

## 氧化石墨:制备及去除阳离子染料的性能

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**摘要:** 以石墨粉为原料按 Hummers 氧化法制备氧化石墨, 借助 X 射线衍射仪(XRD)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)、傅里叶变换红外光谱法(FTIR)和低温氮吸附-脱附对氧化石墨的结构和形貌进行了表征。结果表明, 氧化石墨是不平整的、具有一定层状结构的褶皱片状, 在其表面存在着许多含氧的官能团如: 环氧基、羟基、羧基。此外还研究了氧化石墨对阳离子染料的吸附性能, 结果表明: 吸附过程的等温模型符合 Langmuir 等温式, 对甲基紫、甲基绿、中性红这 3 种阳离子染料的最大饱和吸附量分别为: 741, 446 和 368  $\text{mg}\cdot\text{g}^{-1}$ ; 对阳离子染料的吸附过程符合二级动力学方程。氧化石墨作为一种吸附剂能有效的去除阳离子染料与其较高的比表面积和与阳离子染料的静电吸引有关。

**关键词:** 氧化石墨; 阳离子染料; 吸附; 热力学; 动力学

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## Graphite Oxide :Preparation and Removal Ability of Cationic Dyes

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**Abstract:** This study reports the preparation of Graphite oxide (GO) and GO as an adsorbent for removal of cationic dyes. GO was synthesized by the oxidation of graphite through the modied Hummers approach. The structure of GO was characterized by XRD, TEM, SEM, FTIR and  $\text{N}_2$  adsorption. The results show that GO is a uneven wrinkled flake with certain layer structure and a large quantities of oxygen-containing fuctional groups exists in the form of epoxy, hydroxyl, and carboxyl groups on the surface of GO. In addition, GO has a good capability towards cationic dyes adsorption. The Langmuirian maximum adsorption capacities of GO are 741  $\text{mg}\cdot\text{g}^{-1}$  for methyl violet, 446  $\text{mg}\cdot\text{g}^{-1}$  for methyl green and 368  $\text{mg}\cdot\text{g}^{-1}$  for neutral red. The adsorption processes follow the pseudosecond-order kinetics model. GO could be used potentially as an effective adsorbent for removal of cationic dyes from aqueous solution possibly due to its electrostatic attraction and large specific surface area.

**Key words:** graphite oxide; cationic dyes; adsorption; isotherms; kinetics

Many industries, such as paper, plastics, food, cosmetics, textile use dyes. The presence of these dyes in water, even at very low concentration, is highly undesirable<sup>[1-2]</sup>. Environmental concern about textile waste-water is the heavy pollution of water with dyes. Adsorption has been extensively investigated for the environmental pollutants removal. Active carbon<sup>[3-4]</sup>,

resin<sup>[5-6]</sup>, expanded graphite<sup>[7]</sup> have been reported as an adsorbent for the treatment of dyes. However commercially actived carbons are usually derived from wood or coal, which are considered expensive<sup>[3]</sup>. This has led to search for cheaper adsorbent. Graphite oxide (GO) seems to be a promising material. Recently, GO has been studied as an adsorbent and their ability to

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remove cationic dyes has been demonstrated<sup>[8]</sup>. GO is a highly oxidized, planar material containing 25%~33% oxygen and have good adsorption between layers<sup>[9-11]</sup>. GO is characterized to be a lamellar solid and can be easily prepared by chemical modification. Generally, GO can be synthesized by oxidation of graphite with strong oxidizing agents such as potassium chlorate, permanganate, bichromate and chlorine dioxides<sup>[12]</sup>. The strong oxidation makes GO has multiple oxygen-containing functional groups, for instance carboxyl (C=O), hydroxyl (C-OH), epoxide (C-O-C) could be covalently attached to its layers<sup>[13]</sup>. Moreover, the spatial distribution of functional groups on the carbon skeleton is also diverse. The epoxide and hydroxyl groups are near each other, and the carboxyl is possibly situated at the edges of graphite oxide<sup>[14]</sup>. These oxygen functionalities make GO extensively disperse in water because the functionalities are hydrophilic, thus stabilizing it to be easily exfoliated in aqueous media through strong stirring or ultrasonication<sup>[15]</sup>. GO has important properties, its layered structure and negatively charged surface can dominate the intercalation process<sup>[16]</sup>. Graphite oxide is a promising precursor for the chemical functionalization of graphene<sup>[10,17-24]</sup>. For these reasons, graphite oxide is attracting much attention.

