

Use of Superswelling Acrylamide/Maleic Acid Hydrogels for Monovalent Cationic Dye Adsorption

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ABSTRACT: Acrylamide/maleic acid (AAm/MA) superswelling hydrogels prepared by irradiation with γ radiation were used in experiments on swelling, diffusion, and adsorption of some water-soluble monovalent cationic dyes such as basic red 5 (BR-5), basic violet 3 (BV-3), and brilliant cresyl blue (BCB). The AAm/MA hydrogel containing 60 mg MA and irradiated at 5.20 kGy was used for swelling and diffusion studies in water and aqueous solutions of the monovalent cationic dyes. For this superswelling hydrogel the swelling studies indicated that swelling increased in the following order: BR-5 > water > BV-3 \geq BCB. The diffusion of water and the dyes within the hydrogels was found to have a non-Fickian character. The uptake of the cationic dyes to the AAm/MA superswelling hydrogels was studied by the batch adsorption technique at 25°C. The uptake of dyes within the hydrogel increased in the following order: BR-5 > BV-3 > BCB. In the experiments of the adsorption equilibrium, S-type adsorption in Giles' classification system was found. The binding ratio of the hydrogel/dye systems was gradually increased with the increase of the MA content in the AAm/MA hydrogel and the irradiation dose. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1809–1815, 2001

Key words: hydrogel; poly(acrylamide/maleic acid); swelling; adsorption; cationic dyes

INTRODUCTION

Superswelling hydrogels exhibit a combination of unique physicochemical properties, thus permitting their wide-ranging and often exceptional possibilities in practical applications (high and fine technologies, biotechnology, ecology, medicine, etc.). Gel properties may be programmed by the choice of the main polymer that forms the framework and either the comonomer content or irradiation doses.¹

Synthetic dyes represent a relatively large group of organic chemicals that are met in prac-

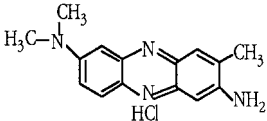
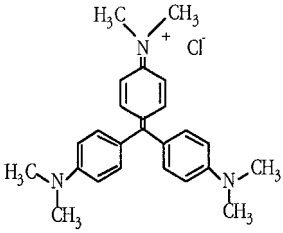
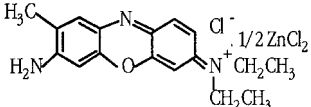
tically all spheres of our daily life. It is therefore possible that such chemicals have undesirable effects not only on the environment but also on humans. In order to minimize the possible damages to humans and the environment arising from the production and applications of cationic dyes, research was carried out around the world. The potential toxicity of some cationic dyes has been known for many decades. Some cationic dyes are not used because they were found to be carcinogenic.²

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 used

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Table I Properties of Water-Soluble Cationic Dyes

Name	Chemical Formula	Molar Mass	Color Index Number or CI Nr.	λ_{\max} (nm)
Basic red 5		288.78	50,040	540
Basic violet 3		407.99	42,555	588
Brilliant cresyl blue		385.96	51,010	622

various adsorbents for the removal of acidic and basic dyes from aqueous solutions.^{3,4}

In our previous studies, adsorptions of protein such as bovine serum albumin,^{5,6} uranyl ions, some heavy metal ions,^{7,8} some cationic dyes,^{9–13} and nicotine¹⁴ by acrylamide/maleic acid (AAM/MA) and AAM/itaconic acid superswelling hydrogels were investigated. The present work was aimed at studying a convenient method for removing some water-soluble monovalent cationic dyes from aqueous solutions by adsorption on a novel polymeric adsorbent such as AAM/MA superswelling hydrogels. The water-soluble monovalent cationic dyes, basic red 5 (neutral red), basic violet 3 (gentian violet), and brilliant cresyl blue resemble the large molecular dyes found in wastewaters.

