaluated as a possible adsorbent for the removal of an anionic dye (MO) from aqueous solution.

## METHODS

### Preparation of PEI-GO

GO was prepared by a modified Hummers method (Cai *et al.* 2012). In brief, concentrated H<sub>2</sub>SO<sub>4</sub> was mixed with graphite powder, P<sub>2</sub>O<sub>5</sub> and KMnO<sub>4</sub> at 35 °C for 2 h, and 30% H<sub>2</sub>O<sub>2</sub> was added. Then, the mixture was washed, centrifuged, filtrated and dried under vacuum to get the GO. PEI with a molecular weight of 10,000 was purchased from Sigma-Aldrich. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl) and *N*-hydroxy-succinimide (NHS) were purchased from Sigma-Aldrich. Methyl orange (MO) was purchased from Aladdin (China). All raw materials were used directly without further purification.

For the preparation of PEI-GO, 100 mg GO was dispersed in 50 mL distilled water under sonication to obtain a clear dispersion. Thereafter, 50 mL PEI solution (20 mg/mL), 200 mg EDC·HCl and 120 mg NHS were added. The pH value of the mixture was adjusted to be 6–7 by adding 0.1 mol/L HCl or NaOH, and was measured using a pH meter (METTLER TOLEDO, FE20). The carboxyl groups of GO were activated by EDC and NHS reagents, and then were conjugated with the amido groups of PEI by carbodiimide chemistry. The mixture was kept at 30 °C for 24 h, after which it was transferred to a dialysis tube (MWCO = 14,000) that was dialyzed against 5 L of deionized water. Moreover, the deionized water was replaced every 12 hours. After 4 days of dialysis, the product was freeze-dried.

The structure was characterized using the Fourier transform infrared spectrometer (FT-IR) spectrum, and the composition was analyzed by thermogravimetry analysis

(TGA) under N<sub>2</sub> with a temperature range of 50–650 °C. The colloidal stability of PEI-GO in an aqueous medium was determined by evaluating the change in absorbance as a function of time at a wavelength of 500 nm (UV-visible spectrometer, S52, China). Moreover, the size and morphology were observed by a JEM-2,100 transmission electron microscope (TEM) (JEOL, Japan). A TEM sample was prepared by dropping colloidal PEI-GO on a copper grid which was dried. The Brunauer–Emmett–Teller (BET) specific surface area of freeze-dried PEI-GO or GO was determined using a Micromeritics ASAP 2010 instrument. Particle size and zeta potential were determined using a PALS Zeta Potential Analyzer (Brookhaven Instruments Co., USA).

### Adsorption of MO

Batch adsorption experiments were performed using 50 mL glass bottles with additions of 20 mg PEI-GO and 20 mL 20 mg/L MO solution. The glass bottles were sealed and placed in a temperature control box to maintain the water temperature. The pH values of the samples were adjusted by adding 0.1 mol/L HCl or NaOH, and were measured using a pH meter. For adsorption kinetic study, the effect of contact time on the adsorbed amount of MO was investigated at different temperatures (298, 313 and 328 K). The adsorbed amount of MO on PEI-GO at any time,  $t$ , was calculated from the concentration of MO in solution before and after adsorption using a spectrophotometer ( $\lambda_{\text{max}} = 470 \text{ nm}$ ). At any time, the adsorbed amount of MO,  $q_t$  (mg/g), onto PEI-GO was calculated from the mass balance equation as follows:

$$q_t = V(C_0 - C_t)/W \quad (1)$$

where  $q_t$  was the adsorbed amount of MO at any time (mg/g);  $C_0$  and  $C_t$  were the initial concentration of MO and liquid-phase concentration of MO at any time (mg/L), respectively;  $V$  was the volume of MO solution (L), and  $W$  was the used mass of PEI-GO sample (g).

