

Interaction of Some Cationic Dyes with Acrylamide/Itaconic Acid Hydrogels

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SYNOPSIS

Acrylamide/itaconic acid (AAm/IA) hydrogels prepared by irradiating with γ radiation were used in experiments on uptake of some cationic dyes such as union green B (UG-B), basic blue 17 (BB-17), basic red 2 (BR-2), and lauths violet (LV). Adsorption of the cationic dyes onto AAm/IA hydrogels is studied by batch adsorption technique at 25°C. In the experiments of the adsorption, Langmuir type adsorption in the Giles classification system was found. Some binding and thermodynamic parameters for AAm/IA hydrogel-dye systems were calculated by using Klotz method. Adsorption studies indicated that monolayer coverages of AAm/IA hydrogel by these dyes were increased with following order BB-17 > UG-B > BR-2 > LV. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Hydrogels are crosslinked hydrophilic polymers that are swollen in water usually to equilibrium. Hydrogels find considerable applications and have been extensively studied because they combine glassy behavior (in their dry state) with elasticity (when sufficient water is absorbed). The behavior of highly swollen hydrogels is, of course, a function of the network characteristic (such as degree of swelling, diffusion coefficient, crosslink density, mesh size, etc.), which in turn is connected with chemical structures. Hydrogels have been used widespread applications in the fields of bioengineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture, photographic technology, and others. It is used as controlled release systems of drugs, for production of contact lenses and artificial organs in biomedicine, as an adsorbent for removal of some agent in environmental applications, immobilized enzyme kinetics in bioengineering, and also as a carrier of water, pesticides, and fertilizer in the agriculture field.¹⁻⁴

The removal of color from textile waste waters is a major environmental problems 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.^{5,6}

In our previous works, adsorption some cationic dyes,⁷⁻⁹ uranyl ions, some heavy metal ions,^{10,11} and protein such as bovine serum albumin^{12,13} by acrylamide/itaconic acid (AAm/IA)^{14,15} and acrylamide/maleic acid¹⁶ hydrogels have been investigated.

The present paper aims to study a convenient method for removing some cationic dyes from water by adsorption on a polymeric adsorbent such as AAm/IA hydrogels. Water-soluble cationic dyes such as union green B (UG-B) (janus green B), basic blue 17 (BB-17) (toluidin blue), basic red 2 (BR-2) (safranin T), and lauths violet (LV) (thionin) resemble the large molecular dyes found in waste waters.

EXPERIMENTAL

AAm and IA monomers were obtained from BDH (Poole, UK). UG-B, BB-17, BR-2, and LV cationic

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dyes were obtained from Merck (Darmstadt, Germany). Some properties of the dyes are listed in Table I.

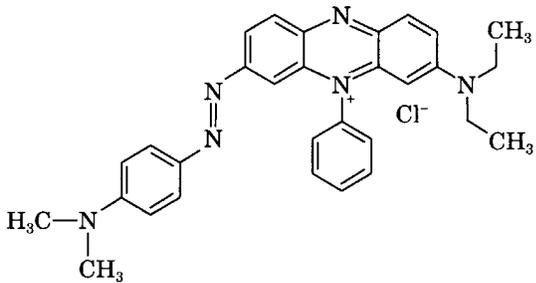
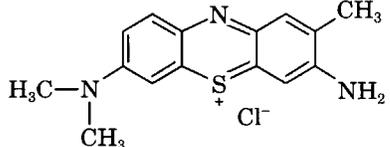
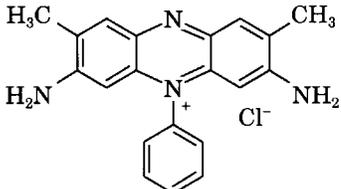
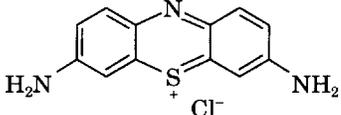
Preparation of Hydrogels

