Self-Assembled Hydrogels Based on Poly-Cyclodextrin and Poly-Azobenzene Compounds and Applications for Highly Efficient Removal of Bisphenol A and Methylene Blue

Yagui Gao,† Rong Guo,† Yao Feng,† Lexin Zhang,†‡ Cuiru Wang,† Jingwen Song,† Tifeng Jiao,*,†‡ Qiuming Peng,‡ Jingxin Zhou,† and Qiuming Peng,‡

1. INTRODUCTION

Cyclodextrins (CDs) are macrocyclic oligosaccharides with the special structure of hydrophobic interior cavity and hydrophilic exterior ring.1 β-Cyclodextrin is composed of seven repeated monomers of glucopyranose units linked by α-(1,4) glycosidic linkages. Due to moderate internal diameter, low price, and negligible toxicity, β-cyclodextrin-based self-assembled materials have been intensively investigated in many fields, such as controlled release drug carriers, self-healing hydrogels, and electrochemical sensors.5−7 However, native cyclodextrins are unable to incorporate certain hydrophilic compounds or large molecules. To overcome these limitations and extend the inclusion capacity, the syntheses of cyclodextrin polymers are necessary.6,8 Cyclodextrin polymers could be prepared by reacting cyclodextrins with cross-linking agents, such as epichlorohydrin, carbonyl compounds (e.g., diphenyl carbonate, dimethyl carbonate, carboxydiimidazole), and organic dianhydrides (e.g., pyromelitic anhydride).7−10 In contrast to CDs, cyclodextrin polymers (poly-CD) exhibited higher efficiency to accommodate high-weight molecules and demonstrated higher stability constants since all of the cyclodextrin units co-operatively participated in the formation process of inclusion complexes.11−13

Polymeric hydrogel is a series of essential soft matter with cross-linked network structure. Stimuli-responsive polymeric hydrogels are significant at present and have potential applications as “smart” materials in many areas owing to well responsiveness to environmental stimuli, such as light, pH, temperature, or solvents.14−16 Compared to the fixed networks constructed by chemical cross-linking, the stimuli-responsive hydrogels showed temporary physical network, which could be inversely transformed into solutions by adjusting the environmental factors.17

Recently, the supramolecular self-assembled hydrogels via host−guest interactions between cyclodextrins polymers and guest molecules have attracted much attention. The hydrophobic cavity of cyclodextrins can obtain host−guest inclusion complexes with suitable hydrophobic guest molecules through hydrophobic interactions, electrostatic interactions, van der Waals forces, and dipole−dipole interactions. Hence, the host−guest interaction via cyclodextrin can be utilized to form hydrogel as adsorbent agents to anchor MB via electrostatic interaction and anchor MB via electrostatic interaction and hydrogen bonding.

Received: July 30, 2018
Accepted: September 13, 2018
Published: September 24, 2018

DOI: 10.1021/acsomega.8b01810
ACS Omega 2018, 3, 11663−11672
coatings.\textsuperscript{18} BPA could be removed using cyclodextrin-based hydrogel through the host–guest interaction to form inclusion complexes. Besides, methylene blue (MB) is a kind of organic dye from aqueous solution, which is harmful to the environment. Now many excellent research works have been achieved about the synthesis of novel composite materials for MB removal. For examples, Jale et al. reported the synthesis of carbonized peanut shell as low-cost adsorbent for adsorption of MB.\textsuperscript{19} Yildiz and co-workers investigated monodisperse Pt/Rh@GO nanocomposites and their adsorption performances for MB with adsorption capacity of 346.79 mg/g.\textsuperscript{20} Han et al. reported the preparation of flower-like MoS\textsubscript{2} nanosheet-based nanostructure and superior dye-adsorption performance.\textsuperscript{21} Sert et al. investigated the synthesis of monodisperse Vulcan carbon-supported Pt nanoparticles via microwave-assisted method and application for MB removal with remarkable adsorption capacity of 271.15 mg/g.\textsuperscript{22}

In this present work, we synthesized cyclodextrin polymers (poly-CD) by cross-linking agents and fabricated photosensitive supramolecular polymeric hydrogel via poly-cyclodextrin (poly-CD) and azobenzene-branched poly(acrylic acid) copolymer (PAA-Azo) to investigate the light-responsive properties of polymeric hydrogel after UV irradiation. These new sol–gel switching hydrogel materials through host–guest interactions could be utilized as light-operated switch and self-healing materials. Moreover, these polymeric hydrogels served as excellent adsorbent agents to remove BPA via hydrophobic interaction and MB via electrostatic interaction and hydrogen bonding, which demonstrated potential applications in dye removal and wastewater treatment.

