Preparation and adsorption properties of magnetic graphene oxide composites for the removal of methylene blue from water

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Keywords: graphene oxide, composites, methylene blue, adsorption

Abstract

Using graphite powder, chitosan, and diatomite as raw materials, graphene oxide was first prepared by Hummer’s method and GO was carboxylated and modified into hydroxylated graphene oxide (GOH). It was then modified into GOH via carboxylation, and then diatomite (DE) and the prepared magnetic chitosan (MCS) were supported on GOH by blending to generate the magnetic graphene oxide composite GOH/DMCS. This novel composite was then studied to determine its methylene blue wastewater adsorption capability. Results showed that at 45 °C, a dosage of adsorbent of 1 g L−1, and a pH of 12, the adsorption of methylene blue dye by GOH/DMCS reached equilibrium after 120 min, and the maximum adsorption amount was 205.34 mg g−1. The adsorbent was then cycled eight times to test its reusability, and the adsorption efficiency remained greater than 86%. The adsorption process of methylene blue by GOH/DMCS fit well to a pseudo second-order kinetic model. These results showed that the adsorption rate was more sensitive to the initial concentration of methylene blue dye, which implies a chemical adsorption process. The adsorption process conformed to the Langmuir isotherm adsorption model, indicating that the adsorption was monolayer surface adsorption.

1. Introduction

Methylene blue (MB) is a thiazine dye that is widely used in dyeing cotton, silk, leather, paper, bamboo, and wood, etc. It can also be used to make inks, lakes, etc [1–4]. The chemical structure of the dye is complex, not easily oxidized or degraded, and its color rendering is high. MB is especially challenging to remove via conventional methods due to its aromatic structure [5, 6]. Therefore, the efficient and harmless treatment of dye wastewater has become an urgent problem to be solved, namely for environmental and ecological safety [7]. At the same time, in the field of medicine, MB can be used to treat hemoglobinemia and cystitis, but excessive inhalation of MB can cause nausea, rapid heartbeat, tissue necrosis, and other adverse reactions. A high concentration of MB in water will destroy the water quality, affect the chroma and transparency of water, and endanger the environment and human health [8–10]. Therefore, methylene blue-containing wastewater must be treated to reduce its concentration to meet national emission standards. At present, the adsorption method, photocatalytic degradation method, biological method, membrane separation method, and electrochemical method are the main methods used to remove MB dye wastewater [11, 12]. However, the poor biochemical properties of dye wastewater lead to long biological treatment time and weak resistance to environmental interference, causing the treatment effects to be unstable. The disadvantage of the chemical method is that the energy consumption is too high and the capital investment is large. Hence, the adsorption method is widely used because of its low environmental pollution, high treatment efficiency, and simple operation [13].

Graphene oxide (GO), a two-dimensional nanomaterial, has characteristics of a large specific surface area and many oxygen-containing functional groups, and has great application potential in the adsorption field [14, 15].
The adsorption mechanism of dye pollutants in water by GO has been studied extensively, among which electrostatic adsorption is considered as the main mechanism of dye adsorption by GO [16–18]. In addition, the π–π stacking effect [19], hydrogen bonding effect [20], and covalent bond formation [21] may also contribute to the adsorption mechanism of GO. The adsorption capacity of GO comes from its surface structure and functional group properties [22–24].

The excellent physical structure of graphene oxide endows it with high hydrophilicity and other characteristics, which also leads to the fact that although graphene oxide has good adsorption performance, it is difficult to be separated from aqueous solution, which increases the adsorption cost and limits its practical application in wastewater treatment. Therefore, modified GO-based composites have become a research hotspot.

In this paper, graphene oxide (GO) was prepared by the improved Hummers’ method and magnetic chitosan (MCS) was prepared by a coprecipitation method. Based on graphene oxide, modified carboxylated graphene oxide (GOH) and carboxylated graphene oxide/diatomite/magnetic chitosan (GOH/DMCS) composites were prepared, which were shown to enhance adsorption capacity and reduce the hydrophilicity of graphene oxide sheets, and could be easily separated from water. Specifically, the adsorption behaviors of MB on diatomite and magnetic chitosan modified graphene oxide-based adsorbents were studied. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), Zeta potential analysis and vibrating sample magnetometry (PPMS-VSM) were used to characterize the materials. Static adsorption experiments of MB with GOH/DMCS were carried out to explore the adsorption of composite materials under different adsorption conditions, and then that analysis was combined with adsorption kinetics, adsorption isotherms and adsorption thermodynamics for a more holistic view of the process from a theoretical point of view. Then, regeneration experiments using adsorption-saturated GOH/DMCS were carried out to evaluate the regenerative performance of the composites.

2. Materials and methods

2.1. Chemicals and reagents

All chemical reagents used for testing were analytically pure or of a higher purity grade, including graphite powder, H₂SO₄, H₃PO₄, K₂MnO₄, H₂O₂, HCl, absolute ethanol, NaOH, C₂H₃COOH, nano Fe₃O₄, and C₅H₈O₂. All aqueous solutions were prepared with deionized water.

