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Behaviors of Acrylamide/Maleic Acid Hydrogels in Uptake of Some Cationic Dyes from Aqueous Solutions

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ABSTRACT

Acrylamide/maleic acid (AAm/MA) hydrogels prepared by irradiating with γ-radiation were used in experiments on swelling, diffusion, and uptake of some cationic dyes such as basic red 9 (BR-9), basic green 4 (BG-4), cresyl violet (CV), and basic blue 20 (BB-20). AAm/MA hydrogel containing 60 mg maleic acid and irradiated at 5.71 kGy has been used for swelling and diffusion studies in water and solutions of basic dyes. For this hydrogel, swelling studies indicated that swelling increased in the following order; BR-9 > BG-4 > CV > BB-20 > water. Diffusion of water and the dyes within hydrogels was found to be of a non-Fickian character. The uptake of the cationic dyes to AAm/MA hydrogels is studied by the batch adsorption technique at 25°C. In the adsorption experiments, Langmuir-type adsorption in the Giles classification system was found. Some binding and thermodynamic parameters for AAm/MA hydrogel–dye systems were calculated by using the Klotz method. Adsorption studies indicated that monolayer coverages of AAm/MA hydrogel by these dyes increased in the following order: BB-20 > CV > BG-4 > BR-9.

Key Words. Hydrogel; Poly(acrylamide/maleic acid); Swelling; Adsorption; Cationic dyes

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INTRODUCTION

Hydrogels are crosslinked hydrophilic polymers that swell in water, usually to equilibrium. If the water content is increased further, the decline in mechanical properties is unacceptable for most purposes. Many authors have emphasized how improved mechanical properties can be achieved by control of chemical (covalent) and physical (especially hydrophobic) crosslinking. It was pointed out that a small cluster of hydrophobic groups in a predominantly hydrophilic network may serve to increase load bearing yet avoid the embrittlement caused by carbon–carbon crosslinks (1). Hydrophobic groups have been introduced by the copolymerization of various hydrophobic monomers with hydrophilic monomers such as acrylamide, vinyl pyrrolidone, and 2-hydroxyethyl methacrylate (1–5).

Hydrogels have widespread application in bioengineering, biomedicine, pharmaceuticals, veterinary, food industry, agriculture, photographic technology, and others. They are used as controlled release systems of drugs, for the production of contact lenses and artificial organs in biomedicine, as an adsorbent for the removal of some agent in environmental applications, for immobilized enzyme kinetics in bioengineering, and as a carrier of water, pesticides, and fertilizer in agriculture (6–18).

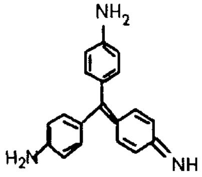
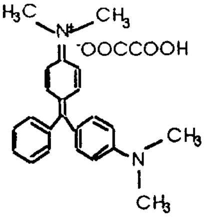
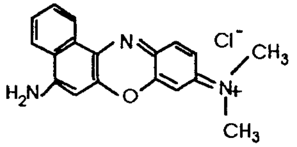
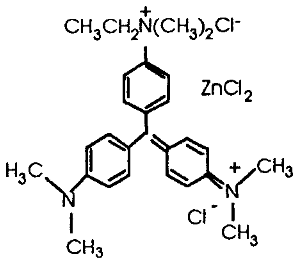
The removal of color from textile wastewaters is a major environmental problem because of the difficulty of treating such waters by conventional methods. Colored waters are also objectionable on aesthetic grounds for drinking and other municipal and agricultural purposes. Some groups have used various adsorbents for the removal of acidic and basic dyes from aqueous solutions (19, 20). The present paper reports a study of a convenient method for removing some cationic dyes from water by adsorption on a new polymeric adsorbent, acrylamide/maleic acid (AAm/MA) hydrogels. The water-soluble cationic dyes basic red 9 (pararosaniline), basic green 4 (malachite green), cresyl violet, and basic blue 20 (methyl green) resemble the large molecular dyes found in wastewaters.

EXPERIMENTAL

Acrylamide (AAm) and maleic acid (MA) monomers were obtained from B.D.H. (Poole, UK). Basic red 9 (BR-9), basic green 4 (BG-4), cresyl violet (CV), and basic blue 20 (BB-20) cationic dyes were obtained from Merck (Darmstadt, Germany). Some properties of these dyes are listed in Table 1.