2. RESULTS AND DISCUSSION

2.1. Preparation and Characterization of Hydrogels.
The photographs of as-obtained poly-CD/PAA-Azo composite hydrogels are showed in Figure 1. It was observed that all hydrogels perform good gelation stability, and the gel with lower concentration of poly-CD becomes more transparent and clearer. To explore the internal structure of the gels, the morphological and spectral characterizations were performed. Figure 2 shows the X-ray diffraction (XRD) patterns of poly-CD and PAA-Azo as well as the five groups of hydrogels. The XRD pattern of pure PAA-Azo has a broad peak with centered position of 23°, which is mainly attributed to the alkyl main chain in the PAA molecule. The XRD pattern of poly-CD shows many diffraction peaks between 2θ values of 10–25° indicating the amorphous state of the cyclodextrin polymer. For the five groups of hydrogels, the obtained XRD patterns of Gel-A and Gel-B are similar to poly-CD, indicating that the concentrations of poly-CD in the hydrogels were excessive. Compared to the formed Gel-C, Gel-D, and Gel-E, the diffraction peaks assigned to poly-CD almost disappeared and there appeared the characteristic diffraction peak at 2θ value of 19.4°, which indicated that the special interaction occurred in the hydrogels (Table 1).

The Fourier-transform infrared (FT-IR) spectra of the five groups of hydrogels are shown in Figure 3. The characteristic peak at 3350 cm\textsuperscript{-1} was mainly owing to the stretching vibration peaks of –OH, –COOH, and –H–OH groups. As for poly-CD, the peak at 2915 cm\textsuperscript{-1} was assigned to the –CH\textsubscript{2} group, which is due to the introduction of the epichlorohydrin as a cross-linking agent. And the peaks at 1650, 1150, and 1095 cm\textsuperscript{-1} originated from C–H bonds, C–O bonds, and C–OH bonds, respectively, which indicated the good hydrophilicity of poly-CD.\textsuperscript{23–25} The characteristic peaks at 1015 and 910 cm\textsuperscript{-1} are attributed to the vibration peaks of the C–O–C bond and the α,1,4 glycosidic bond on the cyclodextrin backbone, respectively. In addition, the above characteristic peaks also appeared in the FT-IR spectra of hydrogels with different concentrations, and the newly appearing characteristic peaks at 1730 and 1660 cm\textsuperscript{-1} were attributed to the stretching vibration peaks of carbonyl and amide bonds, respectively. Therefore, the present obtained FT-IR data demonstrated the successful synthesis of composite materials between poly-CD and PAA-Azo, which occurs through the linkage of amide bonds. It should be noted that due to the component of poly-CD solution with maximum concentration of 100 mg/mL, the formed Gel-A demonstrate cloudy state with a few aggregates, which can be seen in photograph of hydrogels in Figure 1. The concentration ratio of the Gel-E was the minimum gelation concentration between poly-CD and PAA-Azo. Thus, the formed Gel-B and Gel-E were selected as representatives for the next characterization investigation.

It could be seen that the micro/nanosized morphologies of the Gel-B and Gel-E hydrogels are demonstrated in Figure 4. The cross-linked network-like hydrogel system could be formed under the dispersion medium, and the microscopic size changed from several micrometers to hundreds of nanometers. Comparison of Gel-B and Gel-E, it was found that the pore structure existed both in the Gel-B and Gel-E. Due to the poly-CD concentration in Gel-E was lower than...
that in Gel-B, so the more porous structures and larger specific surface area were appeared in Gel-E than that in Gel-B. The porous microstructures of the hydrogels were further investigated by utilizing the nitrogen adsorption–desorption isotherms, and the pore size distributions of poly-CD/PAA-Azo hydrogels were calculated by the Barrett–Joyner–Halenda (BJH) method shown in Figure 5. In the range of relative pressures from 0 to 1, Gel-E shows the hysteresis loops of typical IV isothermal curves at the $p/p_0 = 0.3−0.7$, indicating that the mesoporous structures exist in the Gel-E.\(^{26−28}\) Thus, Gel-E demonstrated more pores and larger specific area than Gel-B. In addition, the BJH method was used to calculate the specific surface areas of the two groups of gels, as shown in Table 2, where the physical properties of nitrogen adsorption and desorption are shown. It can be clearly observed that the specific surface areas of hydrogels in Gel-B and Gel-E are 66.148 and 68.184 m\(^2\)/g, respectively, whereas the average pore diameters are 4.886 and 5.225 nm, respectively, and the average pore volumes are 0.077253 and 0.086408 cm\(^3\)/g. The higher specific surface areas and larger pore diameters and pore volumes can be expected to enhance the enveloped capacity of the organic molecules.