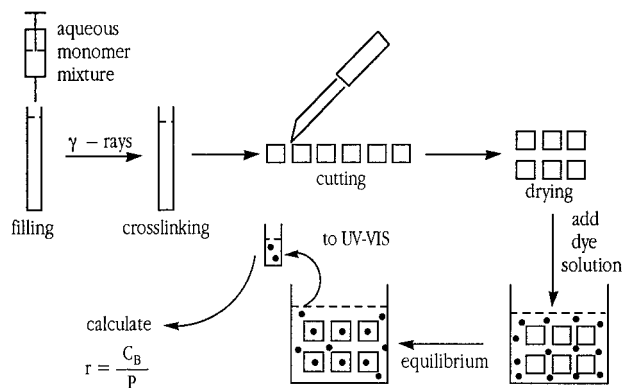
EXPERIMENTAL

The AAM and MA monomers were obtained from BDH (Poole, UK). Basic red 5 (BR-5), basic violet 3 (BV-3), and brilliant cresyl blue (BCB) monovalent cationic dyes were obtained from Merck (Darmstadt, Germany). Some properties of these dyes are listed in Table I.

One gram of AAM was dissolved in 1 mL of the aqueous solutions with 0, 20, 40, and 60 mg MA. These solutions were placed in PVC straws (3-mm diameter) and irradiated to 2.60, 3.73, 4.65, 5.20, and 5.71 kGy in air at ambient temperature in a Gammacell 220 type γ irradiator at a fixed rate of 0.72 kGy h⁻¹. Superswelling hydrogels obtained in long cylindrical shapes were cut and dried in air and then in a vacuum. Preparation and characterization of the AAM and AAM/MA superswelling hydrogels were reported in our previous study.¹⁵

To measure the parameters of diffusion and swelling, the AAM/MA hydrogel containing 60 mg MA and irradiated to 5.20 kGy was accurately weighed and transferred into water, aqueous dye solutions of 20.0 mg L⁻¹ of BR-5, 5.0 mg L⁻¹ of BV-3, and BCB in a beaker. The solution uptake with respect to time was obtained by periodically removing a sample from the solution, quickly blot drying, and reweighing. The measurements were conducted at 25 \pm 0.1°C in a water bath.

The synthetic aqueous solutions of monovalent cationic dyes were prepared in the concentration ranges of 5–40 mg L⁻¹ for BR-5, 2–10 mg L⁻¹ for BV-3, and 10–50 mg L⁻¹ for BCB. The AAM/MA hydrogel containing 60 mg MA and irradiated to



Scheme 1 A diagram of the hydrogel experiment.

5.20 kGy was selected for the adsorption experiments. The dry gel (0.1 g) was transferred into 50 mL of the synthetic aqueous solutions of the dyes and allowed to equilibrate for 24 h at 25°C. These solutions were separated by decantation from the superswelling hydrogels. Spectrophotometric measurements were carried out using a Shimadzu model 160 A UV-vis spectrophotometer at ambient temperature. The absorbances of these solutions were read at the wavelengths given in Table I. Distilled water was chosen as the reference. The equilibrium concentrations of the cationic dye solutions were determined by means of precalibrated scales. A schematic diagram of the hydrogel experiment is presented in Scheme 1.

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

The influences of MA content in the superswelling hydrogel and the irradiation dose were investigated for adsorption of dyes onto AAm/MA hydrogels. Superswelling hydrogel samples weighing 0.1 g and prepared with different concentrations of MA and irradiation doses were added to 50 mL of dye solutions in the desired concentrations and left for 24 h at 25°C. The spectrophotometric method was applied to these dye solutions.

RESULTS AND DISCUSSION

Swelling and Diffusion Behavior

The 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 en-

vironmental, biomedical, pharmaceutical, and agricultural engineering.

The swelling of AAm/MA hydrogel containing 60 mg MA and irradiated to 5.20 kGy in water and in aqueous dye solutions of 20.0 mg L⁻¹ of BR-5, 5.0 mg L⁻¹ of BV-3, and BCB was calculated from the following relation^{15,16}:

$$S (\%) = [(m_t - m_0)/m_0] \times 100 \quad (1)$$

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

The swelling curves of the superswelling hydrogel in water and the monovalent cationic dye solutions are shown in Figure 1(a) and are tabulated in Table II.

