Poly(hydroxamic acid) hydrogels for the removal of dyes from aqueous solutions

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The crosslinker used in the preparation of a poly(hydroxamic acid) hydrogel has a greater effect on its dye-sorbent properties (i.e., the removal efficiency) than does the type of dye.

Hydrogels are a unique class of materials comprised of macromolecular networks. A large fraction of aqueous solvent can be adsorbed into the 3D crosslinked polymeric hydrogel structure, thereby causing the gel to swell in an aqueous environment. For this reason, hydrogels find widespread application in water purification and separation processes.1, 2 It was recently determined that hydrogels with functional groups can also be used as complexing agents for the removal of dyes or other pollutants from aqueous solutions.3, 4 In particular, polyacrylamide (PAAm)-based hydrogels are popular for use in wastewater purification and metal extraction.5, 6 When used as adsorbents, PAAm-based hydrogels achieve superior results compared with other adsorbents (i.e., because their macromolecular structure and modification are controllable). Furthermore, unlike other synthetic and natural adsorbents, PAAm-based hydrogels (e.g., homopolymers; neutral, anionic, or cationic copolymers; composites; and interpenetrating polymer networks), which are easily polymerized, copolymerized, and/or modified, can be used as superadsorbents for cleaning textile wastewaters. A number of PAAm-based hydrogels have achieved good results (e.g., high swelling capacities, high porosity, moderate crosslink density, environmental sensitivity, and good mechanical strength). However, they still fall short in terms of the range of dyes that they can adsorb. 5–10

Therefore, to increase the range of dyes that can be adsorbed from water—and thus improve the performance of hydrogel-based water purification systems (especially for textile-industry wastewater)—we have prepared poly(hydroxamic acid) (PHA) hydrogels by modifying PAAm hydrogels with crosslinkers (i.e., ethylene glycol dimethacrylate, EGDMA, and N,N'-methylenebisacrylamide, NNBis). The PHA hydrogels are able to bind easily via interaction with a number of molecules (e.g., dyes, heavy metal ions, and toxic substances) due to ionizable hydroxamic groups (–NH–OH).11, 12 PHA hydrogels, which are in the form of granules and are insoluble in any solvent, offer a great advantage over other absorbent powders and/or soluble absorbents. Further, they have a very high swelling capacity, great mechanical stability, high adsorption power, and are reusable. We tested the performance of our hydrogels when used for the removal of anthracene-based basic dyes, such as toluylene red (TR, from phenazines), Lauths violet (LV, from phenothiazines), and cresyl violet (CV, from oxazines) from water-based solutions. Details of these dyes and their makeup are shown in Table 1. Cationic groups of dyes such as these are toxic colorants and can have harmful effects in humans and animals (e.g., allergic dermatitis, skin irritation, mutations, and cancer). For this reason, their removal is desirable. We also investigated the influences of hydrogel ionogenity, hydrophilicity, and crosslinker flexibility on the swelling and adsorption of the dyes.

Table 1. Molecular structure of the dyes toluylene red, Lauths violet, and cresyl violet.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Dye structure</th>
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<tbody>
<tr>
<td>Toluylene red (TR)</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>Lauths violet (LV)</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>Cresyl violet (CV)</td>
<td><img src="image3" alt="Structure" /></td>
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Figure 1. A diagram of the hydrogel experiments. First, poly(hydroxamic acid)—i.e., the aqueous monomer, PHA—was prepared by combining a polyacrylamide (PAAm) hydrogel with a crosslinker. The resulting hydrogels were treated in a solution of hydroxylamine hydrochloride and subsequently dried. The hydrogels were then added to a dye solution and analyzed using a spectrophotometer.

