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

Hong Li a, Jinchen Fan b, Zixing Shi a, *, Min Lian a, Ming Tian c, **, Jie Yin a

a School of Chemistry and Chemical Engineering, State Key Laboratory for Metal Matrix Composite Material, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China
b College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, People’s Republic of China
c State Key Lab of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China

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.

© 2015 Elsevier Ltd. All rights reserved.

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 m² 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
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 makes 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 (KMnO₄), concentrated sulfuric acid (95–98%), hydrogen peroxide (H₂O₂, 30%), concentrated hydrochloric acid, sodium borohydride (NaBH₄), sodium nitrate (NaNO₂), 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 NaBH₄ 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 homogenous 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 CuKα radiation (λ = 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 Al Kα radiation (hv = 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>
<thead>
<tr>
<th>Hydrogel</th>
<th>Composition (g)</th>
<th>The fundamental parameters of SP hydrogels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SG</td>
<td>PVA</td>
</tr>
<tr>
<td>PVA</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>S0.1P1</td>
<td>0.001</td>
<td>1</td>
</tr>
<tr>
<td>S0.3P1</td>
<td>0.003</td>
<td>1</td>
</tr>
<tr>
<td>S0.5P1</td>
<td>0.005</td>
<td>1</td>
</tr>
<tr>
<td>S0.7P1</td>
<td>0.007</td>
<td>1</td>
</tr>
<tr>
<td>S1P1</td>
<td>0.010</td>
<td>1</td>
</tr>
<tr>
<td>S2P1</td>
<td>0.020</td>
<td>1</td>
</tr>
</tbody>
</table>

a The as-prepared SP hydrogels.

b The SP aerogel obtained by freeze-drying of the corresponding hydrogel.
with water-change every 12 h. Then, the as-prepared hydrogels were taken out of water and the water on their surfaces was wiped off with a filter paper. Tensile measurement were performed on those SP hydrogels of the sample size (6.5 mm diameter × 70 mm length) using the Instron 4465 instrument. The condition of tensile tests was listed as follows: crosshead speed, 8 mm/min; temperature, 25 °C; initial gauge length, 30 mm. The compressive tests of those SP hydrogels were carried out with the sample size (26 mm diameter × 20 mm height) by the Instron 4465 instrument. The compressive properties of SP hydrogels were obtained under the following conditions: crosshead speed, 10 mm/min; temperature, 25 °C; initial gauge length, 20 mm.

### 2.6. Water content and equilibrium swelling degree (ESD) of hydrogels

All the initial solutions for the preparation of SP hydrogel contained 1 g of PVA, 20 g of DI water and 0–0.02 g of SG. For determining the water content of the SP hydrogels, the as-prepared hydrogels were dried to a constant weight in vacuum at 50 °C. The water content, \( W_c \), was calculated as follows [21]:

\[
W_c = \frac{W_e - W_d}{W_e} \times 100\% \tag{1}
\]

where, \( W_d \) and \( W_e \) represent the weights of dried hydrogels and the hydrogels at swelling equilibrium state, respectively.

To measure the ESD of hydrogels, the as-prepared SP hydrogels were first lyophilized in a freeze drying instrument for 1 week. Then, the SP aerogels were immersed into DI water until their weights became constant. Then, the hydrogels were taken out of water and the water on their surfaces was wiped off with a filter paper. The ESD was calculated as follows [26,27]:

\[
ESD = \frac{W_e - W_d}{W_d} \tag{2}
\]

where, \( W_d \) and \( W_e \) represent the weights of the lyophilized hydrogels and the hydrogels at swelling equilibrium state, respectively.