The equilibrium swelling of the hydrogels is between 1290 and 1890% in the aqueous solutions of the dyes but 1680% in distilled water. The dyes

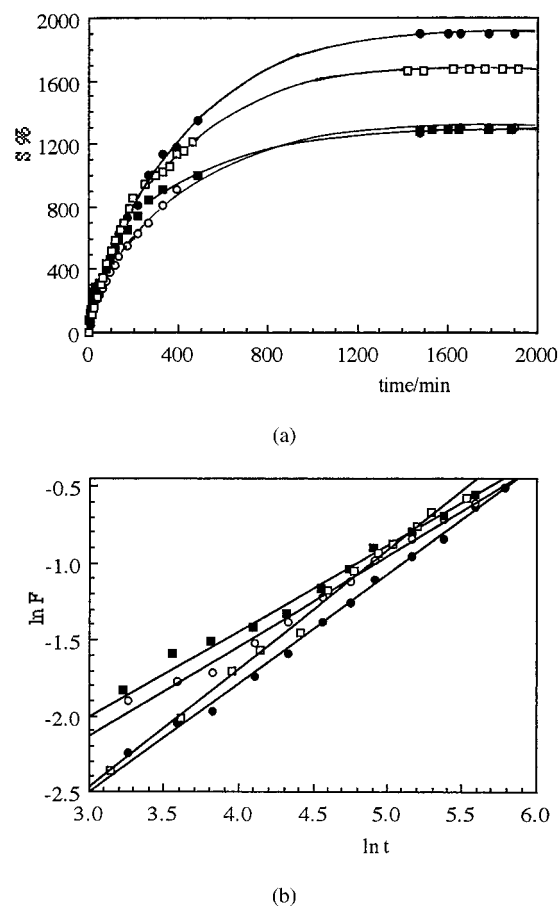


Figure 1 (a) Swelling and (b) swelling kinetics curves of AAm/MA superswelling hydrogels containing 60 mg of MA and irradiated to 5.2 kGy: (●) BR-5, (○) BV-3, (■) BCB, and (□) water.

Table II Parameters of Swelling and Diffusion of AAm/MA Hydrogels Containing 60 mg MA

Solution	S (%)	k_S	$k \times 10^2$	n	$D \times 10^6$ ($\text{cm}^2 \text{s}^{-1}$)	$\mathcal{D} \times 10^6$ ($\text{cm}^2 \text{s}^{-1}$)
Water	1680	0.73	0.90	0.76	2.26	3.29
BR-5	1895	0.58	0.97	0.71	2.25	3.67
BV-3	1300	0.44	2.03	0.59	1.77	2.45
BCB	1295	0.48	2.54	0.56	1.53	2.12

The total dose was 5.20 kGy.

contain the unpaired electrons in the N and O. These atoms behave like a hydrophilic group and form hydrogen bonds with water. Thus, the swelling of AAm/MA hydrogels changes as the dyes bring water into the gels. At the end of these evaluations, the superswelling hydrogel in the aqueous solutions are swollen in the following order: BR-5 > water > BV-3 \geq BCB.

The following equation was used to determine the nature of the diffusion of water and aqueous solutions of dyes into the hydrogels^{15,16}:

$$F = kt^n \quad (2)$$

In this equation F denotes the amount of solvent fraction at time t ; k is a constant incorporating the characteristics of the macromolecular network system and the penetrant; and n is the diffusional exponent, which is indicative of the transport mechanism. This equation is applied to the initial stages of swelling, and plots of $\ln F$ versus $\ln t$ are found in Figure 1(b). The exponent n and k values were calculated from the slope and intercept of the lines, respectively, and are presented in Table II.

In the experiments the number to determine the type of diffusion (n) was found to be over 0.50. Hence, the diffusion of water and monovalent cationic dyes into AAm/MA superswelling hydrogels was taken to be of a *non-Fickian* character.¹⁶ This is generally explained as being a consequence of the slow relaxation rate of the hydrogel matrix.

To determine the swelling rate coefficient the swelling versus the square root of the time were plotted, and the curves are shown in Figure 2. The swelling rate coefficients were calculated from the slopes of the straight portion of the curves¹⁷ in Figure 2 and are tabulated in Table II. The swelling rate coefficients of the hydrogel in the dye solution are parallel to the results of the equilibrium swelling as shown in Table II.