2.2. Preparation of materials

Graphene oxide was prepared using the improved Hummers’ method [25]. The prepared graphite oxide was ultrasonically treated in deionized water for 30 min to fully disperse and exfoliate the graphite oxide to generate a 2 g l⁻¹ GO hydrosol concentration. Then, 2.0 g of sodium hydroxide was added and stirred until completely dissolved, followed by the addition of 3.0 g of chloroacetic acid, which was then ultrasonically dispersed for 1 h. Then, the solution was magnetically stirred for 24 h under constant heating at 25 °C, and the mixed solution was centrifuged and washed with anhydrous ethanol three times. Afterward, the mixture was washed with ample amounts of deionized water several times until the pH was increased to 6.0. The mixed solution was then dried in an oven at 60 °C and then ground and sieved with a 200-mesh sieve to obtain the carboxylated graphite oxide.

To prepare the magnetic chitosan, 0.3 g of chitosan was dissolved in 50 ml of 2% glacial acetic acid solution and heated and stirred until completely dissolved. Then, 0.15 g of nano Fe₃O₄ was added to the above solution and mechanically stirred until it was thoroughly dispersed in the chitosan solution. Then, 2.0 ml of glutaraldehyde was added to the mixed solution and mechanically stirred at 60 °C for 4 h. The obtained product was washed with ethanol and deionized water several times until it reached a pH of 6, and it was then dried in a vacuum drying oven at 60 °C for 12 h. Finally, magnetic chitosan (MCS) was prepared by grinding and sieving with a 200-mesh sieve.

GOH was sonicated in deionized water for 30 min, at which time the GOH hydrosol concentration was 2.0 g l⁻¹. Then, 1.0 g MCS and 3.0 g diatomaceous earth were weighed and added to the GOH solution simultaneously, sonicated for 1 h, and then stirred for 12 h. The obtained product was washed three times with ethanol, washed with a large amount of deionized water until neutral, and then placed in a 60 °C oven to dry for 12 h. Finally, the obtained product was ground and passed through a 200-mesh sieve, stored for use, and then ultrasonically dispersed in deionized water into a certain concentration of GOH/DMCS composite material.

2.3. Testing and characterization

The materials were characterized by SEM, FTIR, XRD, Zeta potential analysis and PPMS-VSM. The main characterization instruments are shown in table 1.
2.4. Adsorption and recycling experiments

We first weighed an amount of sorbent into a 100 ml Erlenmeyer flask. Then, 50 ml of MB solution with a certain concentration was added to the conical flask, and the pH of the solution was adjusted with hydrochloric acid and/or sodium hydroxide. Then, the mixture was suction filtered with a 0.45 μm pore size filter, and the absorbance of the supernatant after suction filtration was measured by arsine azo III spectrophotometry. The adsorption capacity (qe) and adsorption efficiency (w) were calculated according to equations (1).

\[
q_e = \frac{(C_0 - C_e)V}{m} \quad (1)
\]

\[
w = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)
\]

where qe is adsorption capacity (mg/g); C0 is the initial concentration of the solution, mg/L; Ce is the concentration of MB in the solution after adsorption equilibrium is attained, mg l⁻¹; V is liquid volume, mL; m is the amount of adsorbent (mg); and w is adsorption rate (%).

Magnetic separation was carried out on the adsorption-saturated GOH/DMCS composite material from the solution. This material was then placed in 0.2 mol l⁻¹ HNO3 desorption solution at room temperature (25 °C) under an oscillating frequency of 250 r min⁻¹ and oscillated for t min until desorption equilibrium. Then the absorbance of the filtered supernatant was measured by arsenazo III spectrophotometry, and the desorption rate was calculated. After magnetic separation, the GOH/DMCS composite material was cleaned with deionized water several times to attain neutrality, dried in an oven at 60 °C, and the above adsorption-desorption experimental operation was continuously circulated.

According to formula (3), the desorption rate of MB by GOH/DMCS was calculated.

\[
R_d = \frac{V}{M} \frac{C'_e}{q_e} \times 100\% \quad (3)
\]

where \( R_d \) is adsorption rate, %; \( C'_e \) is the concentration of MB in the desorbed solution, mg l⁻¹; V is the volume of liquid, L; M is the amount of adsorbent (g); and \( q_e \) is adsorption capacity (mg/g).

2.5. Adsorption kinetics, adsorption isotherms, and adsorption thermodynamics experiments

The study of adsorption kinetics can be used to describe the speed of dye adsorption by adsorbents, and the adsorption rate is one of the important factors used to judge the adsorption performance of adsorbents. By fitting the experimental data with the kinetic model and understanding its adsorption mechanism, the adsorption rate of the adsorbent can be displayed more intuitively, so as to judge the quality of the adsorbent. In this paper, pseudo first-order, pseudo second-order kinetic and internal diffusion model equations were used to fit the experimental data, and the behavior of the adsorbent was studied [26]:

\[
\ln(q_e - q_t) = \ln q_e - k_1t \quad (4)
\]

\[
\frac{t}{q_t} = \frac{1}{q_e^2k_2} + \frac{t}{q_e} \quad (5)
\]

\[
q_t = k_d t^{1/2} + C \quad (6)
\]

where t (min) is adsorption time, q0 (mg g⁻¹) and qe (mg g⁻¹) are equilibrium adsorption capacity and adsorption capacity at time t, respectively. \( k_1 \) (min⁻¹), \( k_2 \) (g·(mg·min)⁻¹), and \( k_d \) (mg⁻¹·min⁻¹·1/2) are pseudo first-order kinetics, pseudo second-order kinetics and diffusion rate constants in particles, respectively. C is the boundary layer constant.

