

Cationic Dye Adsorption by Acrylamide/Itaconic Acid Hydrogels in Aqueous Solutions

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ABSTRACT

Acrylamide/itaconic acid (AAM/IA) hydrogels containing different quantities of itaconic acid have been irradiated with γ radiation. The hydrogels were used in an experiment concerning the adsorption of cationic dyes such as Basic Blue 9, Basic Violet 1 and Basic Blue 12. In the experiments of the adsorption of dyes from their synthetic aqueous solutions, type S adsorption isotherms were found. One mole of monomeric unit of AAM/IA hydrogels adsorbed 78.5–513.1 μmole of Basic Blue 9, 60.2–641.1 μmole of Basic Violet 1 and, 28.8–593.3 μmole of Basic Blue 12, while acrylamide hydrogel did not adsorb any cationic dye. As a result, it was shown that the AAM/IA hydrogels could be used as an adsorbent for water pollutants such as dyes, and immobilization of these organic contaminants in the hydrogels from waste water can solve one of the most important environmental problems of the textile industry. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Hydrogels are water-swallowable, three-dimensional polymeric networks. The capacity of hydrogels to absorb water is enormous and can be as much as

1000 times the mass of polymer. Hydrogels find considerable applications and have been extensively studied because they combine glassy behavior with elastic. Hydrogels have been used in the fields of medicine, pharmacy, biotechnology, agriculture, food industry, etc. Hydrogels have been most widely used in the controlled release of drugs [1, 2].

The physical and chemical properties of hydrogels will depend upon the monomers and polymers from which they are made. They may be composed of various chemical substances [3]. Some authors have reported that poly(*n*-vinyl pyrrolidone) and poly(vinyl pyridine) hydrogels have been used for adsorption of cationic dyes [4–7].

The removal of color from textile waste waters 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 agricultural purposes. Some groups have used various adsorbents for the removal of anionic and cationic dyes from aqueous solutions [8].

In our previous studies, the adsorption of some cationic dyes [9–12], uranyl ions and some heavy metal ions [13, 14], and protein such as bovine serum albumine [15, 16] has been investigated. The biocompatibility of blood has been investigated by acrylamide–itaconic acid and acrylamide–maleic acid hydrogels [17–19].

The present paper studies a convenient method for removing some cationic dyes from water by adsorption on a new polymeric adsorbent such as acrylamide/itaconic acid (AAM/IA) hydrogels. Water-soluble cationic dyes such as Basic Blue 9 (methylene blue), Basic Violet 1 (methyl violet) and Basic Blue 12 (Nile blue) resemble the large molecular dyes found in waste waters.

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TABLE 1. Some Properties of Monomers in the Preparation of Hydrogels

Name	Generic name	Chemical formula	Molar mass (g/mol)
Acrylamide	Propenamide	$H_2C=CHCONH_2$	71.08
Itaconic acid	Methylene succinic acid	$HOOCH_2C(=H_2)COOH$	130.10

EXPERIMENTAL

Acrylamide and itaconic acid monomers were obtained from BDH (Poole, UK). Basic Blue 9 (BB-9), Basic Violet 1 (BV-1) and Basic Blue 12 (BB-12) cationic dyes were obtained from Merck (Darmstadt, Germany). Some properties of monomers and dyes are listed in Tables 1 and 2, respectively.

Preparation of Hydrogels

One gram of acrylamide was dissolved in 1 ml of the aqueous solutions with 0, 20, 40 or 60 mg of itaconic acid. The chemical structures of monomers are shown in Table 1. These solutions were placed in poly(vinyl chloride) pipettes 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/hr. Hydrogels obtained in long cylindrical shapes were cut and dried first in air and then in a vacuum [19].

Adsorption of Cationic Dyes

The synthetic aqueous solutions of cationic dyes were prepared in the concentration ranges of 1–6 mg/l for BB-9, and 1–10 mg/l for BV-1 and BB-12. Some 0.1 g of AAm/IA hydrogel containing 40 mg IA and irradiated to 5.71 kGy was transferred into 50 ml of the synthetic aqueous solutions of the dyes, and allowed to equilibrate for 24 hr 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 2 [20]. Distilled water was chosen as the reference. The equilibrium concen-

trations of dye solutions were determined with calibration curves obtained with solutions with known concentrations of the dyes.

