



Preparation and characterization of sulfonated graphene-enhanced poly (vinyl alcohol) composite hydrogel and its application as dye absorbent



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ABSTRACT

In this paper, sulfonated graphene (SG) were incorporated into the poly (vinyl alcohol) (PVA) networks to fabricate the SG/PVA (SP) composite hydrogel. The as-prepared SP hydrogel exhibited enhanced mechanical property with a small amount of SG into the PVA matrix. In the meantime, the SP hydrogel showed specific adsorption of cationic dyes, such as Methylene Blue (MB), Malachite Green (MG). Studies on the adsorption isotherm and kinetics of the SP hydrogel showed that the equilibrium and kinetic adsorptions could be well depicted based on Langmuir isotherm and pseudo-second-order kinetics model, respectively. Due to the π - π conjugated structure and sulfonic acids on the SG surface, pH and ionic strength had less impact on the adsorption ability of SP hydrogel toward MB. Furthermore, it was also found that the SP hydrogel could be used as intelligent absorbent in selective adsorption and separation of the dye mixtures.

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1. Introduction

Nowadays, environmental problems have attracted a global attention due to their impact on public health. Improper management of industrial water is one of the main causes of environmental pollution. Especially, many industries such as textiles, paper, leather, food, and cosmetics, generate wastewater with various dyes. Therefore, it is of great importance to develop technologies to purify the water contaminated with the residual dyes. The removal of dyes from aqueous environment has been widely studied and numerous methods such as coagulation, membrane filtration, adsorption, photocatalysis, and advance oxidation, have been developed [1–3]. Among these methods, the adsorption technique is especially attractive because of its high efficiency, simplicity of design, and ease of operation. Many kinds of materials were applied as adsorbents in water purification, such as clays [4], activated carbon (AC) [5], magnetic materials [6], and polymeric materials

[7,8], etc., among which carbon-based materials were regarded as the staple adsorbents. In addition to the conventional AC, some new carbon materials, including carbon nanotubes (CNTs) [9], carbon nanofibers (CNFs) [10], mesoporous carbon [11], and graphene [12,13], have been exploited as high capacity adsorbents for water purification.

Among the carbon based materials, graphene has attracted considerable scientific attention due to its excellent properties such as excellent mechanical, optical, and electrical properties [14]. Graphene can also be used as an excellent adsorbent because of its large theoretical specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) [15] and a large delocalized π -electron system. However, the strong interaction among graphene sheets reduces the surface area of graphene significantly, and the absence of effective ways to disperse graphene in aqueous solution makes it difficult to advance in pollution management. So, great efforts have been devoted to improve the water solubility of graphene. Oxidation of graphite to produce the graphite oxide (GO) is one of good methods to solve this problem. GO having epoxy, hydroxyl, and carboxylic acids groups on the surface [16] bears a remarkable hydrophilic character and can be dispersed homogeneously in water to be used as adsorbents. However, there are several shortcomings associated with GO as

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absorbent. First, the π - π conjugated structure of graphene was damaged by the introduction of oxygen groups, and the adsorption capacity towards aromatic compounds might to be decreased. Second, the solubility of GO make it difficult to totally remove from water and this will cause the second pollution in water due to the residual GO. Therefore, GO was usually attached with magnetic nanoparticles [17] and this hybrid materials could be easily separated from water under the magnetic environment. This method, however, was not suitable for large-scale application in dye adsorption. Sulfonated graphene [18] (SG) with sulfonic acids on the graphene surface would be a good candidate for overcoming the conjugated structure limitation of GO. SG bears the π - π conjugated structure of graphene with good dispersion ability in aqueous solutions. Zhang and co-workers has used the SG nanosheets to adsorb naphthalene and 1-naphthol from aqueous solutions [19,20]. However, these SG nanosheets were also difficult to totally collect from wastewater due to its solubility in water and the residual SG would cause second pollution for water.

An ideal approach to solve the problem above is to encapsulate SG into a loose three-dimensional macroscopic network, which provides channels for pollutant adsorption with easy separation from wastewater. Polymeric hydrogels, consisting of hydrophilic polymers and a large amount of water, would be a perfect choice. There are at least two advantages related with this design. Firstly, SG could absorb dyes from water efficiently without worrying about the second water pollution, associated with the SG residues in water. Secondly, the poor mechanical property of hydrogels could be effectively improved with the presence of derivative graphene nanosheets [21,22], which could increase the duration of hydrogels for their application.

Here, PVA was chosen as the gel matrix material, because PVA has been reported to show no obvious effect on dye adsorption behavior [23] and the true SG absorption behaviors could be investigated without the influence of gel matrix. A novel SG/PVA (SP) composite hydrogel was fabricated by repeatedly freezing and thawing a mixture of SG and PVA aqueous solution. Tensile and compressive tests of the SP hydrogels were used to investigate the reinforced mechanical property with the incorporation of SG. In the meantime, the dye adsorption ability of the SP hydrogels and the influence of pH and ionic strength on adsorption capacity were also examined. Furthermore, the SP hydrogel was also used as intelligent absorbent in selective separation of cationic dyes from anionic dyes.