Figure 6 demonstrates the thermograms of the prepared hydrogels under nitrogen conditions. It could be observed that the first weight loss of four curves was around at 100 °C. This can be normally explained by the removal and evaporation of surface-adsorbed water molecules. From the thermogravimetric curves of PAA-Azo, it can be seen that PAA-Azo mainly loses weight in two stages of 190 and 480 °C, which is mainly owing to the decomposition of the alkyl backbone of PAA molecules and the azobenzene group organics. As for poly-CD, the weight loss of 62% at 300 °C was attributed to the thermal decomposition of cyclodextrin oligosaccharides.\(^{29−33}\) In addition, from the thermogravimetric plots of poly-CD/PAA-Azo hydrogels of Gel-B and Gel-E, it can be seen that there is approximately 10% weight loss between 100−300 °C, which is attributed to poly-CD molecules and the thermal decomposition of alkyl chains in PAA-Azo molecules; and the mass loss approximately 55% between 300 and 400 °C was mainly attributed to the inclusion complexes of the composite hydrogels became thermal decomposition. The rheological behavior of two kinds of obtained hydrogels was characterized, considering the dependence of storage modulus ($G'$) and loss modulus ($G''$) on angular frequency ($\omega$). The storage modulus $G'$ represents the elastic part of stored energy in material and also becomes the elastic modulus; the loss modulus $G''$ reflects the viscosity and energy loss of the material and also becomes the viscous modulus. Comparing Figure 7a,b, the $G'$ and $G''$ values of the Gel-B and Gel-E are equal at shear stresses of 1.02 and 0.43%, respectively. This shows that the Gel-B has relatively wider viscoelastic region and shear strength relative to the Gel-E. At a shear stress of 0.001%, the frequency-dependent oscillating shear rheological behavior of the obtained gels was measured in Figure 7c,d. It was found that $G'$ dominated the detected
frequency range, exhibiting the true gel-state behavior. From the Figure 7e,f curves, it can be seen that the two groups of gels can basically be shear thinned and have good recovery performance.

The photoisomerization performances of the azobenzene group were studied using the minimum gel formation concentration of Gel-E, as shown in Figure 8. Figure 8a shows the Gel-E placed in a quartz cell, and the hydrogel would be exposed to UV light at different time intervals with 365 nm UV lamp in dark conditions. The UV−vis spectra were measured with the irradiation time of 0 s, 15 s, 30 s, 1 min, 5 min, and 10 min, as shown in Figure 8c. Observing the UV−vis spectra of the Gel-E before irradiation, it can be found that the absorption peaks appear at 221, 282, and 433 nm. The characteristic peak at 348 nm was attributed to the π−π* transfer of the azobenzene trans-isomer, whereas the n−π* transfer of the cis-isomer was at 438 nm. With the increase of the irradiation time, the intensity of the π−π* transfer peak gradually decreased and the position of the peak became slowly blue shifts, at the same time, the intensity of the n−π* transfer peak gradually increased. The equilibrium state was basically reached after 5 min of irradiation, indicating that the cis and trans isomers of azobenzene group almost reached equilibrium at this time. Figure 8d is a comparison of circular dichroism (CD) spectra before and after UV light illumination. It could be seen that the hydrogel had a good chiral signal before illumination, indicating that the azobenzene group and the β-CD group in the poly-CD/PAA-Azo hydrogel have the host−guest reaction. The host−guest recognition had formed in a hydrogel system with a stable cross-networking structure. Compared with the CD spectra of the 10 min UV light, the chiral signal was weaker and almost disappeared. This indicated that UV light make the azobenzene group change from trans-isomer to cis-isomer. The conformational conversion of isomer caused the partial host−guest interactions of azobenzene group and β-CD groups to be disassembled, and the stable system of hydrogels was conversed to a sol state macroscopically, as shown in the photograph of Figure 8b.