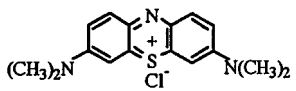
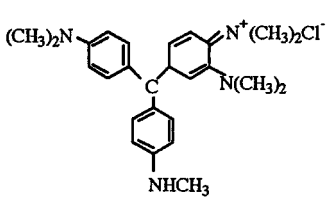
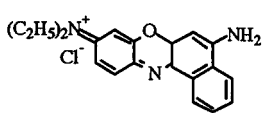
Hydrogels separated from dye solutions were left for three days in distilled water at 25°C to investigate desorption.

In order to understand the effects of content of IA in hydrogel and the effects of irradiation dose on adsorption of the dyes within AAm/IA hydrogels, some experimental studies were made. For this, hydrogels (0.1 g) prepared with different contents of IA and with different irradiation doses were put into 50 ml of dye solutions in concentrations of 4 mg/l for BB-9, 6.6 mg/l for BV-1 and 8 mg/l for BB-12, and left for two days at 25°C. Spectrophotometric methods were used to follow the concentrations of these dye solutions.

RESULTS AND DISCUSSION

For adsorption of some dyes, AAm and AAm/IA hydrogels were placed in aqueous solutions of cationic dyes such as Basic Blue 9, Basic Violet 1 and Basic Blue 12 and of anionic dyes such as Alizarin Yellow R, Congo Red and Indigo Blue, and allowed to equilibrate for two days. At the end of this time, AAm/IA hydrogels in the solutions of Basic Blue 9, Basic Violet 1 and Basic Blue 12 showed dark colorations of the original solutions. AAm hydrogels did not show any sorption from dye solutions and AAm/IA hydrogels did not show any sorption from the "anionic" dye solutions such as Alizarin Yellow R, Congo Red and Indigo Blue. Since poly(acrylamide) is a nonionic polymer [21], ionizable groups on the polymer were increased by adding itaconic acid to acrylamide monomer. So, these hydrogels have many carboxyl groups that can increase the interaction between the cationic groups of cationic dyes and

TABLE 2. Some Properties of Dyes [15]

Name	Chemical formula	Molar mass	Color Index No.	$\lambda_{max}(nm)$
Basic Blue 9 (BB-9)		319.86	52,015	655
Basic Violet 1 (BV-1)		393.96	42,535	560
Basic Blue 12 (BB 12)		354.92	51,180	600

carboxyl groups of hydrogels. On the other hand, there will be anionic repulsion between the anionic groups of anionic dyes and the carboxyl group of itaconic acid in the hydrogels, and little interaction between the anionic dyes and AAm/IA hydrogels.

The other types of interaction between gel and dyes may be hydrophobic and hydrogen bonds. Hydrophobic effects are specifically aqueous solution interactions, which in the present case will involve the aromatic rings and the methyl groups on the dye molecules and the methine groups on the gel. Hydrogen bonding will be expected to occur between the amine group's oxygen atom on the dye molecules and the amine and carbonyl groups on the monomer unit of crosslinked copolymer [22]. But, electrostatic interactions between dye molecules and the hydrogel are dominant due to hydrophobic and hydrogen bonds.

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

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

where C_B is the equilibrium concentration of the solute on the adsorbent in mol/l (bound solute concentration) and C is the equilibrium concentrations of the solute in the solution in mol/l (free solute concentration). The value of the bound concentration may be obtained 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 and P in base mol (moles of monomer units) per liter, r then represents the average number of molecules of solute bound to each monomer unit at that free solute concentration.

P values of the hydrogels were calculated by the following equation:

$$P = m / M \quad (3)$$

where m is mass of hydrogel and M is the average molar mass of repeating units of polymer.

Plots of the binding ratio (r) against the free concentrations of the cationic dyes in the aqueous solutions (C , $\mu\text{mol dye/l}$) are shown in Figs 1–3 for Basic Violet 1, Basic Blue 9 and Basic Blue 12, respectively.

Figures 1–3 show that adsorption of the dyes within AAm/IA hydrogels corresponds to type S adsorption isotherms in the Giles classification system for adsorption of a solute from its solution [23, 24].