### 2.7. Dye adsorption property of hydrogels

Four kinds of dyes were chosen for adsorption experiment (Scheme 1b). 2.0 g of S2P1 hydrogel was mixed with 25 mL of dye solution at 10 mg/L concentration at 25 °C. After reaching adsorption equilibrium, small amounts of the solution were taken to be analyzed by UV-vis absorption spectroscopy by monitoring the absorbance changes at a wavelength of maximum absorbance (Table 2) after being diluted five times. The equilibrium adsorption capacity, \( Q_e \) (mg/g), was calculated as follows [6,28]:

\[
Q_e = \frac{(C_0 - C_e)V_{\text{dye}}}{W_{\text{hd}}} \tag{3}
\]

where, \( C_0 \) and \( C_e \) (mg/mL) were the initial and final concentration of the dye solution. \( V_{\text{dye}} \) (mL) and \( W_{\text{hd}} \) (g) were the volume of the dye solution and the weight of lyophilized hydrogel, respectively.

The effect of pH on the amount of dyes removal was analyzed in the pH range from 1 to 10. The solution pH was adjusted by the using of HCl and NaOH solution. The ionic strength of the dyes solution was adjusted by the addition of NaCl (0.1–1.0 M).

For desorption experiment, first 2.0 g of S2P1 hydrogel was mixed with 25 mL of MB solution at 80.0 mg/L for 8 h. The initial and final MB concentrations were analyzed by UV-vis absorption spectroscopy. The amount of MB adsorbed on the S2P1 hydrogel was calculated to be 13.54 mg/g. Then the S2P1 hydrogel was immersed in DI water to conduct desorption experiment for 75 h.

### 3. Results and discussion

#### 3.1. Characterization of GO and SG

The XRD patterns of pristine graphite, GO and SG were shown in Fig. 1a. The characteristic peak (20) of pristine graphite appeared at 26.3°, corresponding to the layer–layer distance of 0.34 nm. Due to the creation of oxygen-containing functional groups on the GO [29,30], the interlayer distance of GO was increased to 0.83 nm, corresponding to the diffraction peak at 10.7°. For SG, the weak and

![Scheme 1](image-url)
broad diffraction peak around 23.4° was attributed to the effective reduction of GO by sodium borohydride and hydrazine, suggesting the rather limited ordering (only a few layers) in each SG sheet and the uneven interlayer distance over the whole SG samples [31]. And the weak and broad peak at 8.6° of SG implied the sulfonic acid groups were successfully introduced on the GO surface. The Raman spectra of GO and SG were shown in Fig. 1b. The band around 1350 cm⁻¹ was assigned to D band, which was related to the vibration of sp³ carbon atoms of defects and disorder. Meanwhile, the band around 1580 cm⁻¹ was assigned to G band, which was associated with the vibration of sp² carbon atoms in a graphitic 2D hexagonal lattice [32]. The integrated intensity ratio (I_D/I_G) increased from 0.833 for GO to 1.002 for SG, which suggested that the reduction and sulfonation process changed the structure of GO and the SG had a higher content of sp³ carbon atoms than that of GO, which meant that SG had more defects than GO since an increase in sp³ carbon-atoms demonstrated an increased number of defects [33].
XPS measurements were performed to investigate the chemical composition of GO and SG. The C 1s XPS spectrum of GO (Fig. 2a) indicated the presence of four types of carbon bonds: C−C (284.8 eV), C−O (286.8 eV), C=O (287.8 eV), and O−C=O (289.0 eV) [34,35]. Although the C 1s XPS spectra of SG (Fig. 2b) also exhibited the same species, the peak intensities of oxide species were much weaker than those in the spectra of GO, suggesting that most of the oxygen-containing functional groups were successfully removed by the reduction process [31]. In addition, there was an additional component at 285.9 eV, corresponding to carbon bound to nitrogen. The S 2p XPS spectrum of SG (Fig. 2c) demonstrated the existence of benzenesulfonic groups [36]. The atomic ratio of S:C was calculated to be about 1:49 according to the XPS analysis.