For the adsorption isotherm study, 20 mg PEI-GO was added into 20 mL MO solution (the initial concentration ( $C_0$ ) of MO increased from 2.5 to 25 mg/L), and the temperature was held at 298, 313 and at 328 K. At the end of the equilibrium period, the suspension was separated for the later analysis of dye concentration. The adsorbed amount of MO at equilibrium,  $q_e$  (mg/g), was calculated from the following equation:

$$q_e = V(C_0 - C_e)/W \quad (2)$$

where  $C_0$  and  $C_e$  (mg/L) were the liquid-phase concentrations of MO at initiation and equilibrium, respectively;  $V$  (L) was the volume of MO solution and  $W$  (g) was the used mass of adsorbent.

To determine the maximum adsorption capacity, 0.1 g of PEI-GO or GO was put into a conical flask containing 100 mL of 5 g/L MO aqueous solution (pH value was adjusted to 6.0 by adding 0.1 mol/L HCl and was measured using a pH meter). The flask was covered well and shaken in a water bath shaker at 30 °C for 4 days. Then, the adsorbed PEI-GO or GO was filtered using a 0.22  $\mu\text{m}$  membrane filter, and the adsorbed amount of MO was calculated from the concentration of MO in solution before and after adsorption by using a spectrophotometer ( $\lambda_{\text{max}} = 470 \text{ nm}$ ).

For the adsorption mechanism study, a fluorescence spectrum and zeta potential test were carried out for the aqueous PEI-GO/MO mixture. For the fluorescence spectra, 5.0  $\mu\text{g/mL}$  PEI-GO containing 1.0  $\mu\text{g/mL}$  MO was excited at 350 nm using a fluorophotometer (RF-5301, Shimadzu, Japan). For the zeta potential test, the same samples were recorded by a Zeta Potential Analyzer instrument (Zeta-PALS, Brookhaven Instruments Corporation, USA).

The thermodynamic parameters were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_c \quad (3)$$

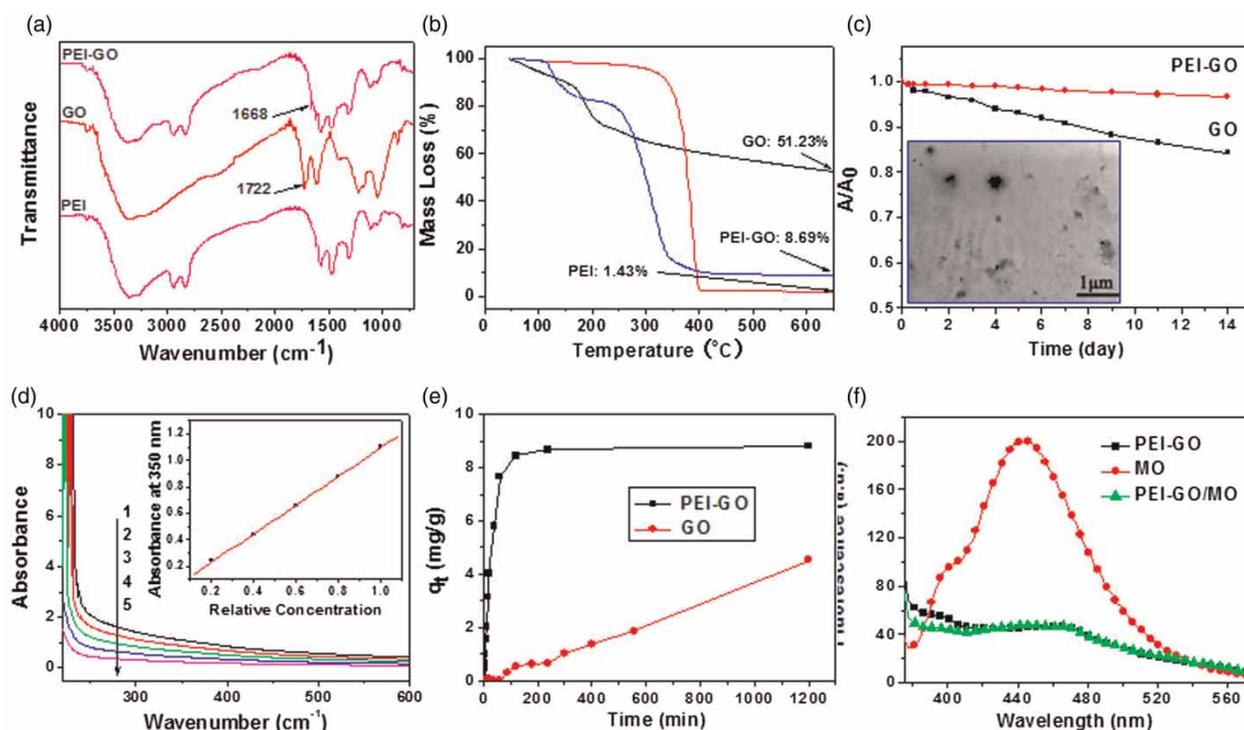
$$\ln K_c = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (4)$$