The preparation and characterization of acrylamide (AAm) and AAm/MA hydrogels were reported in a previous study (16).

TABLE 1
Some Properties of Dyes (21)

Name	Chemical formula	Molar mass	C.I.	λ_{max} (nm)
Basic red 9		305.38	42,500	544
Basic green 4		419.51	42,000	617
Cresyl violet		325.80	51,180	596
Basic blue 20		608.78	42,590	630

Swelling

To measure the parameters of diffusion and swelling, AAm/MA hydrogel containing 60 mg MA and irradiated to 5.71 kGy was accurately weighed and transferred into water, aqueous dyes solutions of 10.0 mg·L^{-1} of BR-9 and BG-4, 12.0 mg·L^{-1} of CV, and 30.0 mg·L^{-1} of BB-20 in a 100-mL beaker. Solution uptake with respect to time was obtained by periodically removing a sample from the solution, quickly blotting dry, and reweighing. The measurements were conducted at 25 ± 0.1°C in a water bath.

Uptake of Dyes

The synthetic aqueous solutions of cationic dyes were prepared in the desired concentrations, and 0.1 g of AAm/MA hydrogel containing 60 mg MA and irradiated to 5.71 kGy were transferred into 50 mL of the synthetic aqueous solutions of dyes and allowed the equilibrate for 24 hours at 25°C. These solutions were separated by decantation from the hydrogels. Spectrophotometric measurements were carried out using a Shimadzu 160 A model UV-VIS spectrophotometer at ambient temperature. The absorbances of these solutions were read at the wavelengths given in Table 1 (21). Distilled water was chosen as the reference. The equilibrium concentrations of dye solutions were determined by means of precalibrated scales.

Hydrogels separated from the dye solutions were left for 3 days in distilled water at 25°C to investigate their desorption.

The influences of MA content in hydrogel and irradiation dose were investigated for uptake of dyes within AAm/MA hydrogels. Hydrogel (0.1 g) prepared with different MA contents and irradiation doses were put into 50 mL of dye solutions in suitable concentrations and left for 24 hours at 25°C. Spectrophotometric methods were used to follow the concentrations of these dye solutions.

RESULTS AND DISCUSSION

Swelling and Diffusion

Analysis of the mechanisms of diffusion in swellable polymeric systems has received considerable attention in recent years because of important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering (2–6).

The swelling of AAm/MA hydrogel containing 60 mg MA and irradiated to 5.71 kGy in water and in aqueous dye solutions of 10.0 mg·L^{-1} BR-9 and BG-4, 12.0 mg·L^{-1} CV, and 30.0 mg·L^{-1} BB-20 was calculated from the following relation (22):

$$\% S = ((m_t - m_0)/m_0) \times 100 \qquad (1)$$

where m_t is the mass of swollen gel at time t, and m_0 is the initial mass of the swollen gel.

Swelling curves of the hydrogel in water and the dye solutions are shown in Fig. 1.

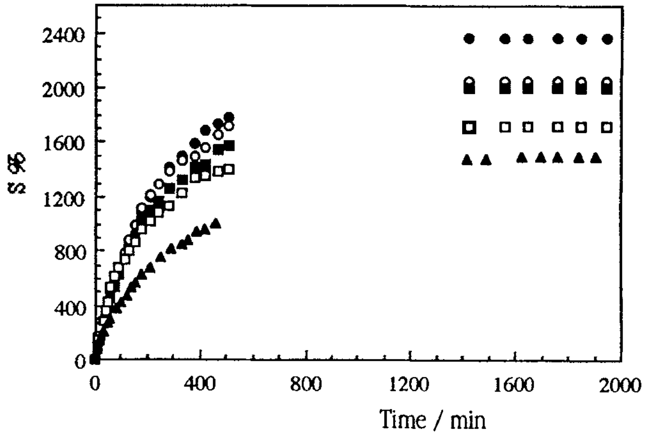


FIG. 1 Swelling curves of AAm/MA hydrogels containing 60 mg of MA and irradiated to 5.71 kGy. (●) Basic red 9, (○) basic green 4, (■) cresyl violet, (□) basic blue 20, (▲) water.

