Facilely Synthesized, Highly Permeable, and Efficiently Recyclable Polycationic Gel with Cohesive State Transformations for Purifying Dyeing Wastewater

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ABSTRACT: A highly permeable polycationic gel (PPG) was designed as a new type of absorbent material, which was prepared by a facile cross-linking copolymerization of 3-chloro-2-hydroxypropylmethyldiallylammonium chloride and dimethyldiallylammonium chloride at 45 °C for 3.0 h. When the PPG absorbent was used for purifying dyeing wastewater, it showed high permeability so that the dyes could fully penetrate into the PPG more easily to be absorbed. Moreover, through Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, optical microscopy, and scanning electron microscopy technologies, the structures of PPG before and after absorption were analyzed, showing that the cohesive states of PPG underwent a great transformation during PPG absorption, and the binding energy of N 1S of PPG increased from 401.66 to 402.15 eV. Because of the new absorption effects of the cohesive state transformations of PPG, the absorption capacity of PPG for absorbing a large-sized dye of Reactive Scarlet 3BS reached 1371.04 mg·g⁻¹, which was 2.07−56.35 times than those of other structural forms of similar cationic absorbents and was 761.69 times higher than that of the frequently used activated carbon. This was the greatest improvement level on the absorption ability of PPG versus the existing absorbents. In addition, PPG achieved excellent recyclability with a mild room-temperature desorption technology, and the absorption capacity of the recycled PPG was 606.76 times higher than that of activated carbon.

1. INTRODUCTION

Dyeing wastewater has high toxicity, high chroma, and high chemical oxygen demands and is regarded as one of the main pollution sources for the global water environments.¹⁻⁵ To purify the dyeing wastewater, it is key to remove the highly toxic and highly colored anionic dyes in the water. Absorption, flocculation, and oxidation decomposition have already been proved to be useful methods for purifying industrial wastewater.⁶⁻¹⁵ Of which, absorption is one of the most widely used and convenient methods for water treatment.¹⁶⁻²¹ The authors have observed that several traditional absorbent materials, for example, activated carbon absorbent, clay mineral (or solid waste) absorbent, and natural product absorbent, are usually used in the field of water treatment.²²,²³ However, the absorption forces of these traditional absorbents are usually weak intermolecular forces, resulting in their relatively weak absorption abilities when being used for water treatment.²⁴,²⁵ Thus, it is necessary to search for new absorbent materials for purifying dyeing wastewater.

In previous studies, the authors had discovered that a series of polycationic materials could be used as excellent absorbents for purifying the dyeing wastewater because their polycationic skeletons could produce efficient electrostatic attractions with the formation of ionic bonds (belonging to the chemical bonds) toward the colored anionic dyes in water during absorption.²⁶⁻³¹ Notably, it was interesting that the absorption capacity of a polycationic gel (PPG) [poly(triallylmethyl ammonium chloride), PTAMAC] had been improved 368.27 times than that of activated carbon in the purification of dyeing wastewater.³² Moreover, compared to the previous absorbent materials, the preparation process of PPG absorbent was a facile polymerization. This novel discovery confirmed that the PPGs would be the better candidates as an absorbent material for purifying wastewater in further works.

The next research goal is to obtain a new type of better PPG absorbent. Through careful observation and analysis, the authors have noticed that the permeability of the previous PPG material in water is a new problem which needs to be solved. For example, the polycationic PTAMAC gel obtained in the

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previous work was not completely transparent when swelling in water, indicating that it is not fully permeable in water. Thus, the authors deduce that it will be a good breakthrough to obtain a higher absorption capacity of a new PPG absorbent by improving the water permeability of the absorbent gel.