In this work, we use three different dye molecules, namely positively charged methyl violet; methyl green and neutral red in an aqueous solution, as a probe to investigate the adsorption between GO and cationic dyes. The results indicate that the adsorption between GO and cationic dyes is efficient, possibly due to the different electrostatic attraction between GO and cationic dyes and large specific surface area of GO.

## 1 Materials and methods

### 1.1 Materials

Natural graphite powder with 99.85% carbon content was used for GO syntheses, purchased from Shanghai Colloid Chemical Plant; Concentrated sulfuric acid (98%) and Concentrated hydrochloric acid (36%) were purchased from Beijing Chemical Plant; All other reagents, including methyl violet, methyl green, neutral red, sodium nitrate, hydrogen peroxide, potassium

permanganate were of analytic purity, purchased from Tianjin Chemical Reagent. Solutions of methyl violet, methyl green and neutral red were prepared using distilled water under natural pH conditions.

### 1.2 Synthesis of Graphite oxide (GO)

Graphite oxide was prepared from graphite powders through the modified Hummers method<sup>[25]</sup>, described as follows: graphite powder (1 g) and NaNO<sub>3</sub> (0.5 g) were introduced to concentrated H<sub>2</sub>SO<sub>4</sub> (23 mL) in an ice-bath. KMnO<sub>4</sub> (3 g) was added gradually under stirring, so that the temperature of the mixture could be kept below 20 °C followed by heating to 35 °C for 2 h. Then deionized water (50 mL) was slowly added into the mixture with stirring, followed by stirring the mixture at 80 °C for 30 min. The suspension was further diluted to 150 mL and stirred for 30 min. The reaction was ended by adding H<sub>2</sub>O<sub>2</sub> (5 mL, 35wt%) under stirring at room temperature. Resulting suspension was centrifuged, washed repeatedly with 5% HCl solution, followed washed by excess deionized water, and dried at room temperature.

### 1.3 Characterization

The X-ray powder diffraction (XRD) patterns were recorded on a MSAL-XD2 X-ray diffractometer with Cu-K $\alpha$  radiation (36 kV, 20 mA,  $\lambda=0.154\ 18\ \text{nm}$ ). The morphology observation of the samples was examined with scanning electron microscopy (SEM, Philips XL-30) and transmission electron microscopy (TEM, Philips Tecnai-10). The Fourier transform infrared spectroscopy (FTIR) spectrum was measured by an EQUINOX 55 (Bruker) spectrometer with the KBr pellet technique ranging from 500 to 4 000 cm<sup>-1</sup>. The BET surface area of the sample was measured on a Tristar 3000 (Micromeritics) instrument. The  $S_{\text{BET}}$  and porosity of the samples were evaluated on the basis of nitrogen adsorption isotherms measured at -196 °C. Prior to the adsorption experiments, all the samples were degassed at 120 °C for 6 h. Total pore volume was calculated at relative pressure  $p/p_0=0.972$ , moreover, the pore size was analyzed by the Barrett-Joyner-Halenda (BJH) method.

### 1.4 Adsorption studies

Adsorption Equilibrium experiments were carried

out by contacting 0.02 g GO with 100 mL solutions of with various initial methyl violet, methyl green and neutral red concentrations under nature pH value at 25 °C in a shaker. At the end of the adsorption experiments, solution samples were centrifuged and the cationic dyes were measured using an UV-Vis spectrophotometer. Adsorption kinetic experiments were basically identical to those of equilibrium experiment, conducted by 100 mL solution of methyl violet, methyl green and neutral red with various initial concentrations and 0.02 g GO. The sample was taken out at appropriate time intervals and the concentration of cationic dyes was also analyzed using an UV-Vis spectrophotometer. The adsorption capacity was calculated from the following expression:

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where  $c_0(\text{mg} \cdot \text{L}^{-1})$  and  $c_e(\text{mg} \cdot \text{L}^{-1})$  are the initial and equilibrium concentrations of cationic dyes,  $q_e(\text{mg} \cdot \text{g}^{-1})$  is adsorption capacity of adsorbent ( $\text{mg} \cdot \text{g}^{-1}$ ),  $V$  (L) is the volume of the solution, and  $m$  (g) is the does of the adsorbent.