To determine of swelling rate coefficient, swelling vs the square root of immersion time was plotted, and representative curves are shown in Fig. 2. Swelling rate coefficients were calculated from the slopes of the straight portion of the curves (23) in Fig. 2, and they are tabulated in Table 2.

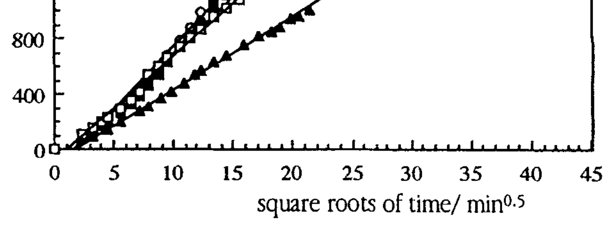


FIG. 2 Plots of swelling vs square roots of immersion time of AAm/MA hydrogels containing 60 mg of MA and irradiated to 5.71 kGy. (●) Basic red 9, (○) basic green 4, (■) cresyl violet, (□) basic blue 20, (▲) water.

TABLE 2
Parameters of Swelling and Diffusion of AAm/MA Hydrogels Containing 60 mg MA. Total Dose Given: 5.71 kGy

Solution	% S	k_s	$k \times 10^2$	n	$D \times 10^6$ $cm^2 \cdot s^{-1}$	$\mathcal{D} \times 10^6$ $cm^2 \cdot s^{-1}$
Water	1495	0.53	1.51	0.63	7.79	11.15
Basic red 9	2360	0.90	1.10	0.72	2.48	4.09
Basic green 4	2050	0.90	1.12	0.75	2.82	4.65
Cresyl violet	2000	0.83	1.18	0.72	2.71	4.26
Basic blue 20	1720	0.76	2.34	0.60	2.55	3.73

The following equation was used to determine the nature of diffusion of water and aqueous solutions of dyes into hydrogels (22):

$$F = kt^n \tag{2}$$

In this equation, F denotes the amount of solvent fraction at time t. The k is a constant incorporating characteristics of the macromolecular network system and the penetrant, and n is the diffusional exponent, which is indicative of the transport mechanism. This equation was applied to the initial stages of swelling, and plots of ln F versus ln t are presented in Fig. 3. The values of exponents n and k were calculated from the slope and intercept of the lines, respectively, and they are presented in Table 2.

Diffusion coefficients are important parameters about the penetration of some chemical species into polymeric systems. The diffusion coefficient (D) gives a measure of the diffusion and mass flow of penetrant into the system (bulk diffusion), but the intrinsic diffusion coefficient ($\mathcal{D}$) gives only diffusion (pore diffusion). Diffusion coefficients were calculated from the following relation (24):

$$D = 0.049/(t/4l^2)_{1/2} \tag{3}$$

where D in is $cm^2 \cdot s^{-1}$, t is the time at which the swelling is one-half the equilibrium value ($V/V_0 = 1/2$), and l is the radius of a cylindrical sample. The intrinsic diffusion coefficient may be expressed as (24)

$$\mathcal{D} = D(1 - V)^{-3} \tag{4}$$

where V is the volume fraction of solvent penetrating the polymer by time t. Values for the parameters of swelling and diffusion, and the diffusion coefficients of AAm/MA hydrogels are listed in Table 2.

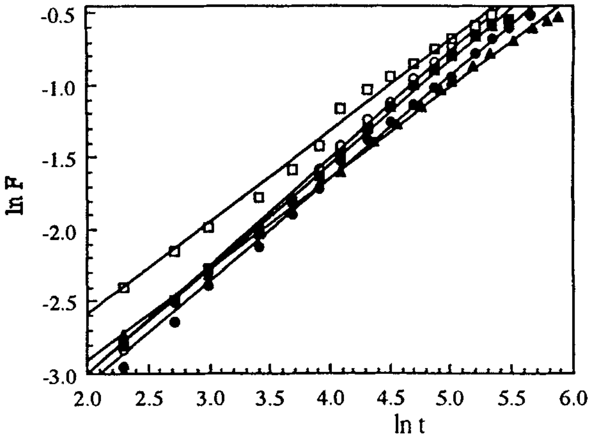


FIG. 3 Plots of ln(F) versus ln(t) of AAm/MA hydrogels containing 60 mg of MA and irradiated to 5.71 kGy. (●) Basic red 9, (○) basic green 4, (■) cresyl violet, (□) basic blue 20, (▲) water.