2.2. Adsorption Performances toward Dye Removal. On the basis of the above characterization analysis, we know that the obtained hydrogels have porous nanostructure and large specific surface area. So, the adsorption properties of present obtained gels to bisphenol A and organic dyes were researched. The Gel-E was chosen as the typical adsorbent to selectively remove MB and BPA mainly owing to the larger specific surface area and more porous structures. The adsorption kinetics was carefully investigated by fitting experimental data with the pseudo-first-order model and pseudo-second-order model adsorption equation, as shown in Figure 9. Classical kinetic models were utilized to show the above adsorption mechanism as follows:

The pseudo-first-order model can be shown by eq 1

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

The pseudo-second-order model can be shown by eq 2

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$
where $q_t$ represents the adsorption capacity at time $t$ and $q_e$ represents the adsorption capacity at equilibrium. $k_1$ and $k_2$ values represent the kinetic rate constants.\(^{38,39}\) The kinetic results are calculated and summarized in Table 3, and demonstrated that the pseudo-two-order model showed a higher correlation coefficient ($R^2 > 0.99$) in MB adsorption process, whereas the pseudo-first-order model seemed more accurate ($R^2 > 0.99$) in BPA adsorption process. Thus, it was hypothesized that Gel-E exhibited the different mechanisms in removal of MB and BPA. In addition, the fitted removal efficiency of Gel-E for MB reached 85.3248 mg/g, whereas for the BPA system, the calculated removal efficiency showed value of 20.7297 mg/g. It should be noted that from previous reports, the removal efficiencies of MB from different composite materials, including sandwiched Fe$_3$O$_4$/carboxylate graphene oxide nanostructure, polydopamine sheathed electrospun nanofibers, and diamond based core–shell nano-

$$t = \frac{1}{k_1 q_e^2} + \frac{t}{q_e}$$

(2)
composites, showed the value range of 34–40 mg/g. In addition, some two-component supramolecular gels based on glutamic acid component and graphene oxide hydrogels demonstrated the maximum removal values of 16.898 and 334.448 mg/g for MB removal. Thus, present obtained composite gel materials exhibited excellent removal capacities for MB molecules. Moreover, durability and regeneration of absorbent materials seemed very important in real industrial conditions.

Figure 8. Photographs of the Gel-E group hydrogel before (a) and after (b) exposure to UV light as well as the corresponding UV–vis spectra (c) and CD spectra (d). Photograph courtesy of Yagui Gao. Copyright 2018.

Figure 9. Kinetic adsorptions of (a) $q_t$ versus $t$ plots and (b) $t/q_t$ versus $t$ plots for BPA and MB.
application. Different composite systems mentioned above can be reused several times or recycled in a controlled way, demonstrating long use in wastewater purification.\textsuperscript{45,46} However, as for present composite hydrogel materials, due to the mass losses of poly-CD and PAA-Azo components in the regeneration process by washing with organic solvents, the durability and reusability performance do not seem promising.

It is well known that cyclodextrin-based compounds also have a good affinity for the binding of BPA mainly due to host−guest interaction, so they can be utilized as specific host molecules for anchoring and removal of BPA from wastewater.\textsuperscript{47} On the other hand, MB belong to a positively charged organic molecule, which interacts with many adsorbents through electrostatic attraction and hydrogen binding.\textsuperscript{41,42} Therefore, present prepared hydrogel materials could remove both kinds of organic molecules with good removal efficiency, which was reasonably attributed to different removal mechanisms. As shown in Figure 10, the prepared gels served as adsorbent agents to anchor MB via electrostatic interaction and hydrogen bonding by functional carboxyl groups linked in molecular skeletons. And the removal of BPA molecules could be attributed to host−guest interactions with versatile adsorption process. Present research work showed new exploration of composite hydrogels used as composite absorbent materials for applications in environmental engineering and wastewater treatment.

| Gel-E | \( q_e \) (mg/g) | \( R^2 \) | \( K_1 \) \((\text{min}^{-1})\) | \( q_e \) (mg/g) | \( R^2 \) | \( K_2 \) \((\text{g/(min mg)})\) |
|-------|-----------------|---------|-----------------|-----------------|---------|-----------------|
| BPA   | 19.0055         | 0.99334 | 1.634 \( \times 10^{-2} \) | 20.7297         | 0.92056 | 1.3274 \( \times 10^{-3} \) |
| MB    | 85.3248         | 0.96126 | 3.2181 \( \times 10^{-3} \) | 84.1750         | 0.99914 | 5.4157 \( \times 10^{-3} \) |

Figure 10. Schematic illustration of the Gel-E adsorption processes of MB (a) and BPA (b).

3. CONCLUSIONS

In summary, new composite hydrogel materials based on poly-CD and PAA-Azo polymers were prepared, and the dye removal capacities of the hydrogels were studied. Various poly-CD/PAA-Azo composite hydrogels with different concentrations ratios were prepared, demonstrating gel−sol conversion process due to the \textit{cis}−\textit{trans} isomerization of azobenzene group. The maximum removal efficiency of present obtained gel reached 85.3248 mg/g for MB and 20.7297 mg/g for BPA, demonstrating excellent anchoring capacities. The prepared gels served as adsorbent agents to anchor MB via electrostatic interaction and hydrogen bonding by functional carboxyl groups linked in molecular skeletons. And the removal of BPA molecules could be attributed to host−guest interactions with versatile adsorption process. Present research work showed new exploration of composite hydrogels used as composite absorbent materials for applications in environmental engineering and wastewater treatment.