## 2 Results and discussion

### 2.1 Characterization of Graphite Oxide

As shown in Fig.1 the diffraction peak of graphite is observed at  $2\theta=26.56^\circ$ . After oxidation the graphite diffraction peak disappears and the XRD pattern for GO shows only one peak at  $2\theta=10.92^\circ$ , indicating that a highly oxidized GO sample has been synthesized.

Fig.2a shows a typical TEM image of GO, as seen from the TEM image, GO has a two-dimensional structure. The uneven wrinkled layer structure is observed on the SEM of the GO in Fig.2b.

Fig.3 show the FTIR spectra of graphite and GO. The result indicate that there are few functional groups on the surface of graphite, while the GO exhibits many functional groups. The broad absorption at  $3\ 200\sim3\ 400\ \text{cm}^{-1}$  for O-H stretching vibrations, a band at  $1\ 721\ \text{cm}^{-1}$  can be assigned to the C=O stretching vibrations,  $1\ 622\ \text{cm}^{-1}$  for water H-O-H bending, the bands at  $1\ 407\ \text{cm}^{-1}$ ,  $1\ 223\ \text{cm}^{-1}$ ,  $1\ 048\ \text{cm}^{-1}$ ,  $987\ \text{cm}^{-1}$  correspond to stretching vibrations of the tertiary alcoholic C-OH

stretching, phenolic C-OH stretching, C-O stretching, epoxy Stretching, respectively<sup>[24,26-30]</sup>. These results