Diffusion coefficients are important parameters of the penetration of some chemical species

into polymeric systems. The diffusion coefficient (D) gives a measure of the diffusion and mass flow of the penetrant to the system (bulk diffusion), but the intrinsic diffusion coefficient (\mathcal{D}) gives only the diffusion (pore diffusion). The diffusion coefficients were calculated from the following relation¹⁸:

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

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

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

where V is the volume fraction of the solvent penetrating the polymer by the time t defined above. The values for the parameters of swelling and diffusion and the diffusion coefficients of AAm/MA superswelling hydrogels are listed in Table II. Table II shows that the values of the intrinsic diffusion coefficient of the superswelling

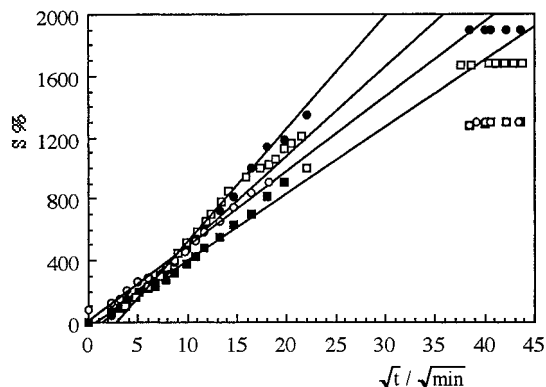


Figure 2 Swelling rate curves of AAm/MA hydrogels containing 60 mg of MA and irradiated to 5.20 kGy: (●) BR-5, (○) BV-3, (■) BCB, and (□) water.

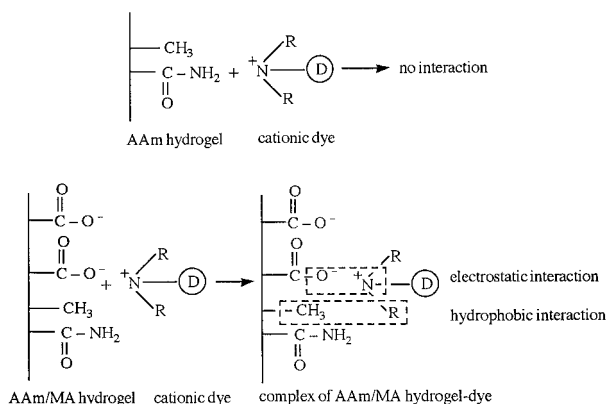
hydrogel in the water and the solution of dyes are bigger than the values of their diffusion coefficient.

Adsorption of Monovalent Cationic Dyes

To observe the adsorption of some dyes, AAm and AAm/MA hydrogels were placed in the aqueous solutions of monovalent cationic dyes such as BR-5, BV-3, and BCB, and the aqueous solutions of anionic dyes such as orange II, azocarmine B, alizarin yellow G, and erythrosin B and allowed to equilibrate for 2 days. At the end of this time, AAm/MA hydrogels in the aqueous solutions of BV-3 (a triarylmethine dye), BR-5 (an azin dye), and BCB (an oxazin dye) showed the dark colorations of the original solutions. The AAm hydrogel did not sorb any dyes from the solutions, and the AAm/MA hydrogel did not sorb the anionic dyes. Because poly(AAm) is a nonionic polymer, ionizable groups on the polymer were increased by the addition of MA to the AAm monomer. Therefore, these hydrogels have many carboxyl groups that can increase the interaction between the cationic groups of the monovalent cationic dyes and the carboxyl groups of the hydrogels. On the other hand, there will be anionic repulsion between the anionic groups of the anionic dyes and the carboxyl group of MA in the hydrogels.

The other types of interactions between the superswelling hydrogel and the monovalent cationic dyes may be hydrophobic and hydrogen bond. Hydrophobic effects are specifically aqueous solution interactions, which in the present case involves the aromatic rings and the methyl and methine groups on the dye molecules and the methine groups on the gel. Hydrogen bonding is expected to occur between the amine group and oxygen atom on the dye molecules and the amine and carbonyl groups on the monomer unit of the crosslinked copolymer.¹⁶ But, electrostatic interaction between the dye molecules and the hydrogel is very dominant because of hydrophobic and hydrogen bonds. As previously stated, the AAm hydrogel did not sorb any dye molecules while the AAm/MA hydrogel sorbed the dyes. A possible complexation process between the AAm/MA superswelling hydrogel and the monovalent cationic dye molecules is presented in Scheme 2.