The equilibrium swelling of hydrogels is high (1720–2360%) in aqueous solutions of the cationic dyes but low (1495%) in water. The dyes contain unpaired electrons of N and O. These atoms behave like a hydrophilic group and form hydrogen bonds with water. Thus, the swelling of AAm/MA hydrogels increases as the dyes bring water into the gels. At the end of these evaluations, the hydrogel in the aqueous solutions were swollen the following order: BR-9 > BG-4 > CV > BB-20 > water.

Swelling rate coefficients of the hydrogel in the dye solution are parallel to the result of equilibrium swelling, as shown in Table 2.

In the experiments, the number that determines the type of diffusion n was found to be over 0.50. Hence, the diffusion of water and cationic dyes into AAm/MA hydrogels was taken to have a *non-Fickian* character (22). This is generally explained as being a consequence of the slow relaxation rate of the hydrogel matrix.

If Table 2 is examined, it is seen that the values of the intrinsic diffusion coefficients of the hydrogel in the water and the solution of dyes are higher than their diffusion coefficient values. On the other hand, the values of the diffusion and intrinsic diffusion coefficients of water in the hydrogel are greater than the values of the dyes, so diffusion of water into the hydrogel is easier than those of the dyes. These results are parallel to the results of swelling.

Uptake of the Cationic Dyes

To observe the uptake of some dyes, AAm and AAm/MA hydrogels were placed in aqueous solutions of cationic dyes (such as BR-9, BG-4, CV, and BB-20) and aqueous solutions of anionic dyes (such as methyl orange, indigo carmine, titan yellow, and amido black), and allowed to equilibrate for 2 days. At the end of this time, AAm/MA hydrogels in the aqueous solutions of BR-9, BG-4, CV, and BB-20 showed the dark colorations of the original solutions. AAm hydrogel had not sorbed any dyes from the solutions, and AAm/MA hydrogel had not sorbed the anionic dyes. Since poly(acrylamide) is a nonionic polymer (25), ionizable groups on the polymer were increased by the addition of maleic acid to acrylamide monomer. Therefore, these hydrogels have many carboxyl groups that can increase interaction between the cationic groups of cationic dyes and carboxyl groups of hydrogels. On the other hand, there is anionic repulsion between the anionic groups of anionic dyes and the carboxyl group of MA in the hydrogels, and therefore there is little interaction between the anionic dyes and AAm/MA hydrogels.

These cationic dye solutions were used in experiments on the uptake of dyes to AAm/MA hydrogels. In a batch adsorption system at equilibrium, total solute concentration (C_I, mol·L^{-1}) is

$$C_I = C_B + C \tag{5}$$

where C_B is the equilibrium concentration of the solute on the adsorbent in mol·L^{-1} (bound solute concentration) and C is the equilibrium concentration of the solute in the solution in mol·L^{-1} (free solute concentration). The value of the bound concentration may be obtained by difference by using Eq. (5). For a fixed free solute concentration, C_B is proportional to the polymer concentration on the binding system; the amount bound can therefore be conveniently expressed as the binding ratio, r, defined by

$$r = C_B/P \tag{6}$$

Thus, with C_B in mol·L^{-1} and P in base mol (moles of monomer units) L^{-1}, r represents the average number of molecules of solute bound to each monomer unit at that free solute concentration.

Plots of the binding ratio (r) against the free concentrations of the dyes in the solutions (C, μmol dye·L^{-1}) are shown in Fig. 4.

Figure 4 shows that adsorptions of the dyes within AAm/MA hydrogels correspond to type L (*Langmuir type*) adsorption isotherms in the Giles classification system for adsorption of a solute from its solution (26, 27).

