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Adsorption of Some Basic Dyes by Acrylamide–Maleic Acid Hydrogels

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ABSTRACT

In this study, acrylamide–maleic acid (AAm/MA) hydrogels containing different quantities of maleic acid have been irradiated with γ-radiation. They have been used in experiments on swelling, diffusion, and the adsorption of basic dyes such as methylene blue, methyl violet, and nile blue. Acrylamide–maleic acid hydrogel containing 40 mg maleic acid and irradiated at 3.73 kGy has been used for swelling and diffusion studies in water and solutions of basic dyes. For this hydrogel, maximum and minimum swellings have been observed with solutions of nile blue (2000% swelling) and water (1480% swelling). Diffusions of water and dyes within hydrogels have been found to be non-Fickian in character. In experiments on the adsorption of dyes, Type III adsorption has been found. One gram of AAm/MA hydrogel sorbed 0.3–2.2 mg of methylene blue, 0.3–3.4 mg of methyl violet, and 1.6–3.9 mg of nile blue, while acrylamide hydrogel has not sorbed any basic dye. This result shows that AAm/MA hydrogel can be used as a sorbent for water pollutants such as dyes, and immobilization of these organic contaminants in the hydrogels from wastewater can solve one of the most important environmental problems of the textile industry.

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

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INTRODUCTION

Hydrophilic polymer networks capable of retaining large volumes of water by swelling, so-called superadsorbent hydrogels, are of great interest for their potential practical uses. Hydrogels have been used in the fields of medicine, pharmacy, biotechnology, agriculture, food industry, etc. Hydrogels have been most widely used for the controlled release of drugs, and often prepared with acrylamide (1–6).

Hydrogels can be defined as polymeric materials that exhibits the ability to swell in water and retain a significant fraction of water within their structure without dissolving (7, 8). The physical and chemical properties of hydrogels depend upon the monomers and polymers from which they are made. They may be composed of various chemical substances (9). Some authors reported that poly(*n*-vinyl pyrrolidone) and poly(vinyl pyridine) hydrogels have been used for the adsorption of acidic dyes (10–13), and acrylamide/itaconic acid hydrogels have been shown to adsorb some basic dyes (14).

Color in drinking water may be due to presence of colored organic substances or highly colored industrial wastes. Pulp and paper and textile wastes are common as sources of coloring in water. The primary importance of color in drinking water is aesthetic, but sensory effects may be regarded as a health effect. Health-related criteria include the association between color and the production of some chlorinated organic compounds, interference with water treatment, and increased chlorine consumption. Few toxicological studies of natural organic color agents have been undertaken (15). Some reactions of dyes, such as neutralization, reduction, and oxidation reactions, consume dissolved oxygen. Thus, the chemical oxygen demand (COD) of water has increased, and this effect decreases the presence of useful aquatic microorganism (15).

The removal of color from textile wastewaters is a major environmental problems because of the difficulty of treating such waters by conventional methods. Some groups have used various adsorbents for the removal of acidic and basic dyes from aqueous solutions (16). The present paper studies a convenient method for removing some basic dyes from water by adsorption on a new polymeric adsorbent: acrylamide–maleic acid hydrogels. Such water-soluble basic dyes as methylene blue, methyl violet, and nile blue resemble the dyes found in wastewaters.

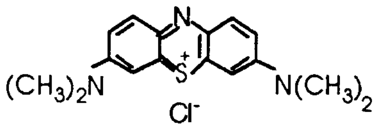
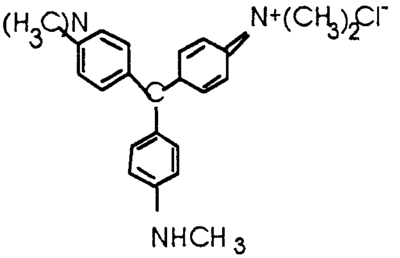
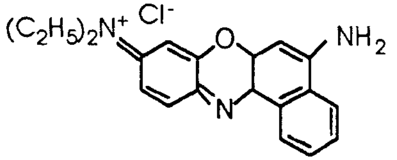
EXPERIMENTAL

Acrylamide and maleic acid monomers were obtained from B.D.H. (Poole, UK). Methylene blue (MB), methyl violet (MV), and nile blue chloride (NB) basic dyes were obtained from Merck (Darmstadt, Germany). Some properties of dyes are listed in Table 1.