In the S curves in the Giles classification system, the initial direction of curvature shows that adsorption become stronger as concentration rises. In practice, the S curve usually appears when three conditions are fulfilled: the solute molecule (a) is

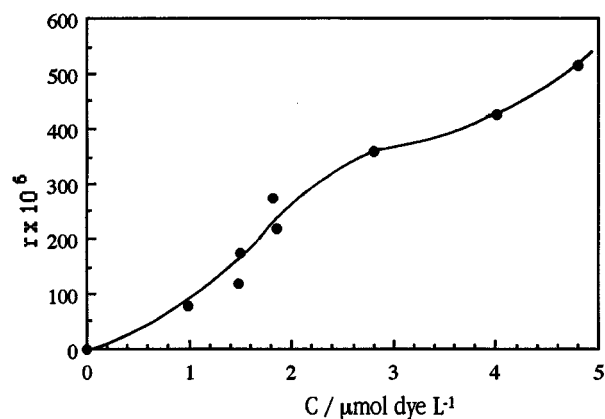


FIGURE 1. Adsorption isotherm of Basic Blue 9 onto AAm/IA hydrogels.

monofunctional, (b) has moderate intermolecular attraction, causing it to pack vertically in regular array in the adsorbed layer, and (c) meets strong competition, for substrate sites, from molecules of the solvent or of another adsorbed species [23, 24].

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 further molecules – a cooperative process – so that the isotherm will become convex to the concen-

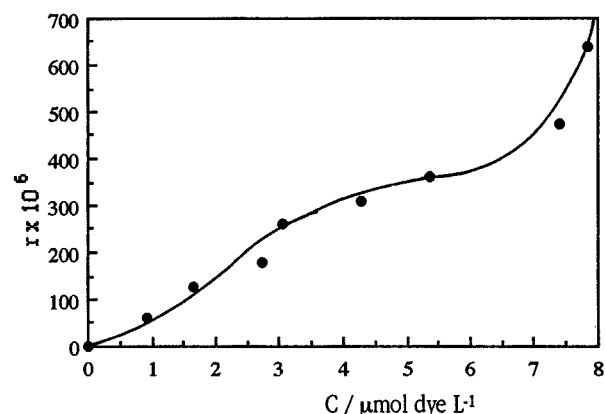


FIGURE 2. Adsorption isotherm of Basic Violet 1 onto AAm/IA hydrogels.

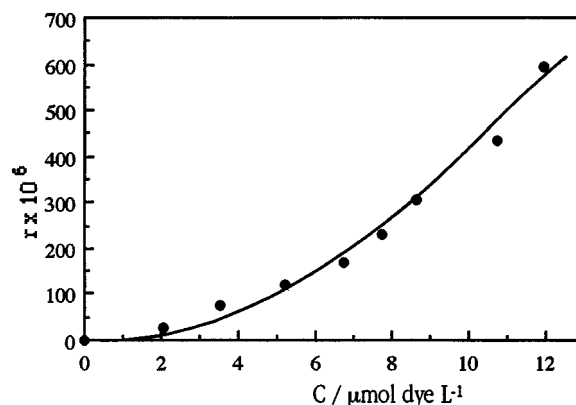


FIGURE 3. Adsorption isotherm of Basic Blue 12 onto AAm/IA hydrogels.

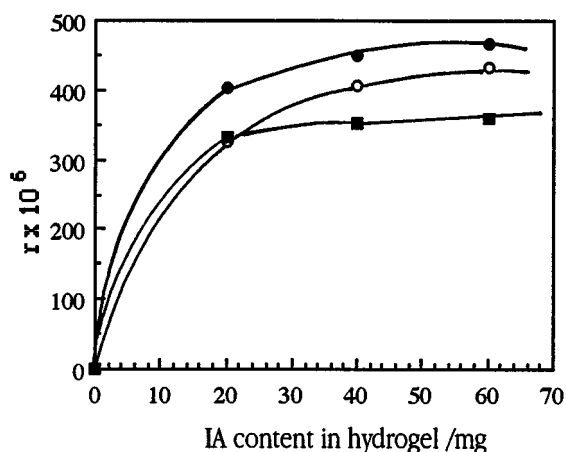


FIGURE 4. The variations of binding ratio of dye – AAm/IA hydrogel systems with content of IA in the hydrogel. Total doses given are 5.20 kGy: ● Basic Violet 1 (6.6 mg BV 1/l), ■ Basic Blue 9 (4 mg BB 9/l); ○ Basic Blue 12 (8 mg BB 12/l).

tration 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 with the polar contribution. Not surprisingly, water provided many examples of type S isotherms.

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 S isotherm should result.

In a system that gives rise to a type S isotherm, however, multiple layers are built up on some parts of the surface while a monolayer is still incomplete on other parts.

Dyes were removed from hydrogels by contact with distilled water for three days. It was observed that desorption of the dyes by the suitable coloration

