

Effects of the oxidation degree of graphene oxide on the adsorption of methylene blue[☆]



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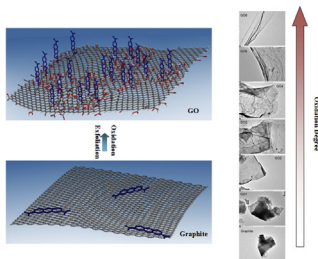
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HIGHLIGHTS

- A series of graphene oxides (GO) with different oxidation degrees (OD) were prepared.
- The GO series shows an overall fast and pH-independent dye adsorption.
- Dye uptakes of GO are exponentially increased with the increase of OD.
- GO would change from Freundlich-type to Langmuir-type adsorption as OD increases.
- Various interactions of dye with GO exist in oxidation and non-oxidation region of GO.

GRAPHICAL ABSTRACT

With increasing oxidation degree of GO, the interaction modes are gradually changed from MB parallel stacking on graphite plane through π - π interactions to vertical standing via electrostatic interactions.



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ABSTRACT

In this current work, a series of graphene oxides (GO) with different oxidation degrees (OD) was prepared using Hummer method. Fundamental adsorption behavior of the GO series for removal of methylene blue (MB) from aqueous solutions has been studied. The GO series shows an overall fast and pH-independent MB adsorption, which is even capable of removing trace levels of dye completely from very dilute solutions. Furthermore, the effects of the oxidation degree (OD) on MB adsorption behavior have been investigated systematically, indicating that the dye uptakes of GO exponentially increase with the increase of OD. Further study on the adsorption mechanism shows that adsorption behavior of GO would change from a Freundlich-type to a Langmuir-type adsorption as the OD increases. It may be due to both the enhanced exfoliation degree of the carbon planes in graphite caused by oxidation and the production of more active adsorption sites. The binding features of the MB loaded GO gradually change from MB molecule parallel stacking on graphite plane through hydrophobic π - π interaction to vertical standing via electrostatic interaction with increasing OD, resulting in a significant improvement of MB uptakes. In addition, the adsorption capacity of the regenerated GO has little loss until four cycles.

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1. Introduction

Recently, the application of nanomaterials in water treatment plants has attracted significant attentions for the advantages of

large surface areas and more activated functionalized sites [1,2]. Among them, two-dimensional (2D) grapheme, with an atomic thickness and a large planar size, is more fascinating. In fact, grapheme-based materials have already made great impacts in many fields ever since its discovery in 2004 [3–8]. Graphene oxide (GO) [9–11] is one of the most important graphene-based materials. Its dispersibility and affinity to many pollutants in water have been greatly enhanced for containing various functional groups in GO, such as hydroxyl, carboxyl and epoxy groups [12–16]. Unlike the special oxidation processes of carbon nanotubes (CNTs), another kind of popular carbon-based nanomaterials, the preparation of

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GO is much easier using Hummers' method [17] and provides the potential of cost-effective and large-scale production [2,11,18]. Moreover, differing from the potential hazard of CNTs to human health [19], GO shows fine biocompatibility [9]. All of the aforementioned outstanding features of GO demonstrate its greatly potential applications as an excellent water treatment agent.

In fact, previous studies [10,11,14,20] have already proven that GO could be efficient removal of various kinds of organic matters and metal ions from water. The role of GO in water treatment is becoming increasingly significant, so well understanding the treatment mechanism is of great importance. Obviously, adsorption is the most commonly involved one, because GO is found to be highly adsorptive activity and bears high affinity to many contaminants, including dyes, heavy metals, and phenols [21,22]. The affinity of GO can be mainly attributed to two aspects: the oxygen-containing functional groups and the aromatic matrix. The former ones are facile to bind hydrophilic species due to electrostatic interactions or hydrogen bonds, and the latter one tends to hydrophobic organics by π - π stacking or hydrophobic interactions [23–25]. However, the relative ration of the two functional regions in GO is flexible and varies greatly with oxidation conditions, making GO a material of structural diversity that bears variant adsorption selectivity and characteristics [26]. Furthermore, it is obvious that the adsorption performance of GO is greatly dependent on its structural features. Therefore, a detailed investigation on the effects of structural features, such as oxidation degree of GO, on its adsorption behavior is very beneficial to understanding of adsorption mechanism and especial interactions between GO and contaminants from molecular levels. As a result, a proper GO-based material could be selected or designed successfully according to the characteristics of targeted contaminants and treatment mechanism.