Suitable quantities of IA and irradiation doses for AAm/IA hydrogels were selected based on results from experiments.¹⁶ One gram of AAm was dissolved in 1 mL of the aqueous solutions with 0, 20, 40, and 60 mg of IA. These solutions were placed in polyvinyl chloride straws of 3 mm diameter and irradiated. Doses of 2.60, 3.73, 4.65, 5.20, and 5.71 kGy in air at ambient temperature in a Gammacell 220 type γ irradiator were applied at a fixed rate of 0.72 kGy h^{-1} . Hydrogels obtained in long cylindrical shapes were cut, washed with distilled water for removal of unreacted monomers, and dried at air and in a vacuum.^{14,15}

Adsorption of Dyes

The synthetic aqueous solutions of cationic dyes were prepared in the concentration ranges 10–80 $mg L^{-1}$ for UG-B, 5–40 $mg L^{-1}$ for BB-17, 4–32 $mg L^{-1}$ for BR-2, and 6–20 $mg L^{-1}$ for LV. AAm/IA hydrogel containing 60 mg IA and irradiated to 4.65 kGy were selected for adsorption studies. Dry crosslinked copolymer, 0.1 g, of AAm/IA transferred into 50 mL of the synthetic aqueous solutions of dyes and allowed the equilibrate for 24 h at 25°C. These solutions were separated by decantation from the hydrogels. Spectrophotometric measurements were carried out using a Shimadzu 160 A model ultraviolet-visible spectrophotometer at ambient temperature. The absorbencies of these solutions were read at the wavelengths given in Table I.¹⁷ Distilled water was chosen as the reference. The equilibrium concentrations of dyes solutions were determined by means of precalibrated scales.

Table I Some Properties of Dyes¹⁷

Name	Chemical Formula	Molar Mass	C.I. Nr.*	λ_{max} (nm)
Union green B		511.07	11,050	660
Basic blue 17		305.83	52,040	626
Basic red 2		350.85	50,240	530
Lauths violet		287.34	52,000	598

* C.I. Nr.: Color Index Number

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

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

RESULTS AND DISCUSSION

To observe uptake of some dyes, AAm and AAm/IA hydrogels were placed in aqueous solutions of cationic dyes such as UG-B, BB-17, BR-2, and LV and the aqueous solutions of anionic dyes such as eosin yellowish, bromocresol purple, naftol green, and evans blue and allowed to equilibrate for 2 days. At the end of this time, AAm/IA hydrogels in the aqueous solutions of UG-B, BB-17, BR-2, and LV showed the dark colorations of the original solutions. AAm hydrogel had not sorbed any dyes from the solutions, and AAm/IA hydrogel had not sorbed the anionic dyes. Because poly(acrylamide) is a non-ionic polymer,¹⁸ ionizable groups on the polymer were increased by the addition of IA to AAm 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 will be anionic repulsion between anionic groups of anionic dyes and carboxyl group of IA in the hydrogels and therefore little interaction between the anionic dyes and AAm/IA hydrogels.

These cationic dye solutions were used in the experiments of uptake of dyes to AAm/IA hydrogels. In a batch adsorption system at equilibrium, total solute concentration (C_I , mol L⁻¹) is

$$C_I = C_B + C \quad (1)$$

where C_B is the equilibrium mol number of the solute on the adsorbent per liter solution (bound solute concentration) and C is the equilibrium concentrations 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. 1. 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

$$r = C_B/P. \quad (2)$$

Thus, with C_B in mol L⁻¹ and P in base mol (moles of monomer units) per liter solution, r then represents the average number of molecules of solute bound each monomer unit at that free solute concentration.¹⁹ Plots of the binding ratio (r) against the free concentrations of the dyes in the solutions (C , μmol dye L⁻¹) are shown in Figure 1.