where  $\Delta G^\circ$  (kJ/mol),  $\Delta H^\circ$  (kJ/mol) and  $\Delta S^\circ$  (J/(mol · K)) were the changes of gibbs free energy, enthalpy and entropy, respectively.  $K_c$  was the ratio of MO concentration on the adsorbent at equilibrium ( $q_e$ ) to the remaining MO concentration in the solution at equilibrium ( $C_e$ ).  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and intercept of the linear plot of  $\ln K_c$  versus  $1/T$ .

## RESULTS AND DISCUSSION

### Preparation and characterization of PEI-GO

In Figure 1(a), the FT-IR spectrum of GO reveals -OH ( $\sim 3400 \text{ cm}^{-1}$ ), C = O ( $1722 \text{ cm}^{-1}$ ), C = C ( $1609 \text{ cm}^{-1}$ ) and



**Figure 1** | (a) FT-IR spectra of GO, PEI and PEI-GO; (b) TGA curves of GO, PEI and PEI-GO with reference to the verification of the PEI-GO material; (c) changes of relative absorbance with respect to the setting time for GO and PEI-GO in aqueous solution at 500 nm (the inset is the TEM image of PEI-GO in water); (d) UV-vis absorption spectra of PEI-GO in water for different relative concentration of  $C_0$  ( $C_0$  denotes the original concentration of PEI-GO in water; 1: 1.0  $C_0$ , 2: 0.8  $C_0$ , 3: 0.6  $C_0$ , 4: 0.4  $C_0$ , 5: 0.2  $C_0$ , and the inset is Lambert-Beer's plot for the absorption at 350 nm) with reference to the characterization/property of the synthesized material; (e) adsorption kinetic analyses of GO and PEI-GO (MO, 20 mg/L; pH = 6.0; 298 K); and (f) fluorescence spectra of PEI-GO, MO and PEI-GO/MO mixture (excitation at 350 nm) with reference to the interaction with MO.

C-O ( $1109\text{ cm}^{-1}$ ) functional groups in GO (Cai *et al.* 2012). After being conjugated with PEI, the resultant PEI-GO shows the absorption features of PEI, and the peak at  $1668\text{ cm}^{-1}$  is attributed to the O = C-NH stretch, indicating that GO had been successfully covalently-modified by PEI. The composition of PEI-GO could be calculated from the residual mass presented in the TGA curve shown in Figure 1(b). Under nitrogen atmosphere, GO remained at about 51.23% residue after it was heated to  $650\text{ }^{\circ}\text{C}$ , while the PEI only remained at about 1.43% residue. PEI-GO began to decompose at approximately  $120\text{ }^{\circ}\text{C}$  and remained at 6.80% residue, from which the content of PEI in PEI-GO could be determined to be 85.4 wt%.

Figure 1(c) shows the changes of relative absorbance with respect to the setting time for GO and PEI-GO samples. It was found that there was little change in relative absorbance for the PEI-GO sample, which indicates that the obtained PEI-GO dispersion had a good colloidal stability. By contrast, pure GO without modification by PEI showed a deposition in water.

The TEM image of PEI-GO (Figure 1(c)) shows that the PEI-GO was well dispersed in water with a diameter of  $463 \pm 171\text{ nm}$  (PALS Zeta Potential Analyzer). In order to confirm the homogenous dispersion of the PEI-GO in aqueous solution, UV-Vis absorption spectra were collected for different PEI-GO concentrations. As shown in Figure 1(d), the intensity of the absorption spectrum had a good linear relation to the concentration of PEI-GO (inset in Figure 1(d)), i.e., following Lambert-Beer's law, indicating that PEI-GO showed a good dispersion in aqueous solution (Wang *et al.* 2007). These results suggest that PEI could function as an effective stabilizing agent for the formation of a stable colloidal GO sample in aqueous solution. In fact, the obtained PEI-GO showed a macroscopically homogeneous dispersion for longer than three months.

