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Characteristics and electrical conductivity of graphene and graphene oxide for adsorption of cationic dyes from liquids: Kinetic and thermodynamic study

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ABSTRACT

Graphene (G) and Graphene oxide (GO) were employed in the present study for the removal of two toxic cationic dye Basic Red 12 (BR 12) and Basic Red 46 (BR 46), from aqueous solutions. Graphene oxide was synthesized by Hummer–Offeman method, and then characterized by XRD (X-ray diffraction), and FT-IR (Fourier Transform Infrared spectroscopy). The influence of various physico-chemical parameters such as electrical conductivity behaviors, contact time, solution pH, dye concentration and temperature were well investigated and elucidated. The kinetics and thermodynamics of the toxic dye removal process were also investigated; results clearly depicts that the kinetics of the removal of BR 12 and BR 46 using G and GO as adsorbents follows a pseudo-second-order model. G and GO exhibited high-adsorption capacity for BR 12 and BR 46. The dye removal depends on the initial pH of the solution with the maximum uptake occurring at about pH 9. Moreover, the thermodynamic results confirmed that adsorption of dye BR 46 on G and GO were exothermic and adsorption of dye BR 12 on G and GO were endothermic in nature. The electrical conductivity behaviors of the aqueous solution were found to be enhanced by oxidation of graphene.

Introduction

Water pollution due to the indiscriminate disposal of dye contaminants has been a rising worldwide environmental concern. For example, wastewater from many industries such as textile and dyeing, etc., contains one or more toxic dyes [1]. For environmental protection, it is necessary to remove this pollution from the wastewater before releasing into the environment [2]. Entire removal of dyes contaminants in natural water resources can not only protect the environment itself, but also stop the toxic contaminant transfer in food chains. Traditional techniques for treatment of dyes include sedimentation, chemical treatment, oxidation, electrochemical methodology [3–7], biological treatment, reduction, precipitation, membrane filtration, ion exchange and adsorption [8,9]. Among the above methods, the most promising process for the removal of dyes is adsorption. So far, researchers have tested many different types of developed adsorbents such as activated carbon [10], zeolite [11] and polymer [12] carbon nanotubes [13–20], MWCNTs [21,22], nanoparticles and nanocomposites [23–27], rubber tire [28,29], and other low cost adsorbents [30–35] etc. are used for the removal of noxious impurities from the aqueous solution. However, these adsorbents have been suffering from either low adsorption capacities or low efficiencies. Therefore, tremendous effort has been made in recent years to seek new adsorbents and develop new techniques. An ideal adsorbent should have the ability to rapidly and efficiently remove toxic contaminants from environments to a safety level.

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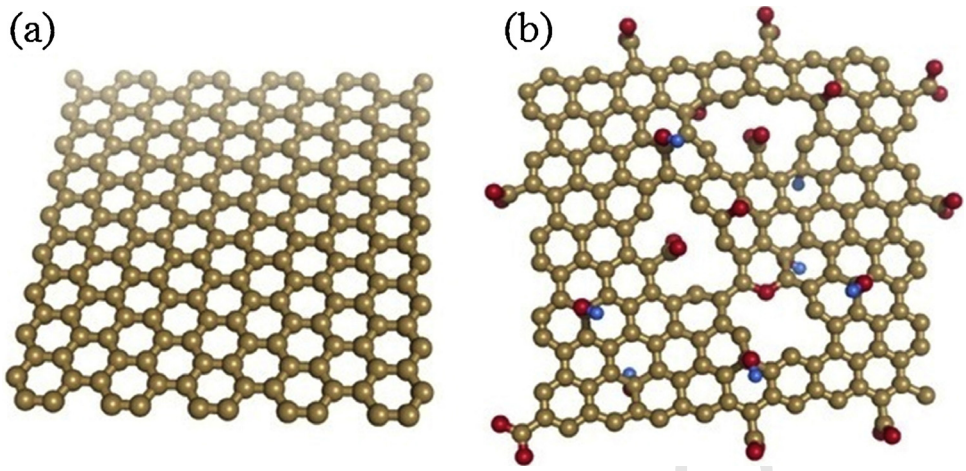
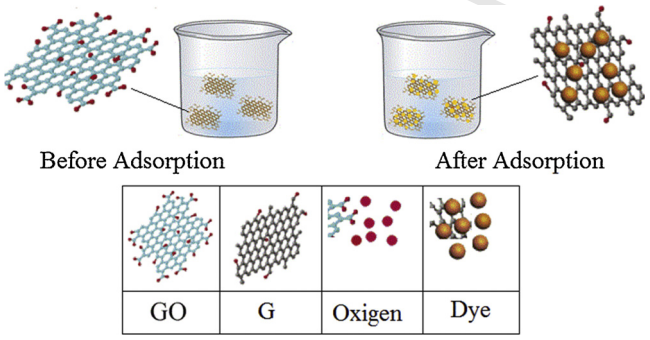