In this type of adsorption isotherm, the initial curvature shows that as more sites in the substrate are filled, it becomes increasingly difficult for

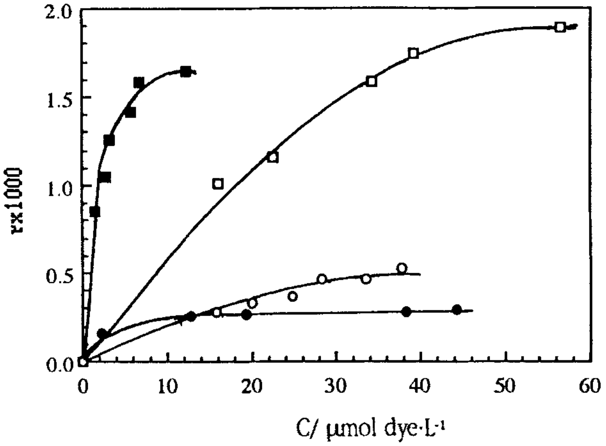


FIG. 4 Binding isotherms of AAm/MA dye systems. (●) Basic red 9, (○) basic green 4, (■) cresyl violet, (□) basic blue 20.

a bombarding solute molecule to find a vacant site available. This implies either that the adsorbed solute molecule is not vertically oriented or that there is no strong competition from the solvent (26, 27).

The types of system which give this curve do, in fact, fulfill these conditions. Thus they have one of the following characteristics: (i) the adsorbed molecules are most likely to be adsorbed flat or (ii) if adsorbed end-on, they suffer little solvent competition. Examples of (ii) are: (a) systems with highly polar solute and adsorbent, and a nonpolar solvent; and (b) systems in which monofunctional ionic substances with very strong intermolecular attraction are adsorbed from water by ion–ion attraction. It is possible that in the system (b) cases the adsorbed ions may have become associated into very large clusters and just adsorption takes place (26).

The binding data were interpreted on the basis of the uniform site-binding model (u.s.b.), which in statistical-thermodynamic terms corresponds to the formation of an ideal localized one-dimensional monolayer of solute on the polymer chains (28). This leads to the hyperbolic (*Langmuir*) form of binding isotherm, which applies to many polymer/solute binding systems (29):

$$r = \frac{nKC}{1 + KC} \tag{7}$$

where K is the binding constant, i.e., the equilibrium constant for the attachment of a molecule of dye D onto a site S by a specific combinationation of noncovalent forces:

$$D + S = D \sim S$$

and n is the site density, i.e., the limiting value of r for "monolayer" coverage, which is thus a measure of the density of the sites S along the polymer chain. The reciprocal of n is the site-size, u, which may be taken to represent either the average number of monomer units occupied by the bound solute molecule or, more generally, the average spacing of solute molecules when the chain is saturated. The initial binding constant K_i is the initial slope of the binding isotherm, and is thus the average binding strength of a solute molecule by a single monomer unit on an occupied chain. In the u.s.b. model it is equal to the product Kn.

The Klotz equation derived on the basis of a uniform site-binding model is

$$\frac{1}{r} = \frac{1}{n} + \frac{1}{nK}\frac{1}{C} \tag{8}$$

where r, C, n, and K are defined above.

Klotz plots of AAm/MA–dye systems are shown in Fig. 5.

Binding parameters of dye–hydrogel systems were calculated from the intercepts and slopes of Klotz plots. The derived values of the binding parameters K and n are listed in Table 3 for cationic dyes with AAm/MA hydrogel. The sixth column contains the derived values of the $\hat{\theta}$, the maximum fractional occupancy attained experimentally, calculated from the definition of fractional occupancy θ:

$$\theta = r/n \tag{9}$$

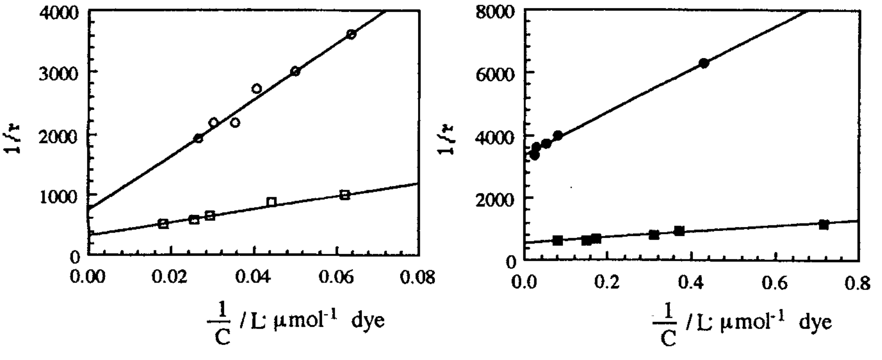


FIG. 5 Klotz plots of AAm/MA dye systems. (●) Basic red 9, (○) basic green 4, (■) cresyl violet, (□) basic blue 20.

