Dodecyl sulphate functionalized magnetic graphene oxide nanosorbent for the investigation of fast and efficient removal of aqueous malachite green

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ABSTRACT

In this study, the ease of magnetic separation was hybridized with the excellent hydrophilicity of both graphene oxide (GO) and dodecyl sulphate (DS) to synthesize a novel nanosorbent (Fe_3O_4@GO–DS; 10–25 nm) for simple, fast and efficient remediation of malachite green (MG) from aqueous media. The structure and morphology of Fe_3O_4@GO–DS were elucidated by FTIR, HRTEM, XRD and TGA techniques. Different analytical parameters including medium acidity, equilibration time, Fe_3O_4@GO–DS dose, initial MG concentration and temperature were optimized for maximum percentage MG removal efficiency. The experimental results indicated that Fe_3O_4@GO–DS had excellent sorption capacity (714.3 mg g^{-1} at pH 7.0 and 25 °C) which decreased from 98.75% to 95.60% after five sorption–desorption cycles. The adsorption isotherm data best-fitted to Langmuir model and the sorption reactions follow second order rate equations. Thermodynamic study is inspected and different mechanistic pathways are proposed for the sorption process.

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1. Introduction

Surface water pollution due to coloured effluents from dyes and pigments industries has attracted many researcher interests. Current treatment technologies for industrial wastewaters from leather tanning, textile dyeing, food; printing, electroplating and cosmetic manufactures are not effective enough to remove these dyes before disposal into main water stream. Malachite green (MG), a triphenyl methane cationic dye is widely used for dyeing of cotton, silk, paper, leather and in manufacturing of paints and printing inks. MG has carcinogenic, mutagenic and teratogenic effects on human health and biota [1]. Dyes remediation based on adsorption onto various carbon sorbents, such as activated carbon, carbon nanotubes, graphene and graphene oxide are more simple and favourable technique than several physicochemical and biological methods.

Graphene oxide (GO) has 2D hexagonal lattices of covalently bonded carbon atoms with a huge specific surface area (>2600 m^2 g^{-1}) and unique physical–chemical properties [2,3]. The huge specific surface area with the excellent electric conductivity, thermal stability, mechanical flexibility and other properties enabled GO for many successful technological applications in different fields. In addition, GO is rich in hydroxyl and epoxide groups on the top and bottom of its surface, besides the carboxyl groups distributed in random manner at the edges of GO sheets [4]. Accordingly, GO has triggered enormous interests, as a polar sorbent in normal solid phase extraction (SPE) for removing different water pollutants, by electrostatic interactions and/or hydrogen bonding through these oxygen functional groups. However, modified GO has been also used for removing environmental pollutants, such as ammonia [5], formaldehyde [6], methylene blue [7], arsenate [8] and tetracyclines [9]. In spite of GO nanoparticles have high dispersibility, it gained limited applications in the field of remediation of water pollutants and this is mainly attributed to the separation difficultly of GO from sample solutions. Magnetic solid phase extraction (MSPE) [10], based on functionalized magnetic graphene oxide nanocomposites has received more attention in the last five years. Magnetic resonance imaging [11,12], drug delivery [13], environmental remediation of various pollutants [14–21], battery and electrode material [22], and magnetic controlled switches [23] are the most attractive application prospects for magnetic GO. In the field of aquatic pollutants remediation, Fe_3O_4–GO nanosorbent was found to be more efficient, chemically stable and environmentally

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safe than common adsorbents. In addition, these types of MSPE has two main advantages, the first is related to time factor of the separation mode and the second one is to the ease of GO separation with the analyte from sample solution.

Based on the 2D structure, large specific surface area and π–π electrostatic stacking property of GO, hydrophilicity of dodecyl sulphate, and strong superparamagnetism of Fe_3O_4 nanoparticles, this study developed $Fe_3O_4@GO$–DS as a novel and effective nanosorbent for fast MG removal by coating dodecyl sulphate moiety with magnetic GO nanoparticles. $Fe_3O_4@GO$–DS is amphiphilic nanosorbent containing charged and uncharged binding sites. The sorption rate, isotherm, mechanism and thermodynamics as well as the factors influencing the MG percentage extraction were extensively studied. Moreover, the reusability of the novel nanosorbent is also determined for different adsorption–desorption cycles.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade and used without further purification. MG was purchased from Sigma-Aldrich. MG stock solution of 500 ppm was used to prepare the desired concentrations. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), sodium dodecyl sulphate; SDS and sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$) were purchased from Sigma-Aldrich. Ultrapure water from a Milli-Q system (Millipore, Billerica, MA) was employed throughout the experiments.