Adsorption isotherm refers to the relationship between the concentrations of solute molecules in two phases when the adsorption process reaches equilibrium at the interface of two phases at a certain temperature. In this

| Instrument | Model   | Manufacturer             |
|------------|---------|--------------------------|
| SEM        | TESCAN MIRA3 | Tesken Trading Co., Ltd    |
| FTIR       | VERTEX70 | Swiss Brook               |
| XRD        | D/MAX-2500/PC | Nippon Neotoku Corporation |
| Zeta potential | Zetasizer  | Malvern Instrument Co. Ltd |
| PPMS-VSM   | PPMS-9  | Quantum Design, USA       |

Table 1. Primary characterization instruments.
In this section, GO, GOH, DE, CS, GCS, GOH/DCS, and GOH/DMCS composites were used to fit the experimental data, and the adsorption characteristics of the adsorbent to the adsorbate were observed [27].

The linear equations of the Langmuir and Freundlich isothermal models are as follows:

\[ \frac{C_e}{q_e} = \frac{C_r}{q_m} + \frac{1}{q_m \cdot K_L} \]  
(7)

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  
(8)

where \( C_e \) (mg l\(^{-1}\)) is the concentration of MB at adsorption equilibrium, \( q_e \) (mg g\(^{-1}\)) is the adsorption capacity at adsorption equilibrium, \( q_m \) is the maximum adsorption capacity (mg g\(^{-1}\)), \( K_L \) is the Langmuir constant (L mg\(^{-1}\)), and \( K_F \) is the Freundlich constant (mg g\(^{-1}\)).

Further analysis of the Langmuir model allows for the calculation of a dimensionless parameter (\( R_L \)) from the experimental data. The calculation is as follows:

\[ R_L = \frac{1}{1 + C_0 K_L} \]  
(9)

where \( C_0 \) is the initial concentration of the solution, mg l\(^{-1}\).

Thermodynamic analysis was performed to further study energy change during the adsorption process to better understand the effect of temperature change on the adsorption reaction [28]. \( \Delta H^0 \) and \( \Delta S^0 \) can be calculated by the van’t Hoff equation:

\[ \ln K_d = -\frac{\Delta H^0}{R T} + \frac{\Delta S^0}{R} \]  
(10)

where \( K_d \) is the dispersion coefficient, L/g; \( \Delta H^0 \) is enthalpy change, kJ·mol\(^{-1}\); \( R \) is gas constant, \( 8.31 \times 10^{-3} \) kJ·mol\(^{-1}\)·K\(^{-1}\); \( T \) is absolute temperature, K; \( \Delta S^0 \) is entropy change, J·K\(^{-1}\)·mol\(^{-1}\).

\( \Delta G^0 \) is calculated using the following equation:

\[ \Delta G^0 = -RT \ln K_d \]  
(11)

\[ K_d = \frac{q_e}{C_e} \]  
(12)

The change in Gibbs free energy of \( \Delta G^0 \) is kJ·mol\(^{-1}\).

3. Results and discussion

3.1. Material characterization

In this section, GO, GOH, DE, CS, GCS, GOH/DCS, and GOH/DMCS composites were analyzed by SEM, FTIR, XRD, Zeta potential, and PPMS-VSM.

As shown in figure 1, the surface of GO(a) prepared by the improved Hummers’ method is smooth but at the same time there are many wrinkles; compared with GO, the surface of GOH (b) is rougher due to the appearance of more wrinkles and cracks of different shapes and sizes, which may be due to the carboxylation of GO treated with chloroacetic acid, which activates the ester group and epoxide, and converts the hydroxyl group of GO into a carboxyl group (−COOH) [14, 29]; the overall appearance of DE (c) is round [30], with many similar small holes on its surface. The purpose of the acidification of diatomite is to remove impurities in it, so that it can better combine with other materials to prepare adsorbents; CS (d) has a relatively rough surface and porous structure. From MCS (e), the magnetically modified chitosan is mostly white round particles with agglomerated distribution [31]. GOH/DMCS (f) has a different surface appearance from DE, which is a porous disk, and its periphery is covered with a thick wrinkle, which may be due to the successful compounding of carboxylated graphene oxide and modified materials. Its surface is obviously rough, the DE structure is intact, and magnetic chitosan particles similar to those in figure (e) are irregularly attached to the surface of GOH/DMCS composite material, indicating that the modified GOH/DMCS composite material was compounded successfully [32].