Preparation of Hydrogels

Suitable quantities of maleic acid and irradiation doses for acrylamide and maleic acid hydrogels were selected based upon results from experiments (18). One gram of acrylamide was dissolved in 1 mL of aqueous solutions with 0, 20, 40, and 60 mg of maleic acid. These solutions were placed in PVC straws of 3 mm diameter and irradiated. Doses of 2.60, 3.73, and 5.2 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 as long cylinders were cut and dried, first in air and then in a vacuum.

TABLE 1
Some Properties of Dyes (17)

Name	Chemical formula	Molar mass	C. I.	λ_{max} (nm)
Methylene blue (MB)		319.86	52015	655
Methyl violet (MV)		393.96	42535	560
Nile blue (NB)		354.92	51180	600

Swelling and Diffusion

Hydrogel containing 40 mg maleic acid and irradiated to 3.73 kGy were swollen in distilled water, aqueous dyes solution of 4.0 $mg \cdot L^{-1}$ MB, 6.6 $mg \cdot L^{-1}$ MV and 8.0 $mg \cdot L^{-1}$ NB at 25°C to measure the parameters of diffusion and swelling. The concentrations of dyes in the solutions were determined from the absorbance (A) of the solutions. The wavelengths used for each dye are given in Table 1. Swollen gels removed from the water bath at regular intervals were dried superficially with filter paper, weighed, and placed in the same bath.

Adsorption

The aqueous solutions of dyes were prepared in the desired concentrations, and 0.1 g of acrylamide–maleic acid (AAm/MA) hydrogels containing 40 mg maleic acid and irradiated to 3.73 kGy were transferred into 50 mL of aqueous solutions of dyes and allowed the equilibrate for 2 days at 25°C. These solutions were separated by decantation from the hydrogels. Spectrophotometric measurements were carried out using a Perkin-Elmer Coleman 295 VIS spectrophotometer at ambient temperature. The absorbances of these solutions were read at the wavelengths given in Table 1. Distilled water was chosen as the reference. The equilibrium concentrations of dyes solutions were determined with calibration curves obtained from solutions with known concentrations of the dyes.

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

The effects of MA content in hydrogels and of irradiation dose were investigated for adsorptions of dyes within AAm/MA hydrogels. Hydrogels (0.1 g) prepared with different MA contents and irradiation doses were put into 50 mL of dye solutions in suitable concentrations at the upper limit of observability and left for 2 days at 25°C. Spectrophotometric methods were used to follow the concentrations of these dyes solutions.

RESULTS AND DISCUSSION

Characterization of hydrogel systems used in this investigation were reported in a previous study (18).

Swelling and Diffusion

The swelling behavior of hydrogels prepared from AAm/MA containing 40 mg MA and irradiated to 3.73 kGy in water and in aqueous dye solutions of 4.0 $mg \cdot L^{-1}$ MB, 6.6 $mg \cdot L^{-1}$ MV, and 8.0 $mg \cdot L^{-1}$ NB were followed gravimetrically. The percentage swelling of each hydrogel was calculated from the following relation (6, 19, 20):

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

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 (6, 19, 20) for distilled water and the dye solutions are shown in Fig. 1.

The following equation was used to determine the nature of the diffusion of water and aqueous solutions of dyes into hydrogels (6, 19, 20):

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

In this equation, F denotes the amount of solvent fraction at time t. The constant k is related to the structure of the network, and the exponential n is a number to determine the type of diffusion. This equation is applied to the initial stages of swelling, and plots of $\ln(F)$ versus $\ln(t)$ are presented in Fig. 2. The exponents were calculated from the slope of the lines.