Figure 1 shows that adsorptions of the dyes within AAm/IA hydrogels corresponds to type L (Langmuir type) adsorption isotherms in Giles classification system for adsorption of a solute from its solution.²⁰⁻²²

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.¹⁹ This leads to the Langmuir form of binding isotherm, which applies to many polymer/solute binding system²³:

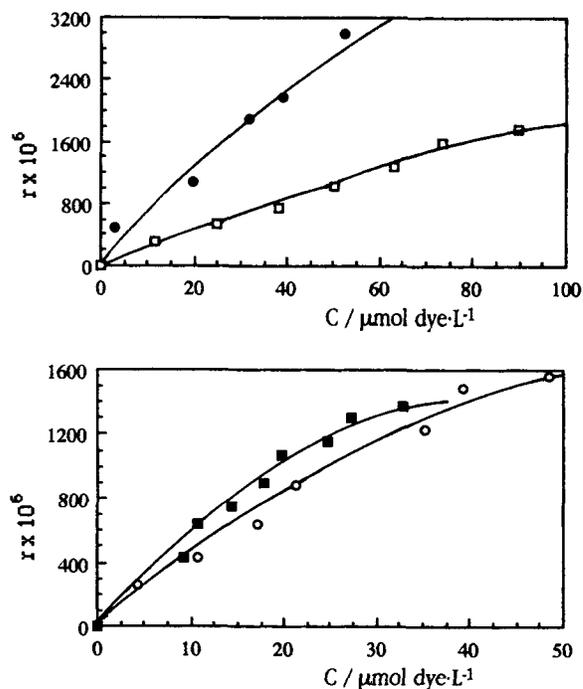


Figure 1 Binding isotherms of AAm/IA-union green B system. □, union green B; ●, basic blue 17, ■, lauths violet; ○, basic red 2.

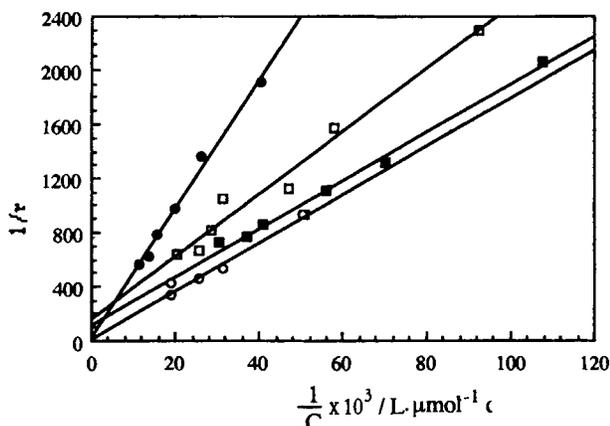
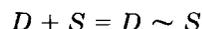


Figure 2 Klotz plots of AAm/IA-dye systems. (●) Union green B, (○) basic blue 17, (□) basic red 2, (■) lauths violet.

$$r = \frac{nKC}{1 + KC} \quad (3)$$

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 combination of noncovalent forces:



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 that may be taken to represent either average number of monomer units occupied by the bound solute molecule or, more generally, the average spacing of solute molecules when the chain saturated. Initial binding constant K_i is 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 is²³

$$\frac{1}{r} = \frac{1}{n} + \frac{1}{nK} \frac{1}{C} \quad (4)$$

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

Klotz plots of AAm/IA-dye systems are shown in Figure 2.

Binding parameters of dye-hydrogel system were calculated from the intercepts and slopes of Klotz plots. The derived values of the binding parameters K and n are listed in Table II for cationic dyes with AAm/IA hydrogel. The fifth column contains the derived values of the $\hat{\theta}$, the maximum fractional occupancy attained experimentally, calculated from the definition of fractional occupancy θ ²³:

$$\theta = r/n \quad (5)$$

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

Adsorption free energies (ΔG^0) of hydrogel-dye systems were calculated following equation:

$$\Delta G^0 = -RT \ln K \quad (6)$$

where R , T , and K are universal gas constant, absolute temperature, and equilibrium constant of adsorption process, respectively.²⁴

If Table II is examined, it is shown that the values of monolayer coverage of the hydrogel by the cationic dyes are increased following order:



All values of ΔG^0 of hydrogel-dye systems are negative and between -6 and -10 kJ mol⁻¹ (Table II); therefore, bindings process of the dyes to the hydrogel is spontaneously.

Dyes were removed from hydrogels by contact with distilled water for 3 days. We have observed that desorptions of the dyes were showed by the suitable coloration in the water and hydrogels also have returned original colors.