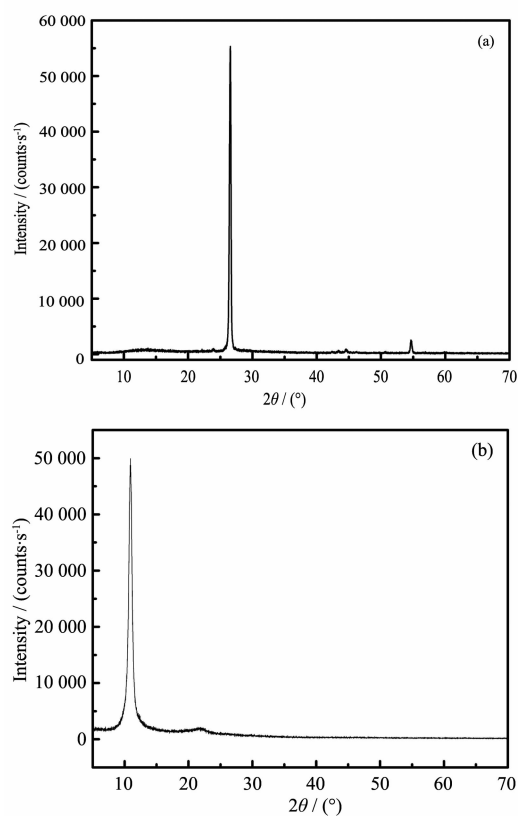


Fig.1 XRD patterns:(a) pristine graphite, (b) graphite oxide

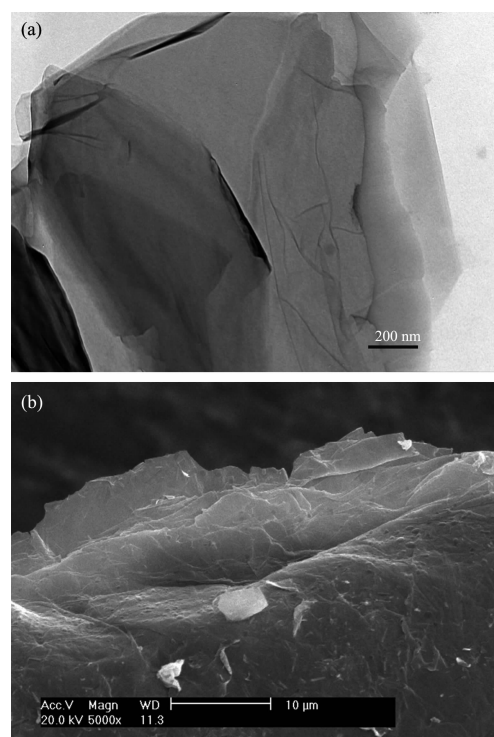


Fig.2 (a) TEM image of GO, (b) SEM image of GO

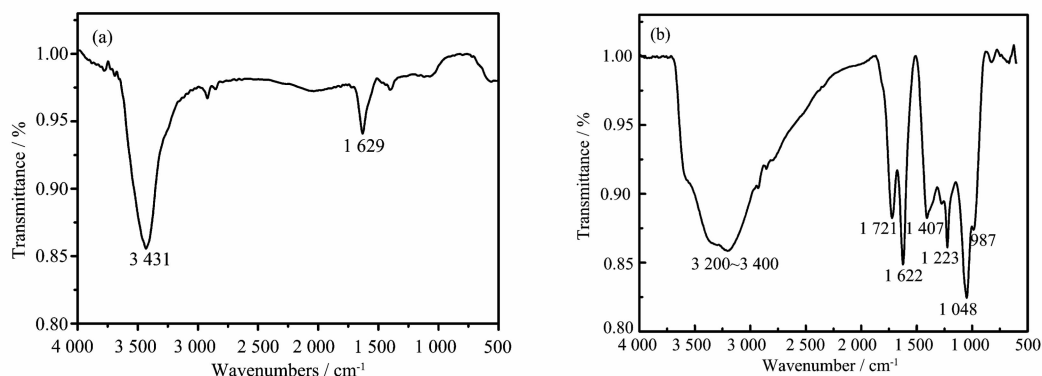


Fig.3 (a) FTIR spectra of pristine graphite, (b) FTIR spectra of GO

indicate that the functional groups of GO are carboxyl, epoxy and hydroxyl groups [10,19,29]. These oxygen functionalities make GO extensively disperses in water [15].

The specific surface areas and the total pore volumes obtained from the nitrogen adsorption

isotherms are listed in Table 1. The specific surface area of GO is  $301 \text{ m}^2 \cdot \text{g}^{-1}$  and better than those in previous reports [8,16]. As shown in Fig.4a the nitrogen adsorption isotherms are type-IV, indicating the presence of mesopores [31-34].

Table 1 Textural Parameters of the GO

Material	$S_{\text{BET}} / (\text{m}^2 \cdot \text{g}^{-1})$	$V / (\text{cm}^3 \cdot \text{g}^{-1})$	Average pore size / nm
GO	301	0.73	13

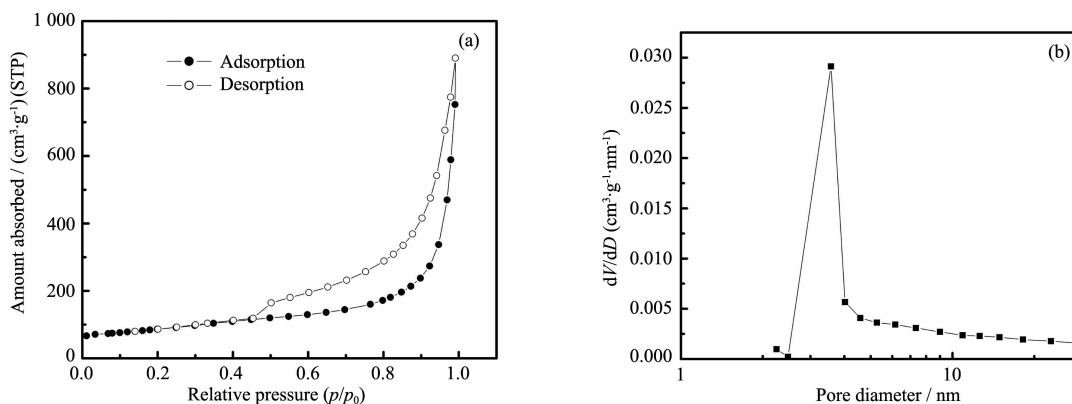


Fig.4 (a) N<sub>2</sub> adsorption-desorption isotherms at 77 K, (b) pore size distribution for the as-prepared GO