The infrared spectra of GO, GOH, DE, CS, GCS and GOH/DMCS are shown in figure 2. From the FTIR spectrum of GO (a), it can be analyzed that the obvious peak at 3406 cm\(^{-1}\) belongs to the −OH asymmetric stretching vibration peak; the vibration at 1650 cm\(^{-1}\) is assigned to the C=O on the carboxyl group of the GO stretching vibration peak, where C=O is attached to the edge of GO; and the peak at 1507 cm\(^{-1}\) reflects the undamaged aromatic region. C=C skeleton vibration absorption peak and OH bond bending characteristic peak; C=O appears at 1260 cm\(^{-1}\) Stretching vibration peak and C=O–C vibration absorption peak [33]. Based on the multitude of oxygen-containing functional groups appearing between GO layers and edges and the above characterization analysis, it is shown that the improved Hummers’ method is successful in preparing GO. Regarding the FTIR spectrum of GOH(b), it can be seen that the characteristic peaks of GO basically appear in
the spectrum, and the characteristic peak at 1171 cm\(^{-1}\) is attributed to the C–O–C antisymmetric stretching vibration; compared with GO at 1600 cm\(^{-1}\), the bending characteristic peak of the –OH bond and the C–O stretching vibration peak of the carboxyl group also appear at the same position. The –OH stretching vibration peak starts to shift from 3406 cm\(^{-1}\), and there is no phenomenon at 3419 cm\(^{-1}\) in the FTIR spectrum of GOH. These peaks indicate that some of the hydroxyl groups in GO are replaced by carboxyl groups in an alkaline environment. The FTIR results clearly confirm the success of the preparation of GOH. In the FTIR spectrum of DE (c), the peak at 3434 cm\(^{-1}\) is attributed to the stretching vibration of the free silanol group Si–OH. The peaks at 1613 cm\(^{-1}\) and 1525 cm\(^{-1}\) are related to the bending vibration of h–O–H water ion \[34\]. The peak at 1090 cm\(^{-1}\) reflects the stretching of the siloxane Si–O–Si group. The peaks at 849 cm\(^{-1}\) and 792 cm\(^{-1}\) are caused by Si–O stretching and SiO–H vibration. The peak at 572 cm\(^{-1}\) reflects the stretching vibration of Si–O–Si \[35, 36\]. In the FTIR spectrum of CS (c), there is an obvious –OH asymmetric stretching vibration peak at 3437 cm\(^{-1}\) and an N-H stretching vibration absorption peak at –NHCO–, a C–H stretching vibration appears at 2992 cm\(^{-1}\); The alcoholic hydroxyl C=O stretching vibration on –NHCO– appears at 1603 cm\(^{-1}\); the peak at 1514 cm\(^{-1}\) is related to the NH stretching vibration on –NH\(_2\); the CH absorption peak appears at 1428 cm\(^{-1}\); the absorption peak at 1078 cm\(^{-1}\) appears as C–O and is caused by the stretching vibration \[37\]. The FTIR spectrum of MCS shows that the characteristic peak of Fe\(_3\)O\(_4\) is located at 580 cm\(^{-1}\), which indicates that the magnetic particles are successfully loaded. The intensity of the hydroxyl peak at 3437 cm\(^{-1}\) on the original CS is significantly weaker, and the peak shifts to the left at 3429 cm\(^{-1}\), indicating that the nano- Fe\(_3\)O\(_4\) particles reacted with the functional groups of chitosan. In the FTIR spectrum of GOH/DMCS, the –OH stretching vibration peak of the carboxyl group appears at 3421 cm\(^{-1}\), which indicates that the hydroxyl groups formed hydrogen bond with one another. The other peaks at 795 cm\(^{-1}\), 1089 cm\(^{-1}\) and 1603 cm\(^{-1}\) correspond to the FTIR of DE. It can be seen that the modified preparation of composite materials still allows the functional group structure of DE to be retained. GOH is covalently bonded to cover the surface of DE, and at the same time, the carboxyl group in GO is also successfully combined with MCS through covalent bonding. According to the electron micrograph, the

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**Figure 1.** SEM images of different materials GO (b) GOH (c) DE (d) CS (e) MCS (f) GOH/DMCS.

**Figure 2.** FTIR spectra of different materials (a) GO (b) GOH (c) DE (d) CS (e) MCS (f) GOH/DMCS.
structure of DE is still retained in the GOH/DMCS composite, which is consistent with the FTIR results. Therefore, the successfully-prepared new composite material maintains the excellent properties of DE.

In this section, XRD (figure 3) is used to analyze the structural changes of crystal materials of each sample. A higher diffraction peak appears in the diffraction spectrum of GO near $2\theta = 10.9^\circ$, indicating that the structure of graphite has been destroyed, the interlayer spacing has become larger, and a new crystal structure has been formed [38]. This peak corresponds to the (001) crystal plane of GO, indicating that GO has been prepared [35]. According to the Bragg formula $2\sin\theta = n\lambda$, the interlayer spacing is 0.81 nm. In the XRD of GOH, the diffraction peak is observed at $2\theta = 10.6^\circ$, and the interlayer spacing is 0.83 nm, which means that the diffraction peak of the same crystal plane shifts to a low angle, and the calculated result shows that the introduction of chloroacetic acid causes the layer spacing of GOH to grow. The dense structure of GO is layered into disordered sheets of GOH to some extent, and the carboxylation treatment increases the number of $-\text{COOH}$ groups at the edges and between the layers of GO. In the XRD of CS (c), there is an obvious characteristic peak of the amorphous structure of chitosan at $2\theta = 19.92^\circ$. The diffraction peak of DE appears near $2\theta = 36.09^\circ$ of the GOH/DMCS composite material, and the diffraction angle is basically unchanged. From the Bragg formula, the layer spacing of the composite material is basically unchanged, which shows that the surface of the GOH/DMCS is successfully loaded with magnetic chitosan and GOH.

