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A facile one-step approach to functionalized graphene oxide-based hydrogels used as effective adsorbents toward anionic dyes

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ABSTRACT

Herein, we used a facile method mainly through self-assemble, hydrogen bonding and electrostatic interaction to synthesize poly(diallyldimethylammonium chloride)/graphene oxide (PDDA/GO) hydrogels, which can be easily used as adsorbents to eliminate anionic dyes. The as-prepared PDDA/GO hydrogels were characterized by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy. In order to research the adsorption kinetics for the removal of anion dyes from water pollution, we further investigated that the effect of concentration, temperature, pH, ionic strength or cycle number on the removal process. The results indicated that due to the strong π–π stacking and anion–cation interaction, there were high removal efficiencies for both ponceau S (PS) and trypan blue (TB). The equilibrium time of adsorption is 30 min and 120 min for PS and TB, respectively, at which the solution could be decolorized to nearly colorless. Meanwhile, the adsorption process was more according with the pseudo-second-order model than the pseudo-first-order model. The hydrogels exhibited high removal efficiency for those two anionic dyes after four repeated adsorption and desorption treatments. It was demonstrated that PDDA/GO hydrogels would have great potential as a freestanding and reusable adsorbent for the practical application in water purification.

1. Introduction

Attributing to the unique structure, excellent physical and chemical properties of graphene and its derivates [1–3], it has aroused general interests in various fields, including sensors [4,5], catalysts [6], energy conversion and storage [7], surface enhanced Raman spectroscopy (SERS) [8], drug delivery [9], and water purification [10]. It is demonstrated that graphene oxide (GO), which exhibits a large surface area, chemical stability and rich surface functional groups, can effectively adsorb pollutants from aqueous solution, such as bisphenol A (BPA) [11], methylene blue (MB) [12], metanil yellow [13], Th (IV) ions [14], Cd (II) and ionic dyes [15], mainly through π–π stacking, hydrogen bond and electrostatic force, etc. Moreover, some graphene-based nanomaterials have been prepared to enhance the removal efficiency [15,44]. Typically, recycled Fe_3O_4/rGO magnetic composites were fabricated for effectively removing As (III), As (V) and dyes [16,17,42,43]. In addition, because dye pollution is one of the important kinds in water pollutions [18,19], using GO and GO-based material as absorbents to remove dyes has been widely studied [20,21]. However, these materials usually exhibit adsorbent capacity toward a certain type of dyes. Ramesha et al. [20] reported that GO showed the removal efficiency up to 95% for cationic dyes, while the removal efficiency is negligible for anionic dyes. In our previous work, we also proved that GO has great adsorption capacity to cationic dyes, such as methylene blue (MB) and rhodamine B (Rho B), but has no adsorption for ponceau S (PS), one of the anionic dyes, at different pH values [21]. Thus how to develop a broad-spectrum adsorbent with high adsorption capacity for anionic dyes is an important issue.

Moreover, two-dimensional (2D) materials have low recovery rate even causing secondary pollution, while three-dimensional (3D) materials can be recycled easily in water purification. In view of this, transforming 2D graphene-based hybrids into 3D materials has attracted a lot of attention [22–29]. Duan and co-workers reported polydopamine-functionalized graphene hydrogels (PDA-GH) as reusable adsorbents to eliminate heavy metals, synthetic dyes, and aromatic pollutants. While the PDA-GH can only remove

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cationic and neutral dyes due to its negatively charged surface [23]. Similarly, the resultant GO-based 3D materials, like other negatively charged adsorbents, exhibit low affinity for anionic dyes, due to the strong electrostatic repulsion between 3D materials and anionic dyes. Recently, Chen et al. [26] reported graphene oxide–chitosan composite hyrogels as broad-spectrum adsorbents for water purification, which could remove cationic and anionic dyes, but the removal efficiency of anionic dyes was still lower than that of cationic dyes, which needed a long time to reach equilibrium. Therefore, it still remains a challenge to develop a broad-spectrum and recycled easily 3D adsorbent with high adsorption capacity for water purification.

Herein, to overcome the challenge mentioned above, we combine the advantages of the two products, GO and poly(diallyldimethylammonium chloride) (PDDA), to synthesize PDDA/GO hydrogels used as effective adsorbents to eliminate anionic dyes. Poly(diallyldimethylammonium chloride) (PDDA) has been used as a flocculating agent to remove the organic pollutants in the water [30–33]. It is detected that the zeta-potential of PDDA/GO hybrid is positive [34], which is good for adsorption of negative organics. Ponceau S (PS) and trypan blue (TB), two kinds of anionic dyes, were applied in the study. In this work, we reported a facile and mild approach to fabricate PDDA/GO hydrogels and evaluated the adsorption kinetics and swelling degree. In order to research the adsorption capability for the removal of anion dyes from water pollution, we also further investigated that the influence of the ratio of PDDA and GO, concentration, pH, ionic strength or cycle number in the adsorption process of the as obtained PDDA/GO hydrogels.