The ATR-FTIR spectra of GO and SG were shown in Fig. 3a. The spectrum of GO showed significant bands around 1050 cm⁻¹ (ν C−O), 1225 cm⁻¹ (ν C−O−C), 1364 cm⁻¹ (ν C−OH), 1619 cm⁻¹ (ν HOD bending in water) and 1728 cm⁻¹ (ν C=O) [37,38]. After reduction with sodium borohydride and hydrazine hydrate, the intensities for these signals were considerably attenuated. For the SG, the peaks around 1170 cm⁻¹, 1122 cm⁻¹, and 1032 cm⁻¹ (two ν S−O and one ν s-phenyl) were the characteristic peaks for a sulfonic acid group and the peaks around 1003 cm⁻¹ (ν C−H in-plane bending) and 831 cm⁻¹ (out-of-plane hydrogen wagging) were vibrations of a p-disubstituted phenyl group [18]. TGA measurement was used to investigate the thermal stability of GO and SG (Fig. 3b). The mass loss of GO is about 40% at 300 °C, which was attributed to the decomposition of labile oxygen-containing groups [39,40]. However, the SG showed only 5.1 wt% mass loss at 300 °C, which was much lower than that of GO and could be ascribed to the efficient removal of oxygen functional groups during the reduction process.

The AFM images of GO and SG were shown in Fig. 4a and Fig. 4b, respectively. The average thickness of GO was about 1.0 nm, which was consistent with the data reported in the literature for single layered GO [18]. After the final reduction step, the thickness of SG

---

**Fig. 3.** (a) The ATR-FTIR spectra of GO and SG. (b) The TGA curves of pristine graphite, GO and SG.

**Fig. 4.** AFM image of GO (a) and SG (b) on freshly cleaved mica.
Fig. 5. (a) The images of SP hydrogels with different SG loading. SEM images of (b) PVA aerogel, (c) a local partial enlarged image of (b), (d) S0.5P1 aerogel, (e–f) local partial enlarged images of (d) and (g) S2P1 aerogel.

Fig. 6. XRD (a) and DSC (b–c) of PVA and SP aerogels and (d) swelling ratio of different SP aerogels at pH 5.9.
was increased to 1.6 nm, indicating the successful introduction of sulfonic acid onto the graphene surface.

3.2. Mechanical property of SP hydrogels

Because of the successful introduction of sulfonic acid onto the graphene surface, the SG nanosheets can be well dispersed in water and PVA aqueous solution, respectively. Then the SP hydrogel was prepared by repeatedly freezing and thawing a mixture of SG and PVA aqueous solution. It could be observed from Fig. 5a that all the SP hydrogel samples showed homogeneous appearance with no noticeable aggregation. As the amount of SG was increased, the colors of SP hydrogels gradually turned to black. The SP hydrogels were immered in DI water for 5 days and then lyophilized in a freeze drying instrument for 4 days. The SEM images of lyophilized hydrogels with different amounts of SG were shown in Fig. S2. For pure PVA hydrogel (Fig. 5b–c), the pore distribution was not uniform and its diameters were 38 ± 15 μm. The connection between the pores was weak and mainly located on the edges of PVA hydrogel. However, after introduction of SG, the SP hydrogels showed different morphology due to the stronger interaction between the sulfonic acids of SG and hydroxyl groups of PVA. For S0.5P1 hydrogel (Fig. 5d–f) and S2P1 (Fig. 5g), the pore size distribution became narrow and the diameters were 35 ± 11 μm and 34 ± 6 μm, respectively. The links between the holes appeared not only on the edges but also on the surfaces. Furthermore, the interconnected pores enabled the diffusion of solute through the hydrogel, which was crucial for the dye adsorption application.