Figure 4 shows the Zeta potential value of GOH/DMCS under in the pH range of 2–12, and it can be seen that the electronegativity of the GOH/DMCS surface gradually increases with increasing pH from $-11.9 \text{ mV}$ at $\text{pH} = 2$ to $-30.4 \text{ mV}$ at $\text{pH} = 12$. When $\text{pH} = 2$, the potential value of GO is $-9.5 \text{ mV}$. In contrast, the high electronegativity of the GOH/DMCS surface is caused by the oxygen-containing functional groups introduced.
during the modification process being negatively charged after ionization in the aqueous solution. This facilitates the adsorption of positively-charged cationic dye MB.

From the hysteresis curve of GOH/DMCS in figure 5, it can be seen that the hysteresis loop of the composite material is a symmetrical S-shaped curve across the origin. GOH/DMCS has superparamagnetism and good functionality in aqueous solution. After removing the external magnetic field, it still shows good water dispersibility. Because GOH/DMCS composites are the non-magnetic materials of GOH and DE and the Fe₃O₄ used in MCS is a nanostructure, by weakening the magnetization of the composite material, the saturation magnetization value of the composite material (13.1 emu g⁻¹) is much lower than that of only Fe₃O₄ (52.70 emu g⁻¹) [39].

3.2. Addition of diatomite and the influence of different materials on adsorption
DE content in composite materials can directly affect the adsorption effects of MB. Several groups of 25-ml MB solutions of 30 mg l⁻¹ concentration were taken, and the pH values of the solutions were adjusted to 6.1 g/l GO, GOH, and GOH/DMCS modified by different diatomite addition amounts (1 g, 2 g, 3 g, 4 g, and 5 g), respectively. The samples were subjected to oscillating adsorption for 2 h at 45° C and oscillation frequency of 250 r min⁻¹. The absorbance of supernatant after filtration was measured by spectrophotometry, and qₑ and ω were calculated to explore the influence of diatomite loading and other materials on the adsorption effect.

It can be seen from figure 6 that when increasing the DE amount from 1 g to 5 g, the adsorption capacity of GOH/DMCS adsorbent for the cationic dye MB gradually increases. The reason may be that with increasing DE, the adsorption function is gradually transferred from the oxygen-containing functional groups on the GO surface to the active sites and hydrogen bonding of DE and CS, thereby causing the adsorption capacity to increase. With increasing time, the active sites for MB are saturated and MB is gradually removed. Therefore, with increasing DE, the adsorption capacity increased first and then remained generally unchanged. In summary, the amount of DE added in subsequent experimental studies was 3 g.
According to the adsorption results of MB by GO and GOH in figure 6, the adsorption capacity of MB by GOH is 102.51 mg/g higher than that by GO, which proves that the carboxylation of graphene oxide provides more effective adsorption sites. In addition, the adsorption effect of GOH/DMCS on MB is obviously better than that of GO and GOH.

3.3. Influence of adsorption time on adsorption and adsorption kinetics
This section will study adsorption time as it can often reflect the conditions needed for adsorption to reach equilibrium and the subsequent desorption process. Twenty-five milliliters of 30 mg l\(^{-1}\) MB solution was neutralized to a pH of six, and then 1 g l\(^{-1}\) GOH/DMCS was added and then oscillated for 10 min, 20 min, 30 min, 40 min, 50 min, 60 min, 120 min, 240 min, 480 min, 720 min and 1440 min at 45 °C and an oscillation frequency of 250 \(\text{r} \text{min}^{-1}\). After filtration, the absorbance of the supernatant was measured by a spectrophotometer, and \(q_e\) and \(\omega\) were calculated to explore the influence of adsorption time on the adsorption effect.

It can be seen from figure 7 that the adsorption results of GOH/DMCS on the MB target show a trend that the adsorption capacity increases rapidly and the adsorption rate is faster over the first 2 h, but then the adsorption capacity remains basically unchanged after 2 h. The adsorption equilibrium was reached at 2 h, and the adsorption capacity of GOH/DMCS for MB was 138.90 mg g\(^{-1}\). At the initial stage of the adsorption reaction, there are many available adsorption sites on the adsorbent surface. Because the adsorbent surface is negatively charged, MB can be effectively removed by the adsorbent through electrostatic action, while the hydrogen bond between composite adsorbents also plays a leading role. At the same time, van der Waals forces and \(\pi-\pi\) bonds may accompany the adsorption process, resulting in fast adsorption rate and high adsorption capacity initially. In addition, the adsorption process is accelerated by the high adsorbate concentration difference between the GOH/DMCS surface and the solution [40]. With increasing adsorption time, the adsorption sites on the adsorbent surface are filled with MB, and the number of functional groups on the adsorbent surface decreases due to this action. At this time, the adsorption process is hindered, and the adsorption capacity is basically unchanged. Based on the above conclusions, 2 h was chosen as the optimal adsorption equilibrium time for follow-up studies. In this section, after studying the influence of adsorption time on adsorption, it is necessary to further study the adsorption kinetics of GOH/DMCS on MB.