In this work, the authors designed a facilely synthesized, highly permeable, and efficiently recyclable PPG as a novel absorbent material. The PPG absorbent was prepared by a facile copolymerization of one cationic cross-linker with strong polar groups (i.e., 3-chloro-2-hydroxypropylmethyldiallylammonium chloride, CMDA) and another cationic monomer (i.e., dimethyldiallylammonium chloride, DMAC). In the structure of PPG, both the strong polar 3-chloro-2-hydroxypropyl groups and the hydrophilic cationic units would

Table 1. L9 (3)4 for Optimizing the Synthesis Conditions of PPG Absorbents

| no. | A (°C) | B (w/w, %) | C (w/w, %) | D (h) | monomer conversion (%) | dye removal percentage (%) |
|-----|--------|------------|------------|-------|------------------------|---------------------------|
| 1   | 40     | 50         | 3          | 3     | 77.29                  | 70.45                     |
| 2   | 40     | 55         | 4          | 4     | 85.57                  | 75.54                     |
| 3   | 40     | 60         | 5          | 5     | 89.40                  | 79.80                     |
| 4   | 45     | 50         | 4          | 5     | 94.26                  | 84.16                     |
| 5   | 45     | 55         | 5          | 3     | 96.18                  | 88.67                     |
| 6   | 45     | 60         | 3          | 4     | 97.83                  | 89.21                     |
| 7   | 50     | 50         | 5          | 3     | 90.77                  | 80.05                     |
| 8   | 50     | 55         | 3          | 5     | 93.65                  | 82.58                     |
| 9   | 50     | 60         | 4          | 3     | 94.95                  | 84.33                     |

*Test conditions for the dye removal percentages: 0.003 g of PPG samples were dispersed in 50 mL of a 100 mg/L dye solution of Reactive Scarlet 3BS assisted by magnetic stirring at 30 °C for 100 h.
increase the water-swelling capacity of PPG, providing the larger accommodation spaces inside PPG to absorb the dyes. Thus, the dyes could fully penetrate into the PPG more easily to be efficiently absorbed, that is, the high permeability of PPG improved the absorption ability toward the dyes. Moreover, the PPG achieved an excellent recyclability with a mild room-temperature desorption technology. In addition, further discovery of the new absorption effects of the cohesive state transformations during the PPG absorption enhanced the absorption intensities of PPG toward the dyes.

2. RESULTS AND DISCUSSION

2.1. Optimizing the Synthesis Conditions and Controlling the Molecular Structures of PPG Absorbents. As designed, the PPG absorbents could be synthesized by a cross-linking copolymerization of CMDA and DMAC monomers, but the optimum synthesis conditions of PPG absorbents should be confirmed. Selecting a model copolymerization system in which the molar ratio of CMDA and DMAC monomers was 50/50, the effects of different conditions on the copolymerization were carried out by an orthogonal L₉(3)⁴ experiment with four factors and three levels as follows: 40–50 °C for the initial reaction temperature (factor A), 50–60% (w/w) of the monomer concentration (factor B), 3–5% (w/w) of the APS initiator amount (factor C), and 3.0–5.0 h for the reaction time (factor D). The monomer conversion percentages and the absorption abilities of the obtained PPG products for absorbing the dye solution of Reactive Scarlet 3BS were monitored and recorded in Table 1. When the monomer conversion percentages and the absorption abilities of the obtained PPG products reached the highest level, the optimum conditions for the synthesis of PPG absorbents were 45 °C for the reaction temperature, 55% (w/w) of the monomer concentration, 5% (w/w) of the APS initiator amount, and 3.0 h for the reaction time.

After achieving optimum synthesis, the molecular structures of PPG products were systemically prepared by adjusting the molar ratios of CMDA and DMAC from 10/90 to 90/10 in the copolymerization. The effects of different molecular structures of BPG products on their absorption abilities were further investigated by absorbing the dye solution of Reactive Scarlet 3BS to confirm the optimum molecular structures of PPG products, and the results are shown in Figure 1. The results showed that the absorption abilities of PPG products varied for their different molecular structure.

When the molar ratio of CMDA and DMAC monomers was 10/90 for copolymerization, the obtained PPG products were slightly cross-linked to be completely soluble in water and play the application characteristic of a polycationic flocculant in the purification of the dye solution of Reactive Scarlet 3BS [Figure 1a]. In this case, only with the dosages of 0.003–0.004 g of the obtained PPG products, the good dye removal percentages (97.83–98.81%) can be achieved. However, the percentages of dye removal were relatively poor (≤92.14%) for dosages of the obtained PPG products that were less than 0.003 g or more than 0.004 g. This indicated that the obtained PPG products only achieved good dye removal percentages within their suitable dosage ranges. This was not adaptable to the changeable water environment in the real application.