Because PVA is a semi-crystalline polymer, its degree of crystallinity has a significant impact on the mechanical properties of SP hydrogels [41, 42]. In this work, XRD and DSC were used to investigate the degree of crystallinity of the SP hydrogels. For the XRD curves (Fig. 6a), there were no obvious differences between the lyophilized PVA and SP hydrogels, which suggested that the SG nanosheets did not have a noticeable effect on the degree of crystallinity of the PVA. Differential scanning calorimetry (DSC) was applied to determine the degree of crystallinity (Xc) of the lyophilized PVA and SP hydrogels by dividing the melting enthalpy of hydrogels (Table S1) by that of 100% crystalline PVA sample (138.6 J/g). The DSC curves (Fig. 6b–c) showed that there was no significant difference in the curves of melting enthalpy and glass transition temperature (Tg). However, an increase in the peak melting point of aerogel with the presence of SG might be ascribed to the fact that the chain mobility of PVA was reduced with the presence of SG due to the strong interaction between each other. Therefore, higher temperature might facilitate the chain’s movement in the melting process [43]. As shown in Table 1, the Xc difference between the pure PVA and SP hydrogels was less than 2.5%, which implied that there was no obvious change of PVA crystallinity. Meanwhile, the Tg of lyophilized PVA and SP hydrogels were not changed on a large scale. Fig. 6d showed the process of the swelling behavior of the lyophilized hydrogels with different SG contents. All the swelling curves were steep at the initial state and then were decreased greatly to reach the similar ESD summarized in Table 1. As listed in Table 1, although the water content of all the SP hydrogels was slightly higher than that of the pure PVA hydrogel, they all also had similar values (95.5–96.6 wt%).

With the introduction of SG, it was expected that the mechanical property of SP hydrogels was better than that of pure PVA hydrogel. As shown in Fig. 7a, the tensile strength of the SP hydrogels was increased obviously with the incorporation of SG. The highest tensile strength was found to be 37.34 kPa at the SG content of 0.5 wt%. With further increase of SG content, the tensile strength was shifted around 35 kPa. Because all the SP hydrogels had similar degree of crystallinity of the PVA and water content, the enhancement in mechanical properties was associated with the dispersion of SG and its interaction towards the PVA matrix [21, 44]. The sulfonic acid groups on the SG could form strong interactions with the hydroxyl groups of the PVA, which provided better load transfer between the SG and PVA matrix, leading to the effective mechanical enhancement. It was also found that the elongation at break (Fig. 7a) increase monotonically with SG content. Therefore, as shown in Fig. 7b, the tensile toughness of SP hydrogels was also increased with increasing SG content since the tensile toughness was defined as the area underneath the tensile stress–strain curve. More SG contents would mean more hydrogen interactions between sulfonic acids of SG and hydroxyl groups of PVA, which would need more energy for the breaking of the hydrogels. Therefore, higher tensile toughness was obtained with the incorporation of SG into PVA matrix.

The compressive strength of SP hydrogels (Fig. S1) was also investigated and all the hydrogels were compressed to 90% of their initial heights. With the incorporation of SG, the compressive strength of SP hydrogel was increased gradually from 0.29 MPa of PVA hydrogel to maximum value 0.58 MPa of S0.5P1 hydrogel. With further SG addition to 2 wt%, the compressive strength shifted around 0.4 MPa, which showed the compressive strength of SP hydrogels was increased by the strong interaction of SG and PVA as illustrated in the tensile strength. Because salt solution can break the hydrogen interaction, so we investigated the compressive property of the S0.5P1 hydrogels soaked in different NaCl concentration (Fig. S2). For S0.5P1 hydrogel, the compressive strength was
improved significantly with the increased NaCl concentration. Although more NaCl would break hydrogen interaction between the SG nanosheets and the PVA matrix, it also reduced the water contained in the S0.5P1 hydrogel, which in turn improved the compressive strength of S0.5P1 hydrogel. This demonstrated that the SP hydrogels could really stand stable in salt solution. Therefore, the incorporation of SG in PVA matrix could enhance the mechanical property of the pure PVA hydrogel, which could facilitate the function of keeping the integrity of hydrogel and expand the scope of the hydrogel’s application area.