Diffusion coefficients are important parameters about the penetration of some chemical species into polymeric systems. Diffusion coefficient (D) gives a measure of diffusion and mass flow of penetrant to the system (bulk diffusion), but intrinsic diffusion coefficient ($\mathscr{D}$) gives only diffusion (pore diffusion). Diffusion coefficients were calculated from the following relation (21):

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

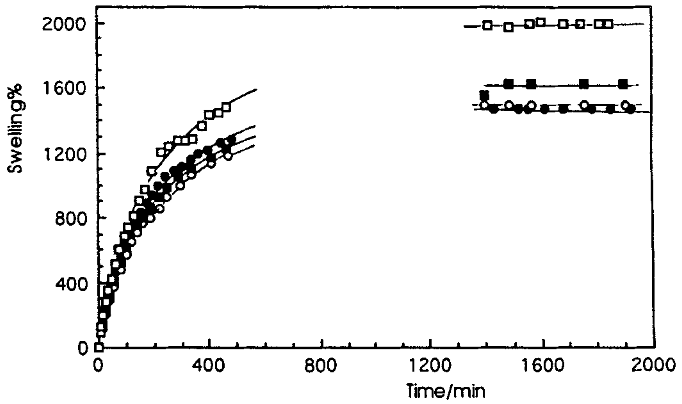


FIG. 1 The swelling curves of AAm/MA hydrogels containing 40 mg MA. Total dose given: 3.73 kGy. (●) Distilled water, (○) methyl violet, (■) methylene blue, (□) nile blue.

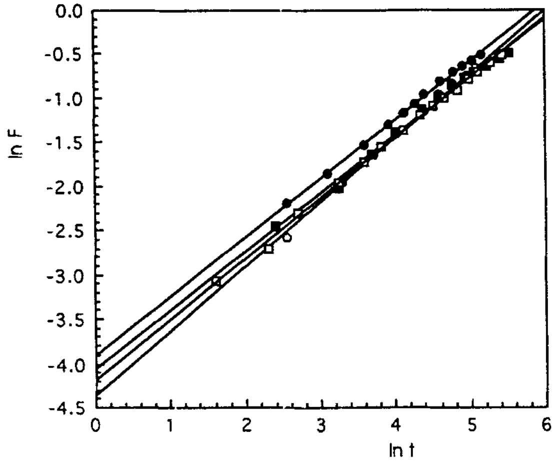


FIG. 2 Plots of ln(*F*) versus ln(*t*) of AAm/MA hydrogels containing 40 mg MA. Total dose given: 3.73 kGy. (●) Distilled water, (○) methyl violet, (■) methylene blue, (□) nile blue.

where D is in $\text{cm}^2\cdot\text{min}^{-1}$, t is the time at which 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 (21)

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

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

The percent swelling of hydrogels is high (1490–2000%) in solutions of dyes but low (1480%) in water. The dyes contain unpaired electrons in

TABLE 2
Parameters of Swelling and Diffusion of AAm/MA Hydrogels Containing 40 mg MA. Total dose given: 3.73 kGy

Solution	% *S*	$k \times 10^2$	n	$D \times 10^3$ $\text{cm}^2\cdot\text{min}^{-1}$	$\mathcal{D} \times 10^3$ $\text{cm}^2\cdot\text{min}^{-1}$
Water	1480	2.0	0.63	5.3	6.8
Methyl violet	1490	1.3	0.72	5.3	7.3
Methylene blue	1630	1.8	0.66	4.9	6.1
Nile blue	2000	1.5	0.68	5.5	8.9

the N, O, and S atoms. 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.

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 basic dyes into AAm/MA hydrogels was taken to have a *non-Fickian* character (19). This is generally explained as a consequence of the slow relaxation rate of the hydrogel matrix. As expected, the diffusion coefficients of dyes in the gels are less than the diffusion coefficients in water.

Adsorption for Removing Dye Pollutants

To observe the adsorption of some dyes, AAm and AAm/MA hydrogels were placed in aqueous solutions of basic dyes such as methylene blue, methyl violet, and nile blue and in aquatic solutions of acidic dyes such as alizarin yellow, congo red, and indigo blue and allowed to equilibrate for 2 days. At the end of this time, AAm/MA hydrogels in the solutions of methylene blue, methyl violet, and nile blue showed the dark colorations of the original solutions. AAm had not sorbed any dyes from the solutions, and AAm/MA had not sorbed the acidic dyes. Since poly(acrylamide) is a nonionic polymer (22), 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 the interaction between the cationic groups of basic dyes and the carboxyl groups of hydrogels. On the other hand, there will be anionic repulsion between the anionic groups of acidic dyes and the carboxyl group of maleic acid in the hydrogels, and therefore little interaction between the acidic dyes and AAm/MA hydrogels.