These monovalent cationic dye solutions were used in the experiments of uptake of dyes by AAm/MA superswelling hydrogels. In a batch adsorption system at equilibrium, the total solute concentration (C_I , mol L⁻¹) is^{19,20}



Scheme 2 A possible complexation process between the AAm/MA superswelling hydrogel and monovalent cationic dye molecules.

$$C_I = C_B + C \quad (5)$$

where C_B is the equilibrium concentration of the solute on the adsorbent in moles in 1 L of solution (bound solute concentration) and C is the equilibrium concentration of the solute in the solution in moles per liter (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

$$r = C_B/P. \quad (6)$$

Thus, with C_B in moles per liter and P in base moles (moles of monomer units) in liters, r then represents the average number of molecules of solute bound to each monomer unit at that free solute concentration.

The binding ratio of the dyes was calculated for the uptake of dyes within the hydrogel in 10 mg dye L⁻¹ of aqueous solutions, and they are presented in Figure 3. Figure 3 shows that the binding ratio of the hydrogel/dye systems increased in the following order: BR-5 > BV-3 > BCB. As expected, this result parallels the result of the equilibrium swelling.

Plots of the binding ratio (r) against the free concentrations of the dyes in the solutions (C , $\mu\text{mol dye L}^{-1}$) are shown in Figure 4.

Figure 4 shows that the adsorptions of the dyes within AAm/MA hydrogels corresponds to type-S adsorption isotherms in the Giles classification system for adsorption of a solute from its solu-

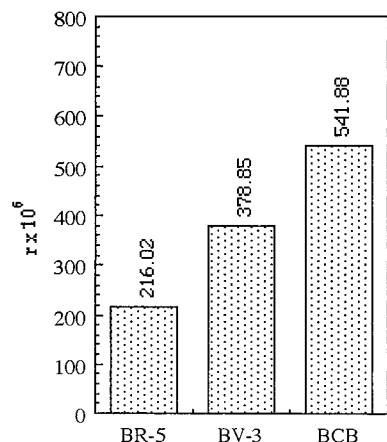


Figure 3 The binding ratios of hydrogel/dye systems in 10 mg dye/L of aqueous solutions.

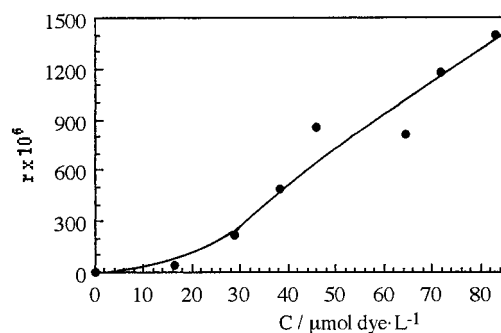
tion.^{21,22} In the S curves in the Giles classification system, the initial direction of curvature shows that adsorption becomes easier as the concentration rises. In practice, the S curve usually appears when three conditions are fulfilled: the solute molecule is monofunctional, has moderate intermolecular attraction, causing it to pack vertically in a regular array in the adsorbed layer, and meets strong competition for substrate sites from molecules of the solvent or of another adsorbed species.^{21,22}

The weakness of the adsorbent–adsorbate forces causes the uptake at low concentrations to be small; but once a molecule has become adsorbed, the adsorbate–adsorbate forces promotes the adsorption of further molecules (a cooperative process) so that the isotherm becomes convex to the concentration axis. Type-S isotherms may originate through the adsorption of either nonpolar molecules or polar molecules, always provided that the adsorbent–adsorbate force is relatively weak. A polar adsorbate of particular interest in this context is water, because the dispersion contribution to its overall interaction energy is unusually small compared to the polar contribution. Not surprisingly, water provided many examples of a type-S isotherm. Once the hydrogel is covered with a layer of adsorbed water, however, the adsorbent–adsorbate interaction is virtually reduced to the weak dispersion energy of water with dyes, so that a type-S isotherm should result. In a system that gives rise to a type-S isotherm, however, the multilayer is being built up on some parts of the surface while the monolayer is still incomplete on other parts.^{21,22}