Fig. 1. Schematic chemical structure of graphene (a) and graphene oxide (b).

Since its discovery by Novoselov et al., in 2004 [36], graphene, a one-atom-thick planar sheet of sp^2-bonded carbon atoms densely packed in a honeycomb crystal lattice, has become a rapidly rising star among carbon materials, triggering a gold rush to exploit its possible applications both in academics and industry (Fig. 1a). Graphene is considered as the mother element of some carbon allotropes, which is a basic building block for graphitic materials of all other dimensionalities, and can be converted into fullerenes, carbon nanotube (CNT), or 3D graphite via wrapping, rolling, or stacking, respectively [37,38]. Because of its unique nanostructure, graphene has many novel properties, such as high surface area, excellent electrical conductivity and electron mobility at room temperature, and unique thermal and mechanical properties [39]. However, graphene is hydrophobic and, consequently, stable dispersions in polar solvents can only be obtained with addition of proper surfactants [40]. Graphene oxide (GO) is similar to graphene, but presents oxygen-containing functional groups (Fig. 1b) [41–43]. The presence of these polar and reactive groups reduces the thermal stability of the nanomaterial, but may be important to promote interaction and compatibility with polar solvents or with a particular polymer matrix [44]. Both G and GO can be modified in order to obtain other functionalized graphene with suitable properties for specific applications [45,46].

In the present study, we investigated the removal property of BR 12 and BR 46 using G and GO as adsorbents in aqueous solutions. The influence of several parameters such as kinetics, thermodynamics, contact time, dye concentration, and solution pH on the removal capacity were evaluated and discussed. Scheme 1 provides an overview about the process we used in this study.



Scheme 1. Interaction between of graphene oxide and dye.

Experimental

Materials and methods

The cationic dye Basic Red 12 (BR 12) and Basic Red 46 (BR 46) (Merck, Germany) were purchased from the market, and were used without any further purification. The stock solutions (1000 ppm) of BR 12 and BR 46 dye were prepared by dissolving accurately weighed quantity of dye in 1 L of double distilled deionized water. The experimental solutions of desired concentration were prepared accordingly by diluting the stock solution with distilled water. The concentration of dyes was measured using UV–visible spectrophotometer (Shimadzu UV-1700 Double Beam). The chemical structure and characteristic of BR 12 and BR 46 dyes are shown in Table 1. Fresh dilutions were used for each experiment. The pH of the working solutions was adjusted to the desired values with dilute HCl or NaOH using a pH-meter.

Purified natural graphene (monolayer graphene film) was purchased from Sigma–Aldrich Inc. Other chemicals unless noted were purchased from Merck Inc.

Batch removal of dyes

Tests for dyes removal were carried out in 100 mL conical flasks containing 20 mL BR 12 and BR 46 solutions in a water bath. The optimum parameters including solution pH (2–9), dye concentration (20–80 mg/L), temperature (20–40 °C), and contact time (0–90 min) have been elucidated. The amount of each adsorbents G and GO used for dye removal was 0.05 g. After each removal, the samples were centrifuged at 2000 rpm for 20 min for separation adsorbents from dye solutions. The residual dye molecules concentrations in solution were analyzed by a UV–vis spectrophotometer at 469 nm for BR 12 and at 530 nm for BR 46. The kinetic and thermodynamic studies were performed by determining the removal conditions. The removal efficiency and adsorption by solid surface, q (mg/g) capacity were calculated using the following equations [47,48]:

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

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$