These basic dye solutions were used in the experiments of adsorption of dyes to AAm/MA hydrogels. Graphs of the mass of absorbed dyes per unit hydrogel mass (q_e, mg dye g^{-1} hydrogel) against the equilibrium concentrations of the dyes (C, mg dye·L^{-1}) are shown in Figs. 3, 4, and 5 for methyl violet, methylene blue, and nile blue, respectively. The figures show that adsorptions of the dyes within AAm/MA hydrogels correspond to Type-III isotherms (23–25).

Type-III isotherms are characterized by convexity toward the concentration axis and are characteristic of weak solute–solid interactions. The weakness of the adsorbent–adsorbate forces will cause the uptake at low concentrations to be small, but once a molecule has become adsorbed, the adsorbate–adsorbate forces will promote the adsorption of more molecules, a cooperative process in which the isotherm becomes convex to the concentration axis. Type-III isotherms may originate through the ad-

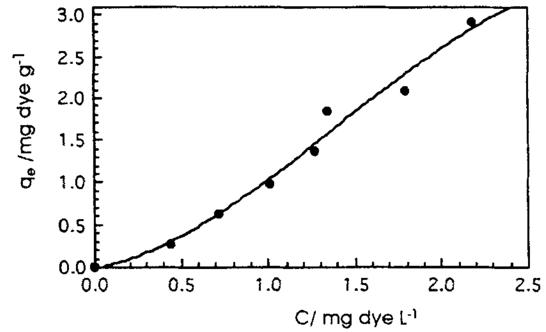


FIG. 3 Adsorption isotherm of methyl violet to AAm/MA hydrogels.

sorption of either nonpolar molecules or polar molecules, 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 in unusually small compared with the polar contribution. Not surprisingly, water has provided many examples of the Type-III isotherm.

The most straightforward case is given by large organic polymers (e.g., polytetrafloroethylene, polyethylene, polymethyl methacrylate, polyacrylonitrile) which gives a well-defined Type-III isotherm with water because of the weak dispersion interactions. In some cases the isotherms have been measured at several temperatures so that q^{st} (isosteric enthalpy of adsorption) could be calculated. The value is somewhat below the molar

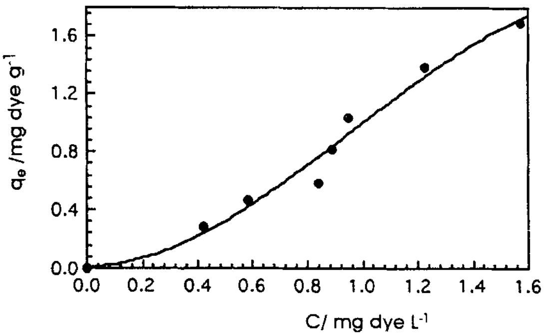


FIG. 4 Adsorption isotherm of methylene blue to AAm/MA hydrogels.

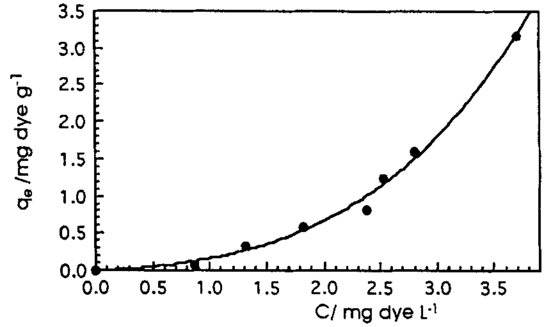


FIG. 5 Adsorption isotherm of nile blue to AAm/MA hydrogels.

enthalpy of crystallization (q_c) and rises to q_c as adsorption proceeds. Thus, ΔH_a (net heat of adsorption) is zero or less.