### Adsorption mechanism

Graphene can invoke strong  $\pi$ - $\pi$  stacking between aromatic compounds and the graphene surface (Wu *et al.* 2011; Cai *et al.* 2012), so it was expected to adsorb the dye and purify the waste water in this paper. Figure 1(e) shows the adsorption kinetic curves of GO and PEI-GO. Both GO and PEI-GO show good adsorption capabilities for MO. However, PEI-GO exhibited significantly a faster kinetic and higher adsorption capacity for MO within the observed time range than did GO. This was likely due to the improved colloidal stability of PEI-GO in aqueous solution and less

aggregation, resulting in a larger specific surface area for the adsorption of MO.

To explore and confirm the interaction between PEI-GO and MO, fluorescence spectrum and zeta potential tests were carried out. In Figure 1(f), PEI-GO shows a weak band at 460 nm while MO shows an obvious emission band at 445 nm in the case of 350 nm excitation. However, upon excitation at the same wavelength, PEI-GO/MO exhibits significant quenching of its emission band, which implies the presence of a photoinduced electron-transfer process or efficient energy transferring along the graphene plane and MO interface (Iurlo *et al.* 2008), which indicates a strong  $\pi$ - $\pi$  stacking interaction between graphene and MO.

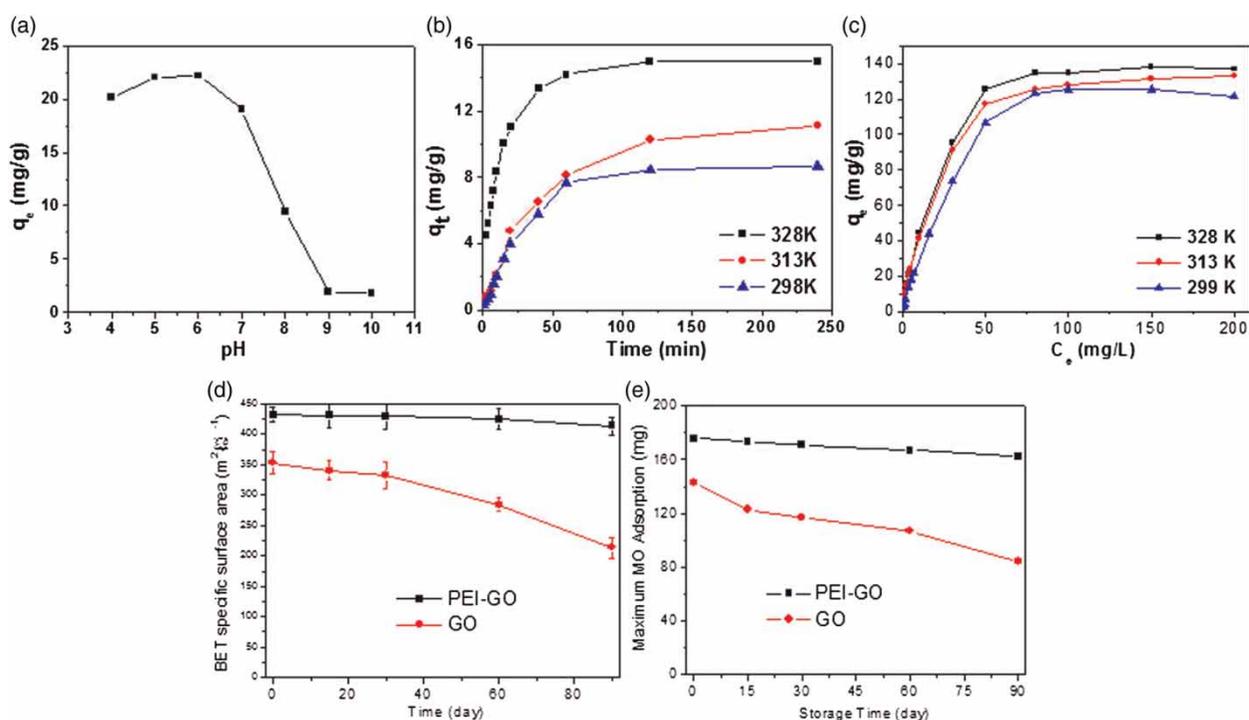
GO showed a negative zeta potential due to the carboxylic groups of plane ( $-30\text{ mV}$ ). After it was modified by cationic PEI, the zeta potential switched to be positive ( $+61\text{ mV}$ ). When PEI-GO was used to adsorb MO, the obtained PEI-GO/MO system showed a lower zeta potential of approximately  $+50\text{ mV}$ , which indicates that PEI and MO might have electrostatic interaction.