## 2.2 Adsorption of Graphite Oxide

In order to analyze the sorption isotherm, two isotherm models are used in this paper. One is the Langmuir model [35-39]. The Langmuir model can be described as:

$$\frac{c_e}{q_e} = \frac{1}{K_a q_{\max}} + \frac{c_e}{q_{\max}} \quad (2)$$

The other is the Freundlich model [35-38]. The Freundlich model can be written as:

$$q_e = K_F c_e^{1/n} \quad (3)$$

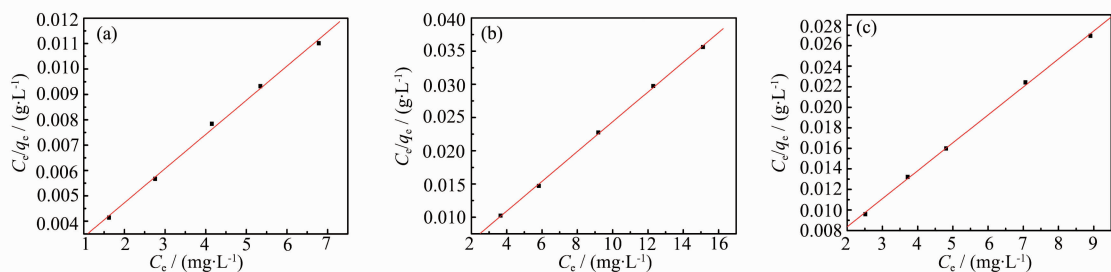
where,  $c_e (\text{mg} \cdot \text{L}^{-1})$  is the equilibrium concentration,

$q_e (\text{mg} \cdot \text{g}^{-1})$  is the adsorption amount at equilibrium,  $q_{\max}$  is the maximum adsorption capacity and  $K_a$  is the Langmuir adsorption constant ( $\text{L} \cdot \text{g}^{-1}$ ), where  $K_F (\text{L} \cdot \text{mg}^{-1})$  is the adsorption capacity at unit concentration and  $1/n$  is the adsorption intensity. The value of  $1/n$  falling in the range of 0~1 indicates favorable sorption [40]. Fig.5 shows the Langmuir isotherm of methyl violet, methyl green and neutral red. The parameters obtained are presented in Table 2.

From Table 2, the equilibrium data are very well described by the Langmuir isotherm model when

Table 2 Parameters of Adsorption Isotherms from Langmuir and Freundlich Models

Dye	Langmuir isotherm			Freundlich isotherm		
	$q_{\max} / (\text{mg} \cdot \text{g}^{-1})$	$K_a / (\text{L} \cdot \text{mg}^{-1})$	$R^2$	$K$	$1/n$	$R^2$
Methyl violet	741	0.665	0.997	344	0.307	0.987
Methyl green	446	1.14	0.999	315	0.111	0.917
Neutral red	368	0.928	0.999	223	0.180	0.989



(a) methyl violet; (b) methyl green; (c) neutral red

Fig.5 Langmuir adsorption isotherms

compared to the Freundlich model. The calculated correlation coefficient values for langmuir model (0.997 ~0.999) are greater than Freundlich model (0.917~0.990) and the value of  $1/n$  falling in the range of 0 ~1 indicates that Freundlich model can also described the equilibrium data. The maximum sorption capacity of methyl violet, methyl green and neutral red are  $741 \text{ mg} \cdot \text{g}^{-1}$ ,  $446 \text{ mg} \cdot \text{g}^{-1}$  and  $368 \text{ mg} \cdot \text{g}^{-1}$ , respectively. The large maximum sorption capacity are mainly due to the different electrostatic attraction between GO and cationic dyes. The maximum sorption capacity of methyl violet was better than those of methyl green and neutral red, possibly due to the different positively charged on the surface of the three cationic dyes. This work remains to be studied.