When the molar ratios of CMDA and DMAC monomers were increased to 20/90–30/70 for the copolymerization, the obtained PPG products were partly cross-linked and partly soluble in water. The polymer systems consisted of the insoluble PPG components (playing the absorbent functions) and the soluble PPG components (playing the flocculant functions). In general, the application stability of the obtained products, in this case, was higher than those with the molar ratio of the CMDA and DMAC units being 10/90 [Figure 1b,c].

When the molar ratios of CMDA and DMAC monomers were further increased to 40/60–90/10 for the copolymerization, the obtained PPG products were highly cross-linked and were completely insoluble in water. The obtained PPG products, in this case, had full absorbent functions for the purification of the dye solution of Reactive Scarlet 3BS, and the dye removal percentages were increased with the increase of the PPG dosages [Figure 1d–i]. Of which, the PPG product with the 50/50 molar ratio of CMDA and DMAC units achieved the good and stable dye removal percentage of ≥99.13% when the dosages were ≥0.004 g (to treat 50 mL of the 100 mg/L dye solution of Reactive Scarlet 3BS) [Figure 1e]. This indicated that this molecular structure of the PPG product with the 50/50 molar ratio of the CMDA and DMAC units achieved the best and most stable absorption ability, thus being the optimum molecular structure for PPG absorbent.

2.2. Comparing the Absorption Abilities of PPG for Purifying Dyeing Wastewater. As the optimum product, the PPG with the 50/50 molar ratio of CMDA and DMAC units was used to purify dyeing wastewater.

Figure 1e shows the absorption results when using 0.001–0.008 g of PPG absorbents to absorb 50 mL of the 100 mg/L dye solution. The maximal absorption capacity (Qₐₘₙₐₓ) for absorbing the dye solution could be calculated by the average absorption values at the saturated absorption states with dosages of 0.001–0.0035 g. The Qₐₘₙₐₓ of the PPG absorbent for absorbing the dye solution was calculated as 1371.04 mg·g⁻¹. Compared to the absorption capacities of the typical and similar absorbents under the same absorption conditions, the PPG absorbent showed a great superiority in the purification of dyeing wastewater (Table 2). The absorption capacity of the PPG absorbent was improved 2.07–56.35 times than those of all other structure forms of similar cationic absorbents (i.e., G-cotton, PF-cotton, LP-cotton, PT-cotton, PA-cotton, and PTAMAC). The absorption capacity of the PPG absorbent was 761.69 times higher than that of activated carbon.²⁶⁻⁻²⁹,³² This was the greatest improvement observed for the absorption ability of this novel PPG absorbent versus the frequently used activated carbon material.
2.3. Recyclability of PPG Absorbents after Absorbing the Dyes. The PPG absorbent with the saturated absorption of the anionic dyes [Figure 2a] could be recycled by using a mild room-temperature desorption technology, adopting the mixture solution of the concentrated hydrochloric acid/H₂O/C₂H₅OH of the volume ratio being 1.5/1.5/2.0 as the new desorption solution. When a certain amount of the PPG samples with the saturated absorption of the anionic dyes were stirred with 50 mL of the desorption solution at room temperature for 8 h, 83.56% of the absorbed dyes were successfully desorbed from the PPG skeletons [Figure 2b].