In this work, a series of graphene oxide with different oxidation degrees was prepared successfully using Hummer method by adjustment of oxidation time and dose of oxidant. The structural features of GO have been characterized by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, wide-angle X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and zeta potential. A typical cationic dye with aromatic structure, methylene blue, was chosen as the model contaminant in investigation of the adsorption performance of GO, whose molecular structure is available in the supplementary information Fig. S1. The effects of pH, dye concentration and adsorption time on removal of MB from aqueous solutions by the GO series have been studied systematically. The adsorption mechanism has been discussed in detail, and the relationship between the oxidation degree of GO and its adsorption performance has been built.

2. Materials and methods

2.1. Materials

Graphite and methylene blue were purchased from Tianjin Institute of Chemical Reagents. Sulfuric acid, KMnO_4 , sodium nitrate, and hydrogen peroxide were all available from Sinopharm Chemical Reagent Co. Ltd. All the reagents are analytical grade.

2.2. Preparation of graphene oxides with different oxidation degrees

Graphene oxides with different oxidation degrees were all prepared based on Hummers method [17]. KMnO_4 was used as oxidant. With some variation in the dose of oxidant and the oxidation time in each preparation process, six GO samples with different oxidation degrees have been obtained successfully and nominated

GO1-6, respectively. The detailed preparation conditions are listed in Table 1.

2.3. Characterization of the graphene oxides

2.3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the GO series and graphite were recorded using a Fourier transform infrared spectrometer (Type TENSOR 27; Bruker Co.; Germany). The range of the scanning wave numbers was 500–4000 cm^{-1} .

2.3.2. Raman spectroscopy

Raman spectra of the GO series and graphite were carried out using a Raman spectrometer (Type LabRAM Aramis; Horiba Co. Ltd.; Japan) with 532 nm excitation wavelength. The scanning range was 300–2000 cm^{-1} .

2.3.3. Wide-angle X-ray diffraction (XRD)

The wide-angle X-ray diffraction patterns were recorded on an X-ray diffraction spectrometer (Type XRD-6000; Shimadzu Co. Ltd.; Japan) at a voltage of 40 kV and a current of 30 mA using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418$ nm). The scanning range (2θ) was 5–50°.

2.3.4. X-ray photoelectron spectroscopy (XPS)

XPS spectra of the GO series were taken on an X-ray photoelectron spectrometer (Type ULVAC-PHI 5000; VersaProbe™, Northrop Grumman Co. Ltd.; USA). The scanning range was 0–1000 eV.

2.3.5. Transmission electron microscopy (TEM)

The surface morphologies of the GO series and graphite were observed using a transmission electron microscope (Type JEM-1011; JEOL Co.; Japan). The acceleration voltage was 100 kV.

2.3.6. Zeta potential analysis

Zeta potential analyses of the GO series were carried out on a zeta potential instrument (Type Nano-Z; Malvern Co. Ltd.; UK). The range of initial pH was 2.0–12.0, adjusted by dilute HCl or NaOH aqueous solutions.

2.4. Methylene blue adsorption experiments

The GO series with different oxidation degrees was applied in removal of methylene blue from aqueous solutions.

2.4.1. Effect of initial solution pH

The effect of initial solution pH on MB adsorption was conducted at 298 K. The initial dye solution pH was ranged from 2.0 to 10.0, adjusted using dilute HCl or NaOH aqueous solutions. At pH higher than 10.0, precipitation of dyes would occur simultaneously, which lead to inaccurate interpretation of adsorption. 0.015 g of GO was firstly dispersed in 15 cm^3 of water and ultrasonicated for 15 min for full exfoliation of GO, then equal volume of MB solution with different solution pH was mixed with the GO suspension, respectively. The mixed solutions were put under continuous stirring for 24 h to achieve adsorption equilibrium. The initial dye concentration of the MB and GO mixture was designed approximate 600 mg dm^{-3} based on the adsorption isotherms.

The dye concentration was analyzed on a 720 Vis spectrophotometer. The analyzing wavelength for MB is 662 nm. Appropriate dilution was performed to ensure that the dye concentration was within the range of the standard curve. MB uptakes (q , mg g^{-1}) are calculated from the dye concentration change in the adsorption process. The equation for calculation is shown below:

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

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