2.2. Synthesis of $Fe_3O_4@GO$–DS nanosorbent

The aqueous dispersion of GO sheets was prepared by chemical exfoliation of graphite powder based on the modified Hummer's method [24]. $Fe_3O_4@GO$ nanoparticles were prepared by the chemical co-precipitation of $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ in the presence of GO. In brief, 50 mg of GO was added to 50 ml water and the dispersed solution was sonicated for 30 min. 0.5 g of $FeCl_3 \cdot 6H_2O$ and 0.2 g of $FeCl_2 \cdot 4H_2O$ were dissolved in 25 ml water and the resultant mixture was added to GO solution. Then, 25% NH_4OH was added in drop wise manner to precipitate the Fe_3O_4 at 40 °C under N_2 gas with magnetic stirring until the pH of solution mixture reached to 10–11. Then, the reaction mixture was stirred rapidly at 60 °C for 2 h and left to cool at room temperature. The black $Fe_3O_4@GO$ product was collected by an external magnet and washed with water for several times. To prepare the dodecyl functionalized magnetic graphene oxide, $Fe_3O_4@GO$ was dispersed in 100 ml of water, sonicated for 30 min and adjusted to pH 7–8 by using 0.1 M NaOH, then 3 ml of 1,2 dibromoethane were added and the mixture was stirred for 2 h. Thereafter, 0.5 g of SDS was added and the reaction mixture was stirred at 60 °C for 2 h. The black–brown $Fe_3O_4@GO$–DS product was collected by magnetic separation, washed with water and anhydrous ethanol. Finally, $Fe_3O_4@GO$–DS was dried in a vacuum at 50 °C overnight. Scheme 1 symbolizes the steps followed for the synthesis of $Fe_3O_4@GO$–DS.

2.3. Characterization of $Fe_3O_4@GO$–DS nanoparticles

$Fe_3O_4@GO$–DS magnetic nanoparticles were examined by X-ray diffraction (XRD) measurements on a D8 Advance diffractometer (Bruker AXS Ltd., Germany) at room temperature. In order to confirm the coating of GO and dodecyl sulphate onto Fe_3O_4 nanoparticles, the compositions of the nanoparticles were examined in dried KBr powder by recording the infrared spectra over the range of 4000–400 cm^{-1} using a Fourier transform infrared (FTIR) spectrophotometer (EQUINOX55, Bruker Co). The morphology and par-

ticle size of the synthesized nanoparticles were investigated by high resolution transmission electron microscopy (HRTEM) using a Philips EM208 microscope operated at an acceleration voltage of 200 kV. The adsorbed mass of dodecyl sulphate on the surface of Fe_3O_4–GO nanoparticles was measured by thermogravimetric analysis (TGA) with a Polymer Lab TGA-1500, from 25 °C to 600 °C using a heating rate of 10 °C min^{-1} in the N_2 atmosphere.

2.4. MG adsorption studies

All batch adsorption experiments were carried out with a shaking rate of 250 rpm. The effect of the nanosorbent dosage on MG removal were conducted using 25 ml of MG solution (10 ppm, pH 7.0) with 1.0, 5.0, 10.0, 15.0, 20.0, 25.0 and 50.0 mg of nanosorbent at 25 °C for 20 min. The effect of pH on MG removal was examined in the pH range (2–10) for contact time 20 min using 15.0 mg of $Fe_3O_4@GO$–DS and 10 ppm of MG solution at 25 °C. The solution pH was adjusted by addition of proper amounts of 0.1 M HCl and 0.1 M NaOH solutions. In order to investigate the effect of contact time on the adsorption of MG for kinetic studies, 25 ml of MG solution (10 ppm at pH 7.0) was shaken with 15 mg of nanosorbent at 25 °C for predetermined intervals of time. The equilibrium adsorption isotherms were established by shaking 25 ml of MG solutions with different initial concentrations (1–25 ppm) at pH 7.0 with 15.0 mg of $Fe_3O_4@GO$–DS at 25 °C until equilibrium was reached. The effect of temperature on the adsorption of MG was carried out in 25 ml of MG solutions (10 ppm, pH 7.0) with 15 mg of $Fe_3O_4@GO$–DS for 20 min at various temperatures (15, 25, 35, 45 and 55 °C). For all determinations, the magnetic nanosorbent was separated from MG solution by an external magnet. The absorbance of solutions was determined using a double beam UV–vis spectrophotometer at wavelength of 616 nm. After equilibrium, the % MG removal efficiency and the equilibrium adsorption capacity (q_e) were calculated according to Eqs. (1) and (2).

$$\%MG\ removal\ efficiency = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

$$q_e = \frac{(C_i - C_e)V}{w} \qquad (2)$$

where C_i and C_e (ppm) are the initial and equilibrium MG concentrations, respectively, q_e (mg g^{-1}) is the equilibrium adsorption capacity, V is the MG solution volume and w (g) is the mass of the nanosorbent.

3. Results and discussion

3.1. Surface morphology and characterization techniques

3.1.1. Surface morphology

Representative HRTEM image of $Fe_3O_4@GO$–DS in Fig. 1a reveals irregular monodispersed nanoparticles with rough spherical surface to elliptical shape while their size is in the range of 10–25 nm. The shell formation in Fig. 1a by GO–DS around Fe_3O_4 showed spherical particles with a lighter core and a darker shell.

3.1.2. FTIR characterization

Fig. 1b exhibits the FTIR spectra of GO, $Fe_3O_4@GO$ and $Fe_3O_4@GO$–DS nanoparticles. GO and $Fe_3O_4@GO$ nanosorbents both showed the O–H stretching vibration adsorption peak at 3227.3 and 3220.2 cm^{-1}, respectively. As to graphene oxide, the peaks at 1711.2 and 1400.2 cm^{-1} were the C=O stretching vibration peaks of carboxyl and carbonyl; the peak at 1583 cm^{-1} was attributed to the stretching vibration of aromatic C=C; the peaks at 1170.1 and 1121.4 cm^{-1} were ascribed to the C–O stretching vibration of epoxy and alkoxy groups [25]. These peaks demonstrated