The fitting results of the kinetic model for GOH/DMCS adsorption of MB are shown in figure 8. It can be seen from the figure that the fitting results of the pseudo second-order kinetic model are better. In addition, It can be seen from table 2 that the correlation coefficient (\(R^2 = 0.9949\)) of the pseudo second-order fitting adsorption results is larger than that of the pseudo first-order fitting adsorption results (\(R^2 = 0.8757\)), which implies that the pseudo second-order kinetic model accurately models the adsorption process and the process is chemical adsorption in nature.

To describe the diffusion of the system in a specific range, an internal diffusion model was used to fit the adsorption process, and the results are shown in figure 9 and table 3. It can be seen from figure 9 that the straight line fitted by \(q_t\) to \(t^{0.5}\) is divided into two sections, and neither section passes through the origin, that is, \(C=0\). This mathematical result shows that the rate of the adsorption reaction was not solely controlled by internal diffusion. As a result of the modification of carboxylate graphene oxide with diatomite and magnetic chitosan, the adsorption of MB using the composite adsorbent is higher. First, through the first stage of intra-particle diffusion, multiple actions such as electrostatic action and hydrogen bonding occur simultaneously. From the adsorption parameters of the internal diffusion model, \(k_{d1}\) of the first stage was greater than \(k_{d2}\) of the second stage.
Stage, which also shows that the adsorption capacity will increase first and then remain basically unchanged with time.

3.4 Influence of pH on adsorption
In this section, experiments were carried out in a pH range of 2–12. Briefly, 25 ml MB solutions with a concentration of 30 mg l\(^{-1}\) were made, and the pH values of the solutions were adjusted to 2, 4, 6, 8, 10, and 12 with NaOH or HCl, respectively. After that, 1 g l\(^{-1}\) GOH/DMCS was added and then oscillated for 2 h at 45 °C. After filtration, the absorbance of the supernatant was measured by a spectrophotometer, and \(q_e\) and \(\omega\) were calculated to explore the influence of pH on the adsorption effect.
It can be seen from figure 10 that with increasing pH, the adsorption capacity of GOH/DMCS for MB increases, reaching a maximum value of 147.62 mg·g⁻¹ at pH = 10, and then plateauing. At the same time, the adsorption rate reaches 81.47% at pH = 10.

When pH = 2–6, H⁺ and cationic organic dyes in the solution compete for adsorption due to the positive charge, and some adsorption sites on the adsorbent surface are occupied by H⁺, resulting in lower adsorption capacity. At the same time, the surface of GOH/DMCS is protonated, and the repulsive force hinders the adsorption process of the adsorbent for the target pollutant. When pH = 6–8, the concentration of OH⁻ in solution increases, and the surface of the GOH/DMCS is negatively charged in an alkaline environment. With increasing pH, the absolute value of Zeta potential increases, and the removal capacity of cationic dye MB increases, so the adsorption capacity and removal rate continue to rise. When pH > 8, the adsorption capacity of MB by GOH/DMCS gradually tends to flatten and reaches its best value near pH = 10. This may be because there is a 'steric effect' between MB molecules adsorbed on the GOH/DMCS surface, which slows down the adsorption process, so the adsorption capacity slowly increases.

3.5. Influence of the dosage of adsorbent on adsorption
This section studies the influence of different dosages of composite adsorbent GOH/DMCS on the adsorption effect of MB. Twenty-five milliliter MB solutions with a concentration of 30 mg l⁻¹ were taken, the pH values of the solutions were adjusted to 10, and GOH/DMCS was added at concentrations of 0.5 g l⁻¹, 1.0 g l⁻¹, 2.0 g l⁻¹, 3.0 g l⁻¹, and 4.0 g l⁻¹, respectively. At 45 °C and an oscillation frequency of 250 r min⁻¹, the samples were oscillated for 2 h. The absorbance of the supernatant after filtration was measured by spectrophotometer, and qₑ and ω were calculated to explore the influence of the dosage of adsorbent on the adsorption effect.

It can be seen from figure 11 that when the dosage of adsorbent is 0.5 g l⁻¹, the adsorption capacity and adsorption rate of GOH/DMCS for MB are 197.73 mg g⁻¹ and 54.93%, respectively. The adsorption capacity and adsorption rate of GOH/DMCS for MB are 34.04 mg g⁻¹ and 94.57%, respectively, when the dosage of adsorbent is 5.0 g l⁻¹. With increasing adsorbent dosage, the adsorption rate of MB by GOH/DMCS increases. On the contrary, the adsorption capacity decreases with increasing adsorbent. With the increased adsorbent...
dosage, the active adsorption sites provided by the adsorbent surface are sufficient, so the adsorption rate continues to rise; however, when the dosage of GOH/DMCS is low, the unit mass of GOH/DMCS can adsorb more MB, and the driving force of mass transfer is large, so the adsorption capacity is higher when the dosage of adsorbent is small. When the dosage of adsorbent increases, the GOH/DMCS may agglomerate, which leads to an overlap and decreased number of adsorption sites on the surface, and the utilization of adsorption sites is insufficient at this time. In addition, with the increased adsorbent dosage, the path of MB diffusion to the adsorbent surface increases, so the adsorption capacity of GOH/DMCS for MB will decrease. In conclusion, the dosage of adsorbent used in subsequent adsorption research was 1 g l\(^{-1}\).