To optimize the pH value for maximum removal efficiency, experiments were conducted in the pH range from 4.0 to 10.0 at room temperature. As presented in Figure 2(a), the PEI-GO had a good adsorption capacity in the acid range, and the highest adsorption of MO occurred at pH = 6.0.

### Adsorption kinetics, isotherms and thermodynamics of PEI-GO and MO

Figure 2(b) gives the adsorption kinetics of PEI-GO at different temperatures. The adsorption capability of PEI-GO increased with an increase in temperature, indicating that the adsorption process was endothermic. The removal of MO by adsorption on PEI-GO was found to be rapid at the initial period and then to become slow and to stagnate with increase of contact time, which was likely because a large number of vacant surface sites were available for adsorption during the initial stage and then the remaining vacant surface sites were difficult to be occupied due to the repulsive force between the MO molecule on the PEI-GO and the free MO (Wu 2007); this will only occur after a certain degree of surface saturation with MO is achieved.

In Figure 2(c), the equilibrium uptake of PEI-GO increases with the increase of equilibrium MO concentration in the range 0–50 mg/L, after which it remains unchanged. When the concentration of MO in solution was higher than 50 mg/L, the active sites of PEI-GO were surrounded by many more MO molecules, and the



**Figure 2** | (a) The effect of pH value on MO adsorption (PEI-GO, 20 mg; MO, 20 mg/L; 298 K); (b) adsorption kinetic analysis of PEI-GO at different temperatures (PEI-GO = 1 mg/L, MO = 20 mg/L, pH = 6.0); (c) adsorption isotherms of MO on to PEI-GO at different temperatures (PEI-GO = 1 mg/L, pH = 6.0); (d) BET specific surface areas of PEI-GO and GO with different storage time; (e) maximum adsorption capacities of PEI-GO and GO with different storage time.

adsorption reaches saturation. Therefore, the  $q_e$  value increases with the increase of equilibrium MO concentration in the range of 0–50 mg/L. The increase of equilibrium adsorption  $q_e$  with increase in temperature indicates that the adsorption of MO onto PEI-GO is endothermic in nature.

In Figure 2(d), the BET specific surface areas of freshly prepared PEI-GO and GO are  $432 \text{ m}^2 \cdot \text{g}^{-1}$ , respectively. After standing for 90 days, the BET specific surface area of GO decreased to  $214 \text{ m}^2 \cdot \text{g}^{-1}$ , while that of PEI-GO almost remained unchanged ( $413 \text{ m}^2 \cdot \text{g}^{-1}$ ). This is attributed to the aggregation of GO during the process of storage because of the unavoidable strong  $\pi$ - $\pi$  stacking interaction between each single layer of GO, and is in accordance with the determined zeta potential. These results suggest that PEI could improve the dispersibility of the GO sheet and prevent its reunion.

In Figure 2(e), at pH 6, the maximum adsorption capacities of MO on freshly prepared PEI-GO and GO are 176 and 143 mg/g, respectively, at  $30^\circ\text{C}$ . After standing for 90 days, the maximum adsorption capacity of MO on stored GO decreases to 84 mg/g at  $30^\circ\text{C}$ , while that on stored PEI-GO decreases to 161 mg/g at  $30^\circ\text{C}$ . The different decrease in maximum adsorption capacities of GO and

PEI-GO is related to the different aggregation degree during the process of storage, since PEI-GO has a better solution stability than GO.