In order to explain the absorption−desorption behaviors of the PPG, the effects of PPG absorption by different pH values were investigated [Figure 2c]. The results showed, when pH ≥ 7.7−11 that the dye removal percentages resulted from PPG absorption were 98.87−99.95%. Conversely, when pH < 7.7−3, the dye removal percentages were plunged to 18.25−25.51%, indicating that the PPG absorption was very sensitive to the pH values and also confirming that the PPG was suitable to be desorbed in the acid systems. Moreover, the zeta potentials of PPG particles when absorbing the anionic dyes in the different pH values were correspondingly analyzed using a Zetasizer nano z90 potential measuring instrument as shown in Figure 2c. The zeta potentials of PPG particles when pH ≥ 7.7−11 were −2.97 to −3.75 mV, all of which were near to the isoelectric points, indicating that the cationic units of PPG could be fully combined with the anionic dyes by the ionic bonds, thus resulting in the good dye removal percentages (98.87−99.95%). However, the zeta potentials of PPG particles when pH < 7.7−3 were +17.57 to +42.38 mV, showing a strong positive charge and suggesting that some of the cationic units of PPG were released and were not combined with the anionic dyes, which was the key factor for PPG to realize the desorption under the acid conditions. Thus, based on the above-obtained results, the desorption mechanisms of PPG could be explained that H⁺ would be first combined with the sulfonate ions in the dye structures to form sulfonic groups, and then, the electrostatic absorption interactions between the cationic units of PPG and the anionic dyes were decreased in turn (Scheme 1), successfully realizing the desorption of the dyes from the PPG phase to water phase. In this case, the PPG absorbents could be regenerated and reused.

Similar to the previous processes in Section 2.2, 0.001−0.003 g of the regenerated PPG absorbents were reused to absorb 50 mL of the 100 mg/L dye solution, and the maximal
absorption capacity ($Q_{\text{max}}$) of the regenerated PPG absorbents could be calculated by the average absorption values [Figure 2d]. The $Q_{\text{max}}$ of the regenerated PPG absorbent was calculated to be 1122.50 mg·g$^{-1}$, which was still 606.76 times higher than that of activated carbon. Thus, the PPG absorbent had excellent recyclability in the purification of dyeing wastewater.

2.4. Absorption Mechanism of PPG for Purifying Dyeing Wastewater. A series of simulation experiments and instrument analysis were carried out to detect the absorption mechanisms and confirm a new absorption effect of PPG for purifying dyeing wastewater.

A series of absorption kinetics models (e.g., eq 1: pseudo-first kinetics equation, eq 2: pseudo-second kinetics equation, eq 3: intraparticle diffusion equation, and eq 4: particle diffusion equation) were selected to further confirm the absorption kinetics behaviors of PPG. The slopes and intercepts of the linear plots of eqs 1–4 could give the corresponding absorption rate constants to evaluate the absorption kinetics behaviors of PPG. The results are shown in Figure 3.

$$\log(q_e - q_i) = \log q_e - \frac{k_1 t}{2.303}$$  \hspace{1cm} (1)

$$\frac{1}{q_i} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$$  \hspace{1cm} (2)

$$q_i = k_3 t^{1/2} + x_i$$  \hspace{1cm} (3)

$$\ln \left( 1 - \frac{q_i}{q_e} \right) = -K_i t$$  \hspace{1cm} (4)

Figure 3a shows the effect of PPG absorption by the different absorption times (0.5–4 h) when using 0.01 g of PPG samples to absorb 50 mL of the 100 mg/L dye solution. The
absorption data obtained at different absorption times were used to fit the absorption kinetics equations (eqs 1−4) as shown in Figure 3b−e, and the absorption kinetics constants of PPG absorbents obtained were further compared to those of the similar cationic absorbents. The results showed that the pseudo-second kinetics model had the best fit to experimental data (R = 1.00), indicating a composite effect of the multiple absorption processes for PPG to absorb the dyes.

The permeable states of PPG before and after PPG absorption were scanned using a 35TV optical microscope instrument as shown in Figure 4I−III. The results showed that PPG was at high transparent state in water because of the high water-swelling effect [Figure 4I], and this transparency was clearly higher than that of the similar polycationic PTAMAC gel in our previous work [Figure 4II]. This indicated that PPG could be highly permeable in water; thus, the dyes could fully penetrate into the PPG more easily to be absorbed [Figure 4III].

A change in the molecular structures of PPG before and after PPG absorption was detected by Fourier transform infrared (FT-IR) spectroscopy analysis technique on a Nicolet FT-IR (510 P, USA) spectrophotometer as shown in Figure 5I. When compared to the FT-IR curve of the original PPG samples (curve "A"), the FT-IR analysis of PPG samples after absorbing the dyes (Reactive Scarlet 3BS) [curve "B" in Figure 5I] showed a different FT-IR curve of the spectrum absorption peaks in a wide spectrum absorption range of 673−1618 cm⁻¹ (peak 5) and a new spectrum absorption of the dye structure at 2355 cm⁻¹ (peak 6). All the changing FT-IR information suggested that the molecular structures of PPG had undergone a great transformation after absorbing the dyes.