Table II 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^0 (kJ mol ⁻¹)
Basic blue 17	55.825	733.986	76.06	13.147	0.039	-7.099
Union green B	21.024	662.164	31.75	31.495	0.055	-6.987
Basic red 2	43.460	7348.700	5.91	169.091	0.263	-9.577
Lauths violet	64.456	14054.900	4.58	218.053	0.301	-10.274

In later experiments, uptake of the dyes to AAm/IA hydrogels were measured effects of different contents of IA and irradiated doses. The initial concentrations of the dyes solutions were 40 mg L^{-1} for UG-B, 20 mg L^{-1} for BB-17 and BR-2, and 10 mg L^{-1} for LV. The binding ratio of dye-hydrogel systems versus percentage weight fraction of IA in feed composition of polymer and irradiation dose are plotted and shown in Figures 3 and 4.

The binding ratio of dye/hydrogel systems gradually increased with the increase of IA content in the hydrogels and irradiation dose. Increasing of carboxyl groups in the hydrogels with increasing of IA contents caused electrostatic interactions between the cationic groups of the dyes and the anionic groups of IA in the hydrogels. On the other hand, the crosslinks of hydrogels increased with the increase of irradiation dose. So, dye molecules in small pores of hydrogel interacted with carboxylic groups of the other chains. It is shown that more interaction are between cationic groups of dye molecules and carboxylic groups of the hydrogel at the higher doses and the amount of adsorbed dye molecules increased.

CONCLUSION

This study has shown that AAm/IA hydrogels adsorb the basic dyes such as UG-B, BB-17, BR-2, and LV, whereas AAm hydrogels do not. Type L (Langmuir) adsorption isotherms in Giles classification system were found. The adsorptions of the dyes are increased with the content of IA in the hydrogels and irradiation dose.

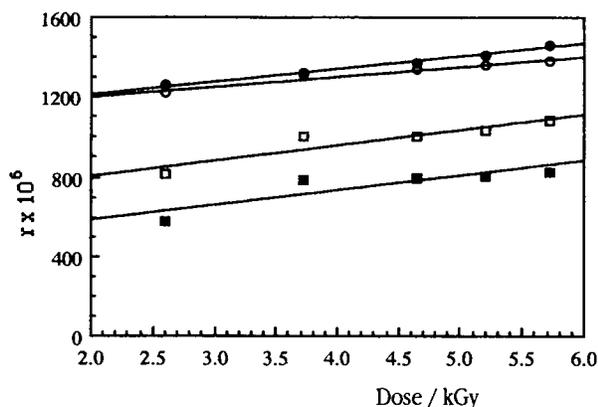


Figure 3 The variations of adsorbed dyes with irradiation dose. Weight fraction of IA is 56.5%. (●) Union green B, (○) basic blue 17, (□) basic red 2, (■) lauths violet.

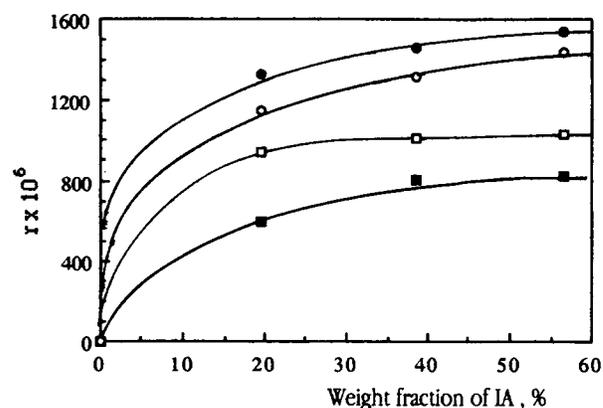


Figure 4 The variations of adsorbed dyes to AAm/IA hydrogels with percentage weight fraction of IA. Total dose given is 5.20 kGy. (●) Union green B, (○) basic blue 17, (□) basic red 2, (■) lauths violet.

As a result, it was shown that the AAm/IA hydrogels could be used as a sorbent for the water pollutants such as cationic dyes, an important problems for the textile industry.

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