The Langmuir model and Freundlich isotherm model were used to fit the data from Figure 2(b). The Langmuir isotherm was represented by the following linear equation:

$$C_e/q_e = 1/q_0K_L + C_e/q_0 \quad (5)$$

where  $C_e$  (mg/L) is the equilibrium concentration;  $q_e$  (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbate;  $q_0$  and  $K_L$  are the Langmuir constants which are respectively related to adsorption capacity and rate of adsorption.

The Freundlich isotherm was represented by the following linear equation:

$$\ln q_e = \ln K_F + \ln C_e/n \quad (6)$$

where  $q_e$  is the amount adsorbed at equilibrium (mg/g) and  $C_e$  is the equilibrium concentration of MO. The favourability of the adsorption process is indicated by  $n$ , and  $K_F$ . It is generally stated that values of  $n$  in the ranges of 2–10, 1–2 and less than 1 represented good,

**Table 1** | Isotherm parameters for removal of MO by PEI-GO at different temperatures and thermodynamic parameters for MO adsorption onto PEI-GO

Temperature(K)	Langmuir model			Freundlich model			$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/(mol·K))
	$K_L$	$q_0$	$R^2$	$K_F$	$n$	$R^2$			
298	0.049	89.7	0.935	4.18	1.11	0.998	- 3.13	20.2	78.28
313	0.369	36.3	0.932	9.16	1.63	0.998	- 4.41	23.5	89.17
328	1.33	25.9	0.949	13.3	2.80	0.999	- 4.99	26.7	96.62

moderately difficult and poor adsorption characteristics, respectively.

From Table 1, the adsorption process can be described by the Freundlich model, and different sites with several adsorption energies are involved. PEI-GO was a good adsorbent for MO ( $n > 2$ ) at a higher temperature.

Table 1 also presents the thermodynamic parameters at various temperatures. The value of  $\Delta H^\circ$  was positive, indicating that the adsorption reaction was endothermic. The positive value of  $\Delta S^\circ$  reflects the affinity of PEI-GO for MO and suggests some structural changes in the dye and PEI-GO. The negative  $\Delta G^\circ$  indicates the spontaneous process of MO adsorption. For instance, the values of enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of adsorption are 20.2 kJ/mol and 78.28 J/(mol K) at 298 K, respectively, which suggests that the adsorption of MO onto PEI-GO was a physisorption process. What is more, the decrease of  $\Delta G^\circ$  with the increase of temperature indicates that the adsorption process of MO on PEI-GO became more favourable at a higher temperature (Yao *et al.* 2010).

## CONCLUSIONS

A PEI-GO material with good colloidal stability was prepared and explored as a new adsorbent for water treatment. The obtained PEI-GO with a diameter of  $463 \pm 171$  nm showed a good adsorption capacity for MO due to the  $\pi$ - $\pi$  stacking and electrostatic interaction between PEI-GO and MO. Under pH = 6.0, the maximum adsorption capacity of MO on freshly prepared PEI-GO with BET specific surface area of  $432 \text{ m}^2 \cdot \text{g}^{-1}$  was 176 mg/g at 30 °C and remained relatively unchanged after standing for 90 days (161 mg/g at 30 °C), while the maximum adsorption capacity of GO decreased from 143 to 84 mg/g after standing for 90 days. The adsorption experiment results suggest that the adsorption of MO on PEI-GO was an endothermic process. The equilibrium data were analyzed and were found to fit well with the Freundlich isotherm equation.

Thermodynamic analyses indicated that the adsorption of MO onto PEI-GO was a spontaneous and physisorption process. These results showed that PEI could improve the colloidal stability of GO in aqueous solution, resulting in the better adsorption capacity of PEI-GO than GO during the process of storage. Moreover, PEI-GO could be used as a preliminary adsorbent in ultrafiltration membrane filtration, thus improving ultrafiltration efficiency and reducing the accuracy requirements for the preparation of the ultrafiltration membrane. The next step in this research will be to study the interaction between the PEI-GO and the ultrafiltration membrane.

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