The strength of dispersion interaction of a solid with a solute molecule is determined not only by the chemical composition of the surface of the solid but also by the surface density of the force centers. If, therefore, this surface density can be sufficiently reduced by the preadsorption of a suitable substance, the isotherm may be converted from Type II to Type III.

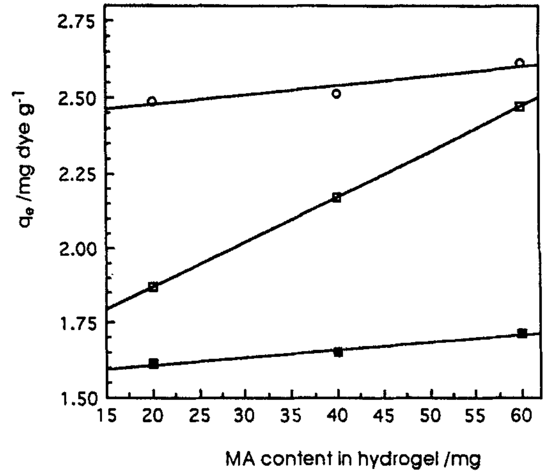


FIG. 6 The variations of adsorbed dyes to AAm/MA hydrogels with content of MA in hydrogel. (○) Methyl violet, (■) methylene blue, (□) nile blue.

Once the hydrogel is covered with a layer of adsorbed water, however, the adsorbent–adsorbate interaction would be virtually reduced to the weak dispersion energy of water with dyes, so that a Type-III isotherm should results.

In a system that give rise to a Type-III isotherm, however, the multilayer is being built up on some parts of the surface while the monolayer is still incomplete on other parts.

Dyes were removed from hydrogels by contact with distilled water for 3 days. We observed that desorptions of the dyes were shown by coloration of the water, and the return of the hydrogels to their original colors.

In later experiments on the adsorptions of dyes to AAm/MA hydrogels, the effects of different MA contents and irradiated doses were measured. The masses of adsorbed dyes per unit mass of hydrogel versus MA content in hydrogel and irradiation dose have been plotted and are shown in Figs. 6 and 7.

The amount of adsorbed dyes to AAm/MA hydrogels increased with increasing content of MA in AAm/MA hydrogels and irradiation dose. Increasing the concentration of carboxyl groups in the hydrogels with increasing MA content caused electrostatic interactions between the cationic groups of the dyes and the anionic groups of maleic acid in the hydrogels. On the other hand, crosslinking of hydrogels increased with an increase of irradiation dose and reduced the size of pores. Dye mole-

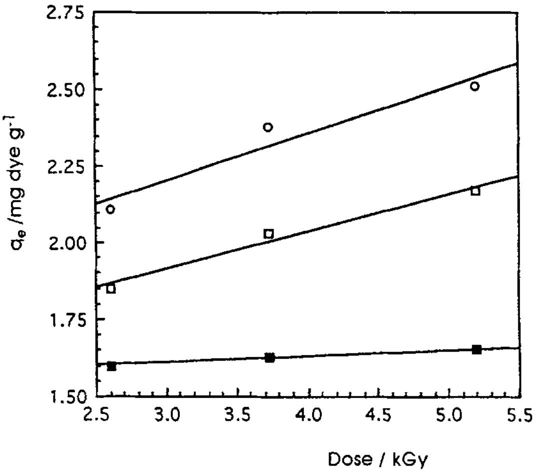


FIG. 7 The variations of adsorbed dyes to AAm/MA hydrogels with irradiation dose. (○) Methyl violet, (■) methylene blue, (□) nile blue.

cules in small pores of hydrogel interacted with hydrophilic groups, and the amount of adsorbed dye molecules increased.

CONCLUSION

This study has shown that AAm/MA hydrogels adsorb such basic dyes as methylene blue, methyl violet, and nile blue, while AAm hydrogels do not. Type-III adsorption isotherms were found and are characteristic of weak solute–solid interaction. Adsorptions of the dyes increase with the MA content in the hydrogels. AAm/MA hydrogels can be used as a sorbent for such water pollutants as basic dyes, an important problem for the textile industry.

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