2. Experimental

2.1. Materials

Graphite powder (100 mesh, 99.995%) was obtained from Alfa-Aesar Co. Ltd. Potassium permanganate (KMnO_4), concentrated sulfuric acid (95–98%), hydrogen peroxide (H_2O_2 , 30%), concentrated hydrochloric acid, sodium borohydride (NaBH_4), sodium nitrate (NaNO_2), sulfanilic acid, hydrazine hydrate and poly(vinyl alcohol) (PVA, AH-26, DP = 2600, alcoholysis degree of 99%) were purchased from Sinopharm Reagent Co. Ltd (SCRC) and used as received. The dyes, Methylene Blue (MB), Malachite Green (MG), Rose Bengal sodium salt (RB) and Ponceau2R (P2R), were also purchased from SCRC.

2.2. Preparation of SG

GO was prepared from the pristine graphite by the modified Hummers method [24,25]. Then, the pre-reduction of GO was performed with NaBH_4 at 80 °C for 1 h to remove the majority of the oxygen functionalities. The sulfonation of GO was then carried

out with the aryl diazonium salt of sulfanilic acid in an ice bath for 2 h, followed by post-reduction with hydrazine at 100 °C for 24 h to remove any remaining oxygen functionalities [18]. The SG can form stable dispersion in water, which makes them form homogeneous mixtures with PVA easily.

2.3. Fabrication of SP hydrogel

The SP hydrogel was prepared by repeatedly freezing and thawing a mixture of SG and PVA aqueous solution. Briefly, appropriate amounts of SG aqueous dispersions were added to PVA solution. After magnetic stirring for 2 days at room temperature, the homogeneous solutions were poured into plastic tubes and frozen at -20 °C for 20 h, followed by thawing for 4 h at room temperature. After three times of freezing-thawing process, the hydrogels, in its cylindrical form, were taken out of the tubes and put into deionized (DI) water for 1 week with water-change every 12 h. In this research, hydrogels were expressed as SxP1, where S and P refer to SG and PVA, respectively, and x stands for the relative weight ratio of SG to the amount of PVA, and 1 represents that the weight of PVA is set as 1 g for all the samples. For instance, the S2P1 hydrogel means that there was 1 g of PVA, 20 mg of SG, which means that the amount of SG accounts for 2 wt% of that of PVA in the SP hydrogel. The detailed compositions of SP hydrogels were illustrated in Table 1.

2.4. Characterization

X-ray powder diffraction (XRD) patterns were recorded on a D/max-2200/PC (Japan Rigaku Corp.) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418$ Å). Raman spectra were recorded on Bruker Optics Senterra R200-L dispersive Raman microscope. X-Ray photoelectron spectra (XPS) were recorded on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with $\text{Al K}\alpha$ radiation ($h\nu = 1486.6$ eV). Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Perkin-Elmer Paragon 1000 PC spectrometer. Thermogravimetric analysis (TGA) was conducted in nitrogen with a Perkin-Elmer TGA 2050 instrument at a heating rate of 20 °C min^{-1} . Atomic Force Microscope (AFM) images were obtained by digital E-Sweep Atomic Force Microscope in tapping mode. Scanning electron microscope (SEM) images were obtained from JSM-7410 (JEOL Ltd, Japan). Ultraviolet visible (UV-Vis) absorption spectra were recorded by UV-2550 spectrophotometer (Shimadzu, Japan).

2.5. Mechanical property of hydrogels

After fabrication of SP hydrogel, the hydrogels, in its cylindrical form, were taken out of the tubes and put into DI water for 1 week

Table 1
Composition, Water content (W_c), Equilibrium swelling degree (ESD), crystallinity (X_c) and T_g of SP hydrogels.

| Hydrogel | Composition (g) | | | The fundamental parameters of SP hydrogels | | | |
|----------|-----------------|-----|----------|--|-----------------------------|------------------------|-------------------------|
| | SG | PVA | DI water | W_c (%) ^a | ESD (pH = 5.9) ^b | X_c (%) ^b | T_g (°C) ^b |
| PVA | 0 | 1 | 20 | 95 ± 0.6 | 10 ± 0.4 | 27.9 | 80.9 |
| S0.1P1 | 0.001 | 1 | 20 | 95 ± 0.9 | 11 ± 0.3 | 30.2 | 79.9 |
| S0.3P1 | 0.003 | 1 | 20 | 96 ± 0.5 | 11 ± 0.8 | 26.0 | 80.4 |
| S0.5P1 | 0.005 | 1 | 20 | 96 ± 0.7 | 12 ± 0.7 | 26.0 | 81.5 |
| S0.7P1 | 0.007 | 1 | 20 | 96 ± 0.5 | 12 ± 0.1 | 28.6 | 80.6 |
| S1P1 | 0.010 | 1 | 20 | 96 ± 0.1 | 11 ± 0.3 | 29.3 | 80.1 |
| S2P1 | 0.020 | 1 | 20 | 96 ± 0.1 | 10 ± 0.8 | 27.6 | 81.1 |

^a The as-prepared SP hydrogels.

^b The SP aerogel obtained by freeze-drying of the corresponding hydrogel.

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