4. EXPERIMENTAL SECTION

4.1. Materials. \( \beta \)-Cyclodextrin (\( \beta \)-CD, 98%), epichlorohydrin (99%), 4-aminoazobenzene (N-Azo), and poly(acrylic acid) (PAA, average MW \( \sim 450 000 \)) were obtained from Alfa Aesar (Tianjin, China) Chemicals, Aladdin Reagent Chemicals (Shanghai, China), and TCI Shanghai Chemicals without further purification. \( N\)-(3-Dimethylaminopropyl)-N-hydroxysuccinimide and methylene blue (MB) and bisphenol A (BPA) were purchased from Beijing Chemicals with analytical reagent grade. The used other reagents, such as toluene and isopropanol, were obtained from Sinopharm Chemical Reagent Co. Ltd. with analytical reagent grade. All aqueous solutions were obtained with water from a double-stage Millipore Milli-Q Plus purification system.
4.2. Preparation of Hydrogels. First, poly(\(\beta\)-cyclodextrin) (poly-CD) was synthesized according to the literature.\textsuperscript{48-50} The final white product solid was obtained after freeze-drying process. The azobenzene-terminated poly(acrylic acid) copolymer (PAA-Azo) was prepared according to our previous work.\textsuperscript{34} Then, aqueous poly-CD solutions with various concentrations (100, 50, 25, 12.5, and 6.25 mg/mL) were prepared and continuously stirred at room temperature until poly-CD molecules was completely dissolved into ultrapure water. Aqueous PAA-Azo solution (10 mg/mL) was also prepared and fully dissolved by sonication for 2–3 min. Then, 1 mL of PAA-Azo solutions was mixed with the different concentrations 0.8 mL of poly-CD solutions, respectively. After sonication for 30 min, the gelation states were formed. The detailed formulations are shown in Table 1, and the prepared samples of hydrogels were named as Gel-A, Gel-B, Gel-C, Gel-D, and Gel-E. It should be mentioned that the concentration ratio of the Gel-E was also the minimum gelation concentration between poly-CD and PAA-Azo.

4.3. Adsorption Experiments. Adsorption performances were performed by utilizing two typical organic molecules, methylene blue (MB) and bisphenol A (BPA). The UV–vis absorption spectra were monitored for the adsorption process at wavelengths of 276 nm (BPA) and 632 nm (MB) using a 752-type UV spectrometer (Shimadzu Corporation, Japan). Absorption spectra were investigated on a Shanghai Luminous Corporation (Shanghai, China) to completely remove water over 2–3 days. The morphology of the hydrogels was characterized via a field-emission scanning electron microscope (SEM) (S-4800II, Hitachi, Japan) with 5–15 kV accelerating voltage. X-ray diffraction patterns were investigated on an X-ray diffractometer (SMART LAB, Rigaku) using Cu K\(\alpha\) radiation. FT-IR spectra were carried out by a Fourier infrared spectroscopy (Thermo Nicolet Corporation) by the conventional KBr disk method. The specific surface areas and pore diameter distributions were measured by using Brunauer–Emmett–Teller measurements (NOVA 4200-P). Thermogravimetrics (TG) were conducted by a Netzsch STA 409 PC Luxxsi multithermal analyzer (Netzsch Instruments Manufacturing Co, Ltd, Germany) in argon gas atmosphere. UV–vis absorption spectra were investigated on a Shimadzu UV-2550 system (Shimadzu Corporation, Japan). Circular dichroism (CD) spectra were obtained by a JASCO J-810 CD spectrometer. Dynamic rheology experiments were measured with an Anton Paar MCR302 rheometer at room temperature.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: zhanglexin@ysu.edu.cn (L.Z.).
*E-mail: tfjiao@ysu.edu.cn (T.J.).

ORCID
Tifeng Jiao: 0000-0003-1238-0277
Qiming Peng: 0000-0002-3053-7066

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We greatly appreciate the financial supports of National Natural Science Foundation of China (Nos 21872119, 21473153, and 51771162), Support Program for the Top Young Talents of Hebei Province, China Postdoctoral Science Foundation (No. 2015MS80214), Research Program of the College Science & Technology of Hebei Province (No. ZD2018091), and Scientific and Technological Research and Development Program of Qinhuangdao City (No. 201701B004).

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