3.6. Influence of temperature and initial concentration of MB solution on adsorption

We also studied the effects of different initial concentrations and temperatures on adsorption efficiency. Twenty-five milliliter MB solutions with different concentrations of 30, 40 and 50 mg l\(^{-1}\) were taken, the pH values of the solutions were adjusted to 10, and 1 g l\(^{-1}\) of GOH/DMCS was added, which was then oscillated for 2 h at 25, 30, 35, 40, and 45 °C, respectively, and an oscillation frequency of 250 r min\(^{-1}\). The absorbance of supernatant after filtration was measured by a spectrophotometer, and \(q_c\) and \(\omega\) were calculated to explore the influence of temperature and initial concentration of MB solution on adsorption.

Figure 12 shows the effects of different initial concentrations and temperatures on MB adsorption by GOH/DMCS. It can be seen from figure 12 that under the same initial concentration, but increasing temperature, the adsorption capacity and adsorption rate both show an increasing trend, indicating that the adsorption reaction of MB by GOH/DMCS is endothermic, and the increasing temperature is beneficial to the adsorption reaction. This may be because the thermal movement of molecules and ions in the solution is intensified at high temperature, so the migration speed of the adsorbate accelerates and the adsorption capacity increases [41].

At the same temperature, with increasing initial concentration of MB solution, the adsorption capacity of MB by GOH/DMCS increases. This may be because the number of active sites on the adsorbent surface is constant, and adsorption is always in an unsaturated state in lowly concentrated MB solution. With increasing initial concentration of MB solution, the adsorbent can remain in the adsorption state until adsorption sites are saturated and adsorption tends to balance, so the adsorption capacity keeps increasing with increasing initial concentration of MB solution until the adsorption reaches equilibrium.

3.7. Adsorption isotherm

Figure 13 shows the fitting results of the adsorption data for the GOH/DMCS using the Langmuir (a) and Freundlich models (b), and table 4 lists the relevant parameters of the fitting results. It can be seen from the graph that the correlation coefficient (\(R^2\)) fitted by the Langmuir model is larger than that fitted by the Freundlich model at different temperatures, so the adsorption process of MB by GOH/DMCS is more in line with Langmuir model, indicating that the adsorption process is more indicative of monolayer adsorption and the surface contains a limited number of uniform adsorption sites [42]. The \(q_{\text{max}}\) values calculated from the fitting curves at different temperatures (298 K, 308 K, and 318 K) are 171.53 mg g\(^{-1}\), 169.49 mg g\(^{-1}\) and 205.34 mg g\(^{-1}\), respectively, which are close to the experimental results of the maximum adsorption capacity. GOH/DMCS positively affects adsorption of MB, which may be due to the following reasons: (1) XRD characterization results show that the interplanar spacing of GOH is larger than that of GO, and this structure will increase the chance of MB entering the adsorbent interlayer and the number of contacts with adsorption
sites and promote the diffusion of cationic dyes to the adsorbent surface or interlayer, which is beneficial to adsorption. (2) With increasing pH, the Zeta potential on the surface of GOH/DMCS increases negatively, so the negative charge on the adsorbent surface is more conducive to adsorption of the cationic dye MB. It can be seen from the dimensionless parameter $R_L$ in the Langmuir model (Table 5) that $R_L$ is between 0 and 1 at three temperatures, so the adsorption of MB by GOH/DMCS is a favorable adsorption process. Table 6 shows a comparison between the adsorption effects of magnetic graphene composites on MB from recent studies, and it can be seen that although the adsorption capacity of magnetized graphene oxide is greater than that of GOH/DMCS, its adsorption time is longer. At the same time, the adsorption capacity of hydroxy-functionalized ionic liquids modified with magnetic chitosan/graphene oxide is also larger, but since GOH/DMCS requires a lower pH value during the adsorption process, it also exhibits more easily achievable conditions and better economic conditions. Therefore, this indicates that the GOH/DMCS composite prepared in this study is a good choice for MB removal and with a wider range of applications.

![Figure 13. Isotherm model of MB adsorption by GOH/DMCS Langmuir model, (b) Freundlich model.](image)

| Table 4. Isothermal parameters of MB adsorption by GOH/DMCS. |
|----------------------------------|
| **Temperature** | **Langmuir model** | **Freundlich model** |
| | $q_{max}$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $R^2$ | $K_F$ (mg g$^{-1}$ L$^{-1/2}$ mg$^{-1/2}$) | $1/n$ | $R^2$ |
| 298 K | 171.53 | 0.1576 | 0.9961 | 34.8131 | 0.4424 | 0.9841 |
| 308 K | 169.49 | 0.3446 | 0.9977 | 54.4498 | 0.3480 | 0.9195 |
| 318 K | 205.34 | 0.3769 | 0.9908 | 65.8402 | 0.9753 | 0.9753 |

| Table 5. Dimensionless parameter $R_L$. |
|----------------------------------|
| **Temperature** | $R_L$ |
| 298 K | 0.1126–0.3882 |
| 308 K | 0.0549–0.2249 |
| 318 K | 0.0504–0.2097 |