To prepare our poly(hydroxamic acid) hydrogel, we added a solution of hydroxylamine hydrochloride to crosslinked PAAm in distilled water and stirred the resulting mixture for 2 hours. The hydrogels were then washed with distilled water and dried in air and under vacuum (see Figure 1). To determine how effective they were at removing the harmful dyes from the solvent, we gravimetrically measured the swelling of the hydrogels in aqueous dye over time. Figure 2 shows that the swelling values of the semi-flexible polymers (modified with NNBis) range from 217 to 243%, while the values for the flexible hydrogels (modified with EGDMA) vary between 2123 and 2817%. The swelling of the PHA/EGDMA is much higher than that of the PHA/NNBis because EGDMA is made up of a greater number of hydrophilic groups.

Our results also showed that the type of dye that is used affects the swelling of the PHA-EGDMA hydrogel, but has no impact on the swelling of the PHA-NNBis hydrogel. The reason for this difference is the hydrophilic character of both the EGDMA crosslinker and the dye molecules. Because the dye molecules have a number of hydrophilic sites, the PHA-EGDMA hydrogels swell to larger volumes in aqueous dye solutions than they do in pure water.

To observe the dye uptake of unmodified PAAm, and thus obtain a base for comparison, we placed both types (i.e., modified and unmodified PAAm) in aqueous solutions of the cationic dyes and a number of anionic dyes (amido black, congo red, orange, titan yellow, and xylidine ponceau) and allowed them to equilibrate. We found that, after equilibrium is reached, the PAAm hydrogels do not show any coloration in any of the dye solutions. In contrast, the PHA hydrogels (i.e., modified PAAm) that contained anionic groups and hydrophilic crosslinkers in the basic (cationic) dye solutions showed a darker coloration, but remained transparent in the anionic dye solutions. Because PAAm is a nonionic polymer, modifying it with hydroxylamine hydrochloride led to an increase in the number of ionizable groups. The resulting hydrogels therefore have many hydroxamate groups, causing an increase in their interaction with cationic dyes. The possible interactions between dye molecules and PAAm or PHA hydrogels are shown in Figure 3.

Based on our findings, we calculated the dye-removal efficiencies of the hydrogels and plotted the results (see Figure 4). We found that the PHA-EGDMA hydrogels had removal efficiencies of 71, 93, and 99% for TR, LV, and CV, respectively. In contrast, the removal efficiencies achieved with the PHA-NNBis hydrogels were 48, 80, and 90%. As can be seen in Figure 4, in both PHA-EGDMA and PHA-NNBis hydrogels, the best binding was achieved for the CV dye.

We attribute the primary influence on hydrogel swelling and dye adsorption to the formation of ionizable groups. Formation of these groups occurs by modification of the amide groups in the polyacrylamide hydrogels (i.e., to hydroxamic acids) and thus causes an increase in the dye removal efficiency (due to hydrogen bonding). The secondary influence is the replacement of NNBis crosslinkers with...
EGDMA crosslinkers, and thus the introduction of a higher number of hydrophilic groups (leading to greater adsorption). The smallest effect on the swelling and adsorption of the dyes arises due to the presence of methyl (i.e., hydrophobic) groups in the dyes. The mechanisms that we have proposed for the binding of the dyes onto PHA hydrogels are presented in Figure 5.

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In summary, we have developed two different PHA hydrogels (i.e., based on NNBis and EGDMA) and have obtained quantitative information on the swelling and binding characteristics of a number of dyes. We found that the crosslinker type in the PHA hydrogel affected the swelling and adsorption properties of the hydrogel more than the nature of the dye. Based on our results, we conclude that PHA hydrogels may be used as a sorbent for the removal of dye molecules. We believe that our results could make the application of these types of hydrogels in biomedicine, controlled drug delivery, pharmaceuticals, agriculture, biotechnology, environment, sorption, separation, purification, immobilization, as well as the enrichment of some species (e.g., heavy metal ions and cationic dyes) more popular. In our future work, we will test the use of PHA-EGDMA hydrogel in the removal of similar cationic dyes from natural and artificial wastewater.

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**References**