3.3. Dye adsorption of SP hydrogels

It has been found the PVA hydrogel has no discernible effect on the absorption of dyes since PVA is a nonionic polymer [23], while SG nanosheets with sulfonic acid onto the graphene surface might have potential application in this field. Therefore, it is highly desirable to select the PVA matrix to encapsulate SG for investigating the true dye absorption behavior of SG without the influence of the hydrogel matrix. In the experiment of dye adsorption, two types of water soluble dyes, including two cationic dyes (MB and MG) and two anionic dyes (RB and P2R), were chosen as representative compounds to investigate the dye adsorption property of S2P1 hydrogel. 2.0 g of S2P1 hydrogel was mixed with 25 mL of dye solution at 10 mg/L concentration for 8 h. Fig. 8 showed the aqueous solution of the four dyes, bright color can be clearly observed. After the addition of S2P1 hydrogel, the color of MB and MG turned obviously light, while that of RB and P2R kept almost no change. In contrast, 2.0 g of PVA hydrogel was also chosen to conduct the above dye adsorption experiment. Based on the different dye adsorption behaviors, the pseudo-first- and pseudo-second-order kinetic models were applied to describe the adsorption process. The pseudo-first-order kinetic model is given as:

\[ \ln (Q_e - Q_t) = \ln Q_e - k_1 t \]

where \( k_1 \) is the rate constant of the pseudo-first-order kinetic model. The pseudo-second-order kinetic model is given as:

\[ \frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \]

where \( k_2 \) is the rate constant of the pseudo-second-order kinetic model.

Fig. 9. (a) Effect of contact time on the adsorption of MB by PVA and S2P1 hydrogels at initial concentration 13.45 mg/L, pH – 6.2 and 25 °C. Plots of (b) first- and (c) second-order rates.
amounts adsorbed on the PVA and S2P1 hydrogel (Table 2), the S2P1 hydrogel was found to have certain specific adsorption ability towards MB and MG. The positively charged MB molecule in solution can be easily adsorbed by negatively charged GO mainly due to electrostatic attraction [45]. Meanwhile, naphthalene and 1-naphthol in aqueous solution can be absorbed by SG due to the π–π conjugated interaction [19]. To further understand the adsorption process of the S2P1 hydrogel, the cationic dyes MB and MG were selected to investigate the adsorption kinetics and isotherms.

The adsorption kinetics of MB on PVA and S2P1 hydrogels were conducted. Typically, 1.0 g of PVA or S2P1 hydrogel was immersed in 50 mL of MB solution at initial concentration 13.45 mg/L, pH = 6.2 and 25 °C. After every interval of 0.5 h, small amounts of the liquids were taken to ascertain the MB concentration by UV-vis absorption spectroscopy. As shown in Fig. 9a, both slopes were high at initial adsorption period of hours, which may be ascribed to the availability of large number of vacant sites that saturates with time. However the adsorption efficiency of MB on PVA hydrogel was significantly lower than that on S2P1 hydrogel. For pure PVA hydrogel, it has no discernible effect on the absorption of dyes. But for S2P1 hydrogel, the interactions were the electrostatic attraction between the negative SG nanosheets and cationic MB and the π–π electron donor acceptor interactions originated from the benzene rings in both MB and SG surface. Two famous adsorption models, pseudo-first and pseudo-second order equations, were used to investigate the adsorption kinetics of MB on PVA and S2P1 hydrogels [46,47]. The integrated form of pseudo-first order equation was listed as follows

\[ \ln(Q_{eq} - Q_t) = \ln Q_{eq} - k_1T \]  

where, \( Q_{eq} \) and \( Q_t \) (mg/g) are the amounts of dye adsorbed at the equilibrium and time \( T \), respectively; \( k_1 \) is the pseudo-first-order rate constant. For pseudo-second order equation, the integrated form could be described below

\[ \frac{T}{Q_t} = \frac{1}{k_2Q_{eq}^2} + \frac{T}{Q_{eq}} \]  

where, \( Q_{eq} \) and \( Q_t \) (mg/g) are the amounts of dye adsorbed at the equilibrium and time \( T \), respectively; \( k_2 \) is the pseudo-first-order rate constant. According to the pseudo-first-order equation, the correlation coefficients of PVA and S2P1 hydrogels for MB were 0.978 and 0.944, respectively (Fig. 9b). As for the pseudo-second-order equation, the correlation coefficients of MB on PVA and S2P1 hydrogels were 0.989 and 0.997, respectively (Fig. 9c). Therefore, the adsorption kinetics was in good agreement with the pseudo-second-order model, which could be utilized to forecast the amount of dye adsorbed on hydrogel at T hour.