TABLE 3
Binding and Thermodynamic Parameters for Hydrogel–Dye Systems

Solution	K_i (L·mol^{-1})	K (L·mol^{-1})	$n \times 10^3$	u	$\hat{\theta}$	ΔG (kJ·mol^{-1})
Basic red 9	145.5	490,376	0.30	3370	0.992	−32.46
Basic green 4	22.1	16,551	1.34	748	0.390	−24.08
Cresyl violet	1070.5	569,366	1.88	532	0.874	−32.95
Basic blue 20	91.1	29,411	3.10	255	0.612	−25.49

using the value of r at the maximum experimental free dye concentration and with the site-density obtained for the u.s.b. model.

Adsorption free energies (ΔG) of hydrogel–dye systems were calculated from the equation

$$\Delta G = -RT \ln K \tag{10}$$

where R, T, and K are universal gas constant, absolute temperature, and equilibrium constant, respectively (30).

If Table 3 is examined, it is seen that the values of monolayer coverage of the hydrogel by the cationic dyes increase in the following order: BB-20 > CV > BG-4 > BG-9. As expected, the results is the inverse of the swelling results.

All values of adsorption free energies of hydrogel–dye systems are negative (Table 3), therefore, the binding process of the dyes to the hydrogel is spontaneous.

Dyes were removed from hydrogels by contact with distilled water for 3 days. We observed that desorption of the dyes was shown by suitable coloration in the water. The hydrogels also returned to their original color.

In later experiments, the uptake of dyes to AAm/MA hydrogels were measured for the effects of different contents of MA and irradiation doses. The binding ratio of dye–hydrogel systems versus the MA content in the hydrogel and irradiation dose are plotted in Fig. 6.

The binding ratio of dye–hydrogel systems gradually increased with an increase of the content of MA in AAm/MA hydrogels and the irradiation dose. Increasing the number of carboxyl groups in the hydrogels by increasing the MA content caused electrostatic interactions between the cationic groups of the dyes and the anionic groups of MA in the hydrogels. On the other hand, the number of crosslinks in the hydrogels increased with an increase of the irradiation dose and reduced the size of the pores. So, the dye molecules in small pores of the hydrogel interacted with hydrophilic groups, and the amount of adsorbed dye molecules increased.

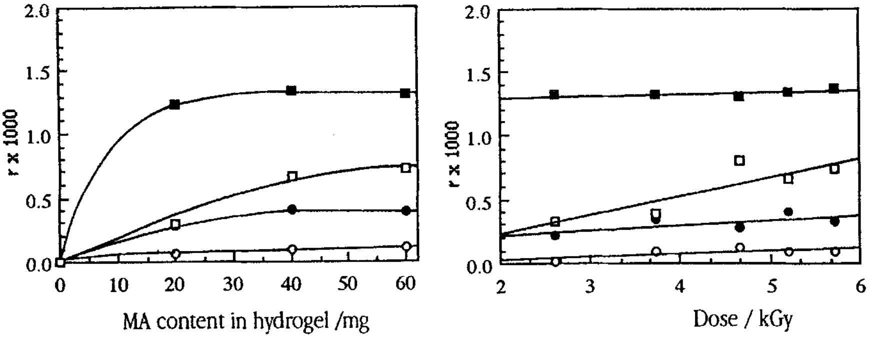


FIG. 6 The variations of adsorbed dyes to AAm/MA hydrogels with MA content in the hydrogel and irradiation dose. (●) Basic red 9, (○) basic green 4, (■) cresyl violet, (□) basic blue 20.

CONCLUSION

This study has shown that AAm/MA hydrogels adsorb such basic dyes as BR-9, BG-4, CV, and BB-20, while AAm hydrogels do not. Type L adsorption isotherms in the Giles classification system were found. The adsorption of the dyes increased with an increase in the MA content in the hydrogels and the irradiation dose.

As a result, it was shown that AAm/MA hydrogels can be used as sorbents for water pollutants such as cationic dyes, which are an important problem for the textile industry.

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