When compared to the XRD curve of the original PPG samples (curve "A"), the X-ray diffraction (XRD) analysis of PPG samples after absorbing the dyes (Reactive Scarlet 3BS) [Figure 5II] showed a different XRD curve (curve "B"). After absorbing the dyes, the width of the diffraction peak of PPG samples was wider, and the height of the diffraction peak was much higher than those before absorbing the dyes [curve "A" vs curve "B" in Figure 5II]. This was a new sign that the cohesive structures of the PPG samples had been transformed after absorbing the dyes. Before absorbing the dyes, the cationic units in the PPG skeletons were repellent because of the repulsive effects of the same cationic charges, resulting in a relatively weak cohesive state for the structure of PPG. After
absorbing the dyes, the repulsive effects of the same cationic charges disappeared because the cationic units in the PPG skeletons would strongly interact with the anionic dyes by the ionic bonds to form the isoelectric combinations (Scheme 2). In this case, the PPG skeletons were strongly cohesive. Thus, the cohesive states of PPG before and after absorption were different.

The scanning electron microscopy (SEM) analysis using a JSM-5610 SEM instrument further showed that the surface of PPG after absorbing the dyes was smoother than the original PPG samples [Figure SIII vs Figure SIV], further confirming a cohesive structure transformation of PPG during the absorption.

The X-ray photoelectron spectroscopy (XPS) analysis from a Thermo VG multilab 2000 spectrometer [Figures 6 and 7] showed a change in the binding energy of the PPG absorbents after absorbing the dyes. The binding energy of N 1s of PPG was increased from 401.66 to 402.15 eV [Figure 6c vs Figure 7c], indicating that the cationic units (i.e., the N-containing units) of the PPG absorbents formed stronger interactions (ionic bonds) with the anionic dyes during absorption, thus enhancing the absorption intensity of PPG toward the dyes.

Scheme 2. Modeling the Cohesive State Transformations of the PPG Absorbent before and after Absorbing the Dyes

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**Figure 6.** XPS analysis of PPG samples before absorbing the dyes. (a) Overall scanning of PPG before absorbing the dyes. (b) Scanning the binding energy of C 1s of PPG before absorbing the dyes. (c) Scanning the binding energy of N 1s of PPG before absorbing the dyes. (d) Scanning the binding energy of O 1s of PPG before absorbing the dyes.

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“−SO₃⁻” the anionic dye of Reactive Scarlet 3BS, HI the electrostatic absorption interaction.
Generally, the above results confirmed that the new absorption effects of the cohesive state transformations occurred during the PPG absorption. Besides, the high permeability of PPG could make the dyes in water penetrate into the PPG more easily to be absorbed, and the cohesive states of PPG had undergone a great transformation during the PPG absorption. This was the key factor for the PPG absorbent to achieve excellent absorption ability in the purification of dyeing wastewater.

3. CONCLUSIONS

A highly permeable PPG has been successfully synthesized as a new type of absorbent by facile cross-linking copolymerization of one cationic cross-linker of CMDA, and another cationic monomer of DMAC at 45 °C for 3.0 h. The PPG absorbent showed a high transparent state in water because of the high water-swelling effect, indicating high water permeability.

When the PPG absorbent was used to purify dyeing wastewater, the absorption capacity was improved 2.07–56.35 times those of all other structure forms of similar cationic absorbents reported in a previous series of studies and was 761.69 times higher than that of activated carbon. Moreover, the PPG absorbent achieved excellent recyclability by using a mild room-temperature desorption technology, and the absorption capacity of the recycling recycled PPG was 606.76 times higher than that of activated carbon.