The adsorption isotherm of MB and MG onto S2P1 hydrogels were conducted to understand how those dyes interact with the SP hydrogel. The equilibrium adsorption data were analyzed by
using the Langmuir and Freundlich isotherm models [48] (Fig. S3 and Table S2). Based on the results obtained from these two models, the data on adsorption of MB and MG follow Langmuir isotherm better than Freundlich isotherm, which indicates that adsorptive sites of the S2P1 hydrogel have the same affinity for MB or MG and can only be occupied once in a one-on-one manner, the adsorption of MB or MG is on a homogeneous, flat surface of S2P1 hydrogel [49].

The effects of pH and ions strength on the adsorption behaviors of MB by S2P1 hydrogels were also studied. As shown in Fig. 10a, the pH had almost the similar effect on the MB adsorption capacity of S2P1 and PVA hydrogels. Actually, the adsorption capacity of S2P1 hydrogel for MB did not change greatly and shifted around 6.87 mg/g during a wide pH range. The influence of ionic strength on the adsorption was shown in Fig. 10b. When the concentration of NaCl increased to 1.0 M the adsorption capacity of S2P1 hydrogel for MB decreased by only 13.1%. Actually 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, which implied the practical dye adsorption potential of S2P1 hydrogel.

Desorption experiment could provide direct insight into the overall adsorption mechanism [42]. As shown in Fig. 10c, although the desorption experiment in DI water was lasted for 75 h, the final desorption efficiency of MB absorbed on S2P1 hydrogel was very low (around 4%). Because of the electrostatic and the π–π interactions between the negative SG nanosheets and cationic MB, the majority of MB adsorbed on S2P1 hydrogel could stand stable for a long time. However, the low desorption efficiency (4%) in DI water suggested that there was also weak physisorption between MB and S2P1 hydrogel.

Motivated by the excellent mechanical property and specific dye adsorption ability of the SP hydrogels, the obtained SP hydrogels can be extended into practical application in dye selective adsorption and intelligent separation [50]. As shown in Fig. 11a–b, the mixture solution became black immediately after the addition of blue (in web version) MB solution into the red P2R solution. With S2P1 hydrogel immersed in the mixture solution for 24 h, the color of the mixture solution turned from black to red (Fig. 11e). The UV–vis spectra were used to trace the separation process and to check the change of dye concentration in solution. As shown in Fig. 11c and f the concentration of P2R kept almost the same after 24 h of dye adsorption, while the concentration of MB in solution decreased to almost zero. Due to the main interactions between MB and S2P1 hydrogel (discussed in adsorption kinetics), the as-fabricated hydrogel could form strong interaction with specific cationic dyes. Therefore, the obtained SP hydrogels could be used in selective adsorption and intelligent separation of cationic dyes especially in the mixture with different kinds of ionic dyes.
4. Conclusions

Based on strong interaction of sulfonic acids and hydroxyl groups, SG has been successfully encapsulated into the PVA hydrogels for the application as smart absorbent to remove the cationic dyes from water. The incorporation of SG could improve the mechanical property of the PVA hydrogel substantially with maximum tensile strength of 37.34 kPa, almost 89.3% increase. The enhanced mechanical property of the pure PVA hydrogel could expand the scope of the hydrogel's application area. It was found that the SP hydrogel showed specific adsorption of certain cationic dyes: MB and MG. The adsorption isotherm and kinetics of the SP hydrogels could be well-modeled using Langmuir isotherm and pseudo-second-order kinetics model, respectively. As result, the prepared SG based hydrogel could successfully separate the cationic dyes from anionic dyes based on its special adsorption behaviors.

Acknowledgements

We thank the National Nature Science Foundation of China (No.51473091) for financial support. Additionally, we also acknowledge the staff at the Instrumental Analysis Center of Shanghai Jiao Tong University for the measurement.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.12.069.

References