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Removal of methyl green dye molecule from aqueous system using reduced graphene oxide as an efficient adsorbent: Kinetics, isotherm and thermodynamic parameters

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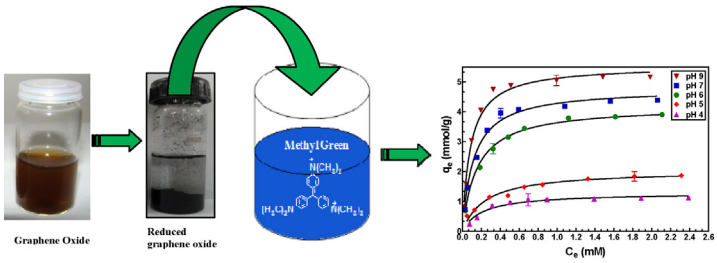
HIGHLIGHTS

- The C—C bond distance of graphene oxide and reduced graphene oxide was calculated.
- Investigation of the adsorption behavior of methyl green, a cationic dye molecule onto reduced graphene oxide nanosheets.
- Effect of time, temperature, pH, presence of other ions in solution on adsorption was studied.
- The mechanism of adsorption was investigated using FTIR and XRD analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Dyes released from different industries are one of the major pollutants in the water system. So removal of dye before disposal to the main water stream is necessary. In this study, adsorption technique was adopted for removal of the cationic dye from aqueous system using reduced graphene oxide (rGO) as adsorbent material. The kinetic study of adsorption shows that the present system follows pseudo second order kinetic (linear) model. Adsorption isotherm investigation indicates that the adsorption of methyl green onto rGO nanosheets follows the isotherm models in the order Toth > Sips > Dubinin–Radushkevich (D–R) > Scatchard > Langmuir > Temkin > Freundlich model in the pH range 4–6. However, the order changes to D–R > Scatchard > Toth > Sips > Langmuir > Temkin > Freundlich model at pH 7 and 9. The adsorption capacity of methyl green onto the rGO nanosheets increases with increasing pH of the medium due to the change in the surface properties. Presence of other ions like Na^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} also influenced on adsorption due to the change in the surface properties. The magnitude of ΔG° values are found to be in the characteristic range of physisorption nature of adsorption. Further, the mechanism of the adsorption process was investigated by FTIR spectroscopy and it indicates that the adsorption is due to electrostatic interaction between methyl green dye molecule and rGO nanosheets. X-ray radial distribution function (RDF) analysis revealed the formation regular molecular packets of graphene. X-ray diffraction (XRD) analysis of the rGO nanosheets before and after adsorption of the dye molecule indicates that some textural changes occur in the rGO nanosheets upon adsorption of the methyl green dye molecule.

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1. Introduction

Graphene is one of the most fascinating advanced materials with two dimensional honeycomb of carbon atoms used in different research area. This excitement is greatly attributed to its excellent mechanical and physicochemical properties [1]. The high surface area and presence of sp^2 hybridized carbon atoms make graphene a promising material for application in a number of fields such as catalysis, sensor, adsorption and so on. It is also extensively studied that the use of graphene and its derivative as template for synthesis of the nanomaterials. Graphene has a very good potential as adsorbent material due to the electronic conjugation present at its basal plane.

Water pollution has become a subject of global environmental concern in recent years. Dyes from the different industries such as dye synthesis, paper, printing, electroplating, food and cosmetic are one of the major source of water pollution. Many of the dyes and their products are harmful to flora and fauna; some of which have mutagenic or carcinogenic effect [1]. Therefore, removal of these dyes before disposal into main water stream is extremely important. Adsorption is the most widely used in this regard due to its simple operation procedure and cost effectiveness [1–5]. A number of adsorbents have been studied for removal of dye molecules from water system. Development of new effective and eco friendly adsorbent materials for removal of dye and other pollutants from water system is always getting special interest of worldwide researchers. In this regard, the efficiency of graphene and its derivatives toward removal of dye molecule are being studied in recent few years. Ramesha et al. reported adsorption of a number of cationic and anionic dye molecules such as methylene blue, methyl violet, rhodamine B, and orange G onto graphene oxide (GO) and graphene in aqueous medium [6]. Liu et al. reported the adsorption of methylene blue onto graphene surface [7]. So, the details investigation of adsorption parameters is very important to develop an adsorbent material with optimum efficiency. However, so far of our knowledge, only limited kinetic and isotherm models have been studied in dye molecule–graphene system. In this paper, we have investigated the adsorption behavior of cationic dye molecule from aqueous system onto graphene nanosheets by taking methyl green as model molecule. The adsorption behavior was investigated by considering different parameters such as kinetics, isotherm, effect of pH, temperature and presence of different inorganic ions. The adsorption kinetics was studied with different models namely pseudo first order, pseudo second order (linear), pseudo second order (non–linear), Elovich, Richi and Bajpai models. In this study, seven different isotherm models namely Langmuir, Freundlich, Sips, Toth, Temkin, Scatchard and Dubinin and Radushkevich (D–R) models were used to analysis the adsorption isotherm experimental data.