2. Materials and methods

2.1. Materials

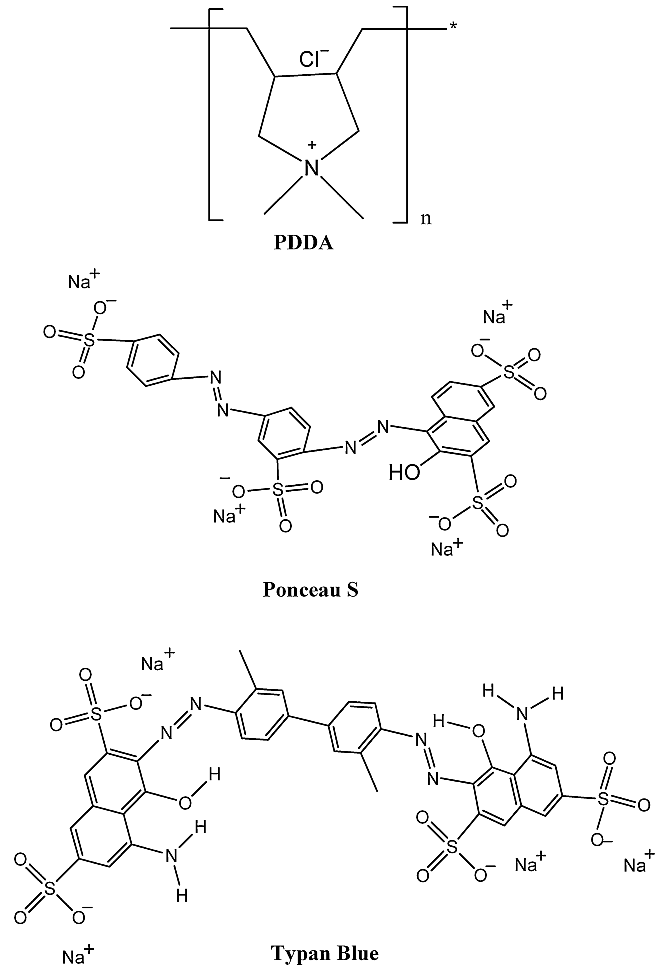
Graphite flake was purchased from Shanghai Yifan Graphite Co., Ltd. PDDA, Ponceau S (PS) and trypan blue (TB) were purchased from Sigma Aldrich of analytical grade and used as received without further purification (Scheme 1). All chemical reagents were used without further purification. Deionized water (Milli-Q System, Millipore, USA) was used in all experiments.

2.2. Synthesis of PDDA/GO hydrogels

Graphene oxide (GO) was prepared following the modified Hummers method [35–37]. PDDA functionalized graphene oxide gel (PDDA/GOG, namely, PDDA/GO hydrogel) was prepared by the following procedure. Typically, GO dispersion (4 mg/mL) was prepared by dispersing 40 mg of graphene oxide powder in 10 mL of de-ionized (DI) water by sonication for 40 min. 900 μL GO dispersion (4 mg/mL) was then added into 300 μL PDDA (1 mg/mL) aqueous solution. Then, the blend was quietly placed for a few seconds. The formation of the hydrogel was examined by a tube inversion method. And the as-prepared hydrogel was freezed drying overnight using a freeze dryer to get the xerogel.

2.3. Characterization

Transmission electron microscopy (TEM) was performed by a JEM-2100HR transmission electron microscopy (JEOL, Japan) operated at 200 kV. Atomic force microscope (AFM) was used for characterization of graphene oxide sheet size and thickness. The morphology of the prepared hydrogel lyophilized for at least 24 h was examined by field-emission scanning electron microscope (SEM) (ZEISS Ultra 55). The ultraviolet–visible (UV–vis) spectra were measured by an UV–vis absorbance spectrometer (NanoDrop, ND-1000). Raman spectra were collected using a confocal Raman microspectrometer (Renishaw InVia, Derbyshire, England) with an excitation wavelength of 514.5 nm generated by an Ar+ laser. A 20× objective was used to focus the laser beam and a charge-coupled device (CCD) array was used as the detector. The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer. FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer.



Scheme 1. Chemical structures of PDDA, PS, and TB.

2.4. Determination of swelling degree

The as-obtained xerogel (the ratio of PDDA and GO is 1:5, that is to say the concentration of GO is 3.33 mg/mL) was weighted and recorded as m_0. After soaking in water overnight, the hydrogel was carried out and then weighed, recording as $m_{eq.}$ The equilibrium swelling degree (SD_{eq}) [40], which can indirectly indicate the adsorption capacity, could be calculated using Eq. (1):

$$SD_{eq} = \frac{(m_{eq} - m_0)}{m_0} \quad (1)$$

2.5. Adsorption of PS and TB by PDDA/GO hydrogels

To measure the adsorption capacities of PDDA/GOG, three kinds of PDDA/GOGs with different ratios of PDDA and GO (1.5:5, 1:5, 1:9) were prepared. The concentrations of GO were separately 3.08 mg/mL, 3.33 mg/mL and 3.6 mg/mL. Then the as-prepared hydrogels were mixed with PS or TB dye solutions (500 μL, 0.1 mM, pH = 6), respectively. The mixtures were shaked at 150 rpm for 30 min and then filtered. The filtrates were detected by the UV–vis absorbance spectrometer. For PS and TB solutions, the

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