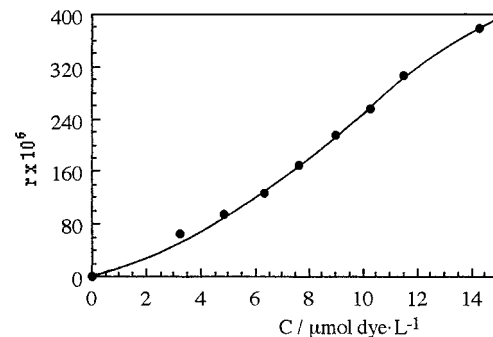
Dyes were removed from superswelling hydrogels by contact with distilled water for 3 days. We

observed that desorptions of the dyes were shown by coloration in the water and the hydrogels also returning to their original colors. Hence, the adsorptions of the monovalent cationic dyes onto the superswelling hydrogel can be the physical type.

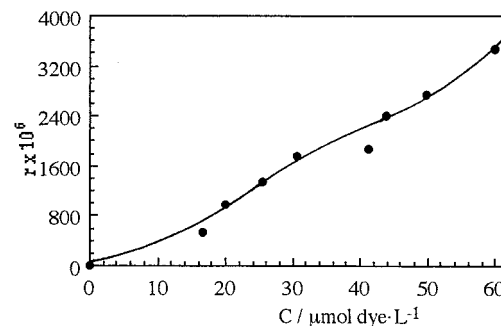
In later experiments the uptake of dyes to AAm/MA hydrogels were measured as effects of the contents of MA and irradiation doses. The binding ratio of hydrogel/dye systems versus the MA content in the hydrogel and the irradiation dose are plotted and shown in Figure 5. The binding ratio of the dye/hydrogel systems gradually increased with the increase of MA content in the AAm/MA hydrogels and the irradiation dose. The



BR-5



BV-3



BCB

Figure 4 Binding isotherms of AAm/MA hydrogel/dye systems.

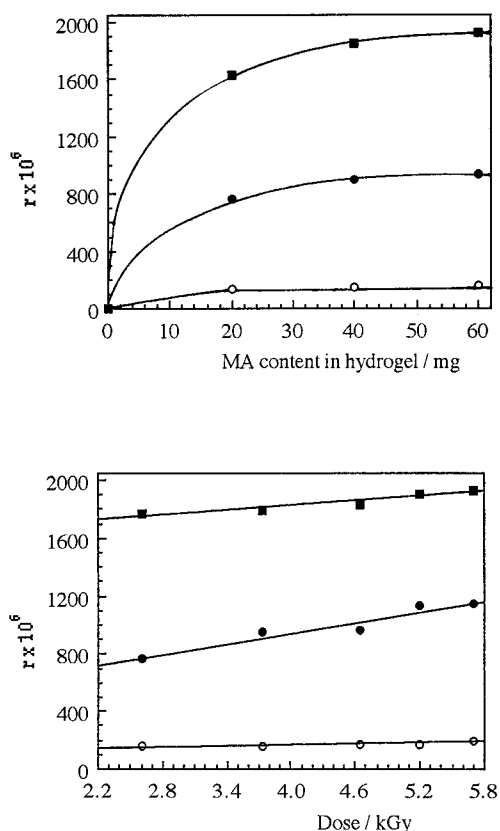


Figure 5 The variations of the binding ratios of adsorbed dyes onto AAm/MA superswelling hydrogels with the content of MA in the hydrogel (total dose = 5.20 kGy) and the irradiation dose (40 mg MA): (●) BR-5, (○) BV-3, and (■) BCB.

increase of the carboxyl groups in the hydrogels with the increase of MA contents caused electrostatic interactions between the cationic groups of the dyes and the anionic groups of MA in the hydrogels. On the other hand, the crosslinks of the hydrogels increased with the increase of the irradiation dose and reduced the size of the pores. So, dye molecules in the small pores of the hydrogel interacted with the hydrophilic groups and the amount of adsorbed dye molecules increased.

CONCLUSION

This study showed that AAm/MA superswelling hydrogels adsorb monovalent cationic dyes such as BR-5, BV-3, and BCB but AAm hydrogels do not. Type-S adsorption isotherms in Giles' classification system were found. The adsorptions of the dyes were increased with the content of MA in the hydrogels and the irradiation dose.

As a result, AAm/MA superswelling hydrogels can be used as sorbents for water pollutants such as cationic dyes, which is an important problem for the textile industry.

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