To develop a good adsorbent material, its synthesis method should be eco-friendly and cost effective. In this method, graphene was synthesized by reduction of GO using ascorbic acid as reducing agent under ultrasonication. The X-ray radial distribution function (RDF) method is also applied for the first time to calculate the C—C bond distance of the chemically derived GO and graphene.

2. Experimental

2.1. Materials

Graphite powder (<20 μm) was purchased from Sigma-Aldrich and used as-received. Sulfuric acid (AR grade, Qualigens, India), hydrochloric acid (AR grade, Qualigens, India), H_2O_2 (30%, Qualigens, India), potassium permanganate (>99%, E-Merck, India), NaOH (99%, Qualigens, India), ascorbic acid (99%, Fisher Scientific, India), ethanol (≥99.9%, E Merck, Germany) and methyl green (LobaChemie, India) were used as received without further purification. Deionized water was used throughout the whole experiment.

2.2. Methods

GO nanosheet was synthesized from powder graphite adopting the Hummers and Offeman method [8]. The synthesis method of GO nanosheets is discussed in detail in our previously published papers [9,10]. Graphene nanosheets were synthesized by reduction of GO using ascorbic acid as eco-friendly reducing agent under ultrasonication [11]. The synthesis method is described elsewhere in detail [12]. However, complete reduction of GO cannot be obtained by this method and the synthesized graphene contains few oxygen functionalities. Therefore, the synthesized graphene is thereafter termed as reduced graphene oxide (rGO).

To get knowledge about effect of time on adsorption of methyl green onto rGO nanosheets, the adsorption kinetic experiments were performed at pH 5 and at four different temperatures (18, 25, 30, and 35 °C) in aqueous medium. Methyl green shows maximum stability in the pH range 3.5–5 [13]. Therefore, the upper limit of maximum stability of methyl green was selected for this adsorption kinetic study. We have adopted batch adsorption technique to carry out the adsorption experiments. The experimental procedure adopted for kinetics of adsorption was explain in details in our previous publications [10,12]. The batch adsorption isotherm experiments were adopted in the pH range 4–9 and at 25 °C. The influence of the background electrolyte on the adsorption of methyl green onto the rGO nanosheets were investigated by carrying out the adsorption isotherm experiments in presence of four different salts namely NaCl, $MgCl_2$, $CaCl_2$ and Na_2SO_4 at pH 5 and 30 °C.

2.3. X-ray analysis

The X-ray diffraction (XRD) measurement was carried out by Rigaku X-ray diffractometer (Model: ULTIMA IV, Rigaku, Japan) with Cu *K*α X-ray source (λ = 1.54056 Å) at a generator voltage 40 kV, a generator current 40 mA with the scanning rate 2° min^{-1}.

2.4. Mechanism of adsorption

FTIR spectroscopic and XRD analysis of rGO nanosheets were performed before and after adsorption of the methyl green dye molecule to understand the adsorption mechanism of methyl green onto the rGO nanosheets. For these studies, 1 mM methyl green was equilibrated with 100 mg/L of rGO nanosheets at pH 5 and 25 °C maintaining total volume of the solution 100 mL following the same procedure adopted for adsorption experiment. The suspension was centrifuged and the residue was dried in a vacuum desiccator over fused calcium chloride and then the FTIR and XRD spectra were recorded. The FTIR spectra was recorded in a Perkin Elmer 2000 (640 B) spectrometer in KBr pellets.

3. Results and discussion

3.1. Characterization of GO and rGO nanosheets

The complete characterization of the GO and rGO nanosheets was described in our previous publications [9,10,12].

3.2. X-ray radial distribution function analysis

The X-ray radial distribution function (RDF) analysis was carried out to evaluate the basic chemical structure of the synthesized