| Table 6. Comparative adsorption capacity of several magsorbents for the removal of MB. |
|----------------------------------|
| Reaction conditions |
| Magsorbent | Dose (g/L) | pH | Time (min) | Temperature (°C) | $q_m$ (mg/g) | References |
| Magnetized graphene oxide | 0.15 | 9 | 360 | 25 | 306.50 | [43] |
| Hydroxy-functionalized ionic liquids modified with magnetic chitosan/graphene oxide | 1 | 12 | 60 | 30 | 243.31 | [44] |
| Magnetic chitosan/graphene oxide | 2 | 10 | NR | 30 | 180.83 | [45] |
| Fe$_3$O$_4$ graphene nanosheet | 0.4 | NR | 20 | 25 | 43.82 | [46] |
| Fe$_3$O$_4$ graphene/MWCNTs | 0.2 | 7 | 30 | 10 | 65.79 | [47] |
| Carboxylated graphene oxide/diatomite/magnetic chitosan | 1 | 10 | 120 | 45 | 205.34 | Present work |

![Figure 13. Isotherm model of MB adsorption by GOH/DMCS Langmuir model, (b) Freundlich model.](image)
3.8. Adsorption thermodynamics
Figure 14 and table 7 show the thermodynamic model and parameters of MB adsorption using GOH/DMCS. It can be seen from table 6 that the enthalpy changes of the adsorption reaction \( \Delta H^0 \) are more than 0, indicating that the adsorption process of MB by GOH/DMCS is an endothermic reaction. When \( \Delta H^0 < 20 \text{ kJ} \cdot \text{mol}^{-1} \), the adsorption process is controlled by physical adsorption. When the enthalpy change \( \Delta H^0 = 20 - 80 \text{ kJ} \cdot \text{mol}^{-1} \), chemical adsorption gradually participated in the reaction, and the fitting parameters show that chemical adsorption participated in the adsorption process [48]. At three different temperatures, 298 K, 308 K, and 318 K, the Gibbs free energy change \( G^0 \) is \( < 0 \), and it can be seen from table 6 that the absolute value of \( G^0 \) increases with increasing temperature, which indicates that the adsorption process of MB by GOH/DMCS proceeds spontaneously, and rising temperature is beneficial to adsorption. The entropy change \( \Delta S^0 \) of this reaction is 87.1615 J \cdot (\text{mol} \cdot \text{K})^{-1}, which indicates that the disorder degree of the solid-liquid interface increases during the adsorption of MB by GOH/DMCS.

3.9. Analysis of the experimental results of the adsorption-desorption cycle
Although the adsorption and removal of pollutants are very important for wastewater treatment, the separation of adsorbent from target pollutants and the availability of recycling are also very critical.

After separating dyes from nanocomposites, recycled nanocomposites can be regenerated and reused in various environments. Because of the potential risks of nanocomposites to the environment and health, reusing recycled nanocomposites can solve environmental risks and reduce the consumption of adsorbents.

In this section, the recycling performance of GOH/DMCS adsorbent was studied by desorption, magnetic separation, filtration, drying, and recovery. It can be seen from figure 15 that the desorption rate of GOH/DMCS...
can still reach more than 86% under the action of 0.2 mol \textsuperscript{-1} eluent. Due to the efficient recovery of composite material, the adsorption capacity of GOH/DMCS has not obviously decreased after four adsorption-desorption cycle experiments, which shows that the composite GOH/DMCS provides effective desorption effects and can be used as an effective adsorbent that can be reused.

4. Conclusions

GO was prepared by an improved Hummers’ method and then carboxylated and modified into GOH. Thus, GOH/DMCS was prepared by loading DE and magnetic chitosan with stable chemical properties, large specific surface area, and high porosity. According to the characterization results, modified GOH/DMCS was successfully prepared and can be quickly separated and recovered as an adsorbent. Through MB adsorption experiments, the influence of different factors on the adsorption effect was explored and fitted. The results are as follows: When the pH value of the solution was 10, the adsorption effect and rate were optimal. Due to the gradual saturation of adsorption sites and the decreased contact area per unit mass of adsorbent, with increasing dosage, the adsorption rate increases and the adsorption capacity gradually decreases. With increasing temperature and initial concentration of MB, the adsorption capacity of MB on the composite adsorbent also gradually increased. The second-order kinetic model fit better to the adsorption process of MB by GOH/DMCS, and the correlation coefficient $R^2$ reached 0.9949. The adsorption process of MB by GOH/DMCS was more in line with the Langmuir model, which shows that the adsorption process belongs to monolayer adsorption and the surface contains a limited number of uniform adsorption sites. According to the thermodynamic model, the adsorption process was an endothermic reaction, and chemical adsorption was involved in the adsorption process. Thermodynamically, $\Delta S^\text{f} > 0$ indicates that the disorder at the solid-liquid interface increases. After four adsorption-desorption cycle experiments, the adsorption capacity of GOH/DMCS composites for MB decreased relatively slowly, and the desorption rate of GOH/DMCS could still reach more than 86%. It can be seen that the GOH/DMCS composite not only can be simply prepared and perform well at mild reaction conditions, but its composition is inexpensive, can be recycled, and has a good removal capability for MB, so it has good application prospects.

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