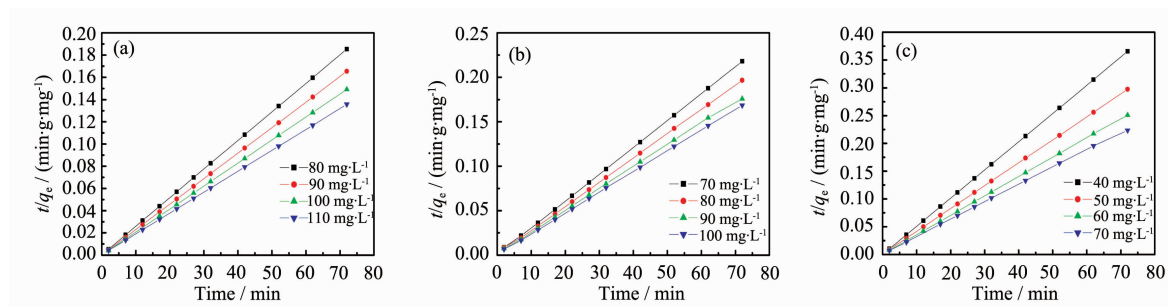
Several experiments were undertaken to analyze the effect of varying the initial cationic dyes concentration on the dye-removal kinetics from

solution. The adsorption kinetics of cationic dyes is studied according to the pseudosecond-order model, which can be expressed as:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (4)$$

where  $k (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$  is the rate constant of the pseudosecond-order adsorption,  $q_e (\text{mg} \cdot \text{g}^{-1})$  and  $q_t (\text{mg} \cdot \text{g}^{-1})$  are the quantities of cationic dyes adsorbed at equilibrium and at any time  $t$ . Fig.6 shows the adsorption kinetics of methyl violet, methyl green and neutral red. The parameters obtained are presented in Table 3.

From Table 3, we can see that the good calculated correlation coefficient values for cationic dyes agree well with the pseudosecond-order kinetics. Also these suggest the assumption behind the pseudosecond-order model that the dye uptake process is due to chemisorption<sup>[35]</sup>. An increase in initial cationic dyes



(a) methyl violet; (b)methyl green; (c)neutral red

Fig.6 Adsorption kinetics

**Table 3** Parameters of Pseudosecond-Order Kinetics for methyl violet, methyl green and neutral red adsorption and GO

	$C_0 / (\text{mg} \cdot \text{L}^{-1})$	$q_e / (\text{mg} \cdot \text{g}^{-1})$	$k / (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$	$R^2$
Methyl violet	80	389	$2.37 \times 10^{-2}$	1
	90	437	1.36	1
	100	483	$1.61 \times 10^{-1}$	1
	110	532	$1.21 \times 10^{-2}$	1
Methyl green	70	332	$1.11 \times 10^{-2}$	0.999
	80	369	$8.36 \times 10^{-3}$	0.999
	90	408	$3.87 \times 10^{-3}$	0.999
	100	429	$7.50 \times 10^{-3}$	0.999
Neutral red	40	197	1.02	1
	50	243	$3.58 \times 10^{-2}$	0.999
	60	287	$1.65 \times 10^{-2}$	0.999
	70	322	$6.86 \times 10^{-3}$	0.999

concentration leads to decrease in the rate constants values. The difference in rate constants is significant.

### 3 Conclusions

We present a method of preparing GO and characterize the GO, we find that GO is with the uneven wrinkled flake layer structure and the large quantities of oxygen exists in the form of epoxy, hydroxyl, and carboxyl groups on the surface of GO. The adsorption behavior of methyl violet, methyl green and neutral red follows the Langmuir adsorption isotherm with a maximum adsorption capacity of  $741 \text{ mg} \cdot \text{g}^{-1}$ ;  $446 \text{ mg} \cdot \text{g}^{-1}$  and  $368 \text{ mg} \cdot \text{g}^{-1}$ , respectively. The good linear relationship for three cationic dyes indicates that the adsorption agree well with the pseudosecond-order kinetics model.

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