A series of simulation experiments and instrument analysis were carried out to detect the absorption mechanisms of PPG. Besides, the PPG could be highly swelling, and the dyes could penetrate into the BPG more easily and be absorbed, our data confirmed that the cohesive states of PPG underwent a transformation after absorbing the dyes. After absorbing the dyes, both the FT-IR and XRD analysis curves differed greatly from the original PPG samples. The XPS technology revealed that the binding energy of N 1s of PPG was increased from 401.66 to 402.15 eV after absorbing the dyes. The SEM analysis further showed that the surface of PPG after absorbing the dyes was smoother than the original PPG samples. The new cohesive state transformations had enhanced the absorption intensities of PPG toward the dyes. This was the key factor for the PPG absorbent to achieve excellent absorption ability in the purification of dyeing wastewater.

4. EXPERIMENTAL SECTION

4.1. Materials. CMDA was prepared by the condensation of methylallylamine and epichlorohydrin at pH = 7–8 according to our previous study. DMAC (industrial purity) was purchased from Luyue Chemical Co., Ltd (China) and treated by vacuum distillation before usage. Ammonium persulfate (APS, AR) was supplied by Tianjin Jinhai Chemical Co., Ltd (China). Reactive Scarlet 3BS (industrial purity) was supplied by Shandong Hongfu Chemical Co., Ltd (China). Hydrochloric acid (AR) was supplied by Tianjin Damao Chemical Co., Ltd (China).

4.2. Facile Synthesis Process of the PPG Absorbent. In a 50 mL round-bottomed flask, a cross-linking monomer of CMDA, a cationic monomer of DMAC, and deionized water were added to form a reaction solution, and the monomer concentration of CMDA and DMAC in the solution was controlled to be 55% (w/w). Subsequently, an APS initiator accounting for 5% (w/w) of the monomer mass was added. The reaction temperature was 45 °C to run the cross-linking copolymerization of the CMDA and DMAC monomers for 3.0 h and obtain the colloid of PPG absorbent. The PPG colloid was dried at 90 °C for 8 h and was crushed with a bowl to finally obtain the power products of PPG absorbents for reservation. The synthesis route of PPG is shown in Scheme 3.

As described in the previous work, the monomer conversions (C%) could be measured by a bromine labeling technique and could be calculated based on the following eq. 5.

\[
C\% = \left(1 - \frac{x_1}{x_0}\right) \times 100\%
\]
where \( x_i \) was the moles of residual bonds and \( x_0 \) was the total moles of double bonds.

### 4.3. Absorption Studies of the PPG Absorbents

First, the absorption effects of PPG absorbents by the different absorption processes were carried out as follows: 0.01 g of the PPG absorbents were mixed with 50 mL of the 100 mg/L dye solution under magnetic stirring, and the absorption interactions were run for 0.5–4 h. The absorption solutions at a corresponding absorption time of 0.5–4 h were filtered to detect the effect of each absorption time interval (\( t \)). As described in detail in a previous series works,26–32 the dye concentration in the solution (\( C_t \)), the dye removal percentage (\( R \)), and the amount of dye absorption (\( q_t \)) at time \( t \) could be calculated by a spectrophotometer technique. The absorption data at time \( t \) were used to fit the absorption kinetics models to investigate the absorption kinetics behaviors of PPG absorbents.

Subsequently, the isotherm absorption experiments of the PPG absorbent toward a large-sized anionic dye of Reactive Scarlet 3BS were conducted as follows: 0.001–0.008 g of the PPG absorbents were mixed with 50 mL of the 100 mg/L dye solution of Reactive Scarlet 3BS under magnetic stirring to run the absorption interactions for 100 h. Subsequently, the absorption solutions were filtered to detect the absorption effects. As described in detail in a previous series works,26–32 the concentration of the dye residue in the solution (\( C_0 \)), the dye removal percentage (\( R \)), and the equilibrium absorption capacity (\( q_e \)) could be measured and calculated by a spectrophotometer technique. All the dye removal percentages (\( R \)) mentioned could be calculated by the following eq 6

\[
R\% = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\%
\]

where \( A_t \) was the dye absorbance residue in the solution after PPG absorption and \( A_0 \) was the dye absorbance in the original solution.

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**Notes**

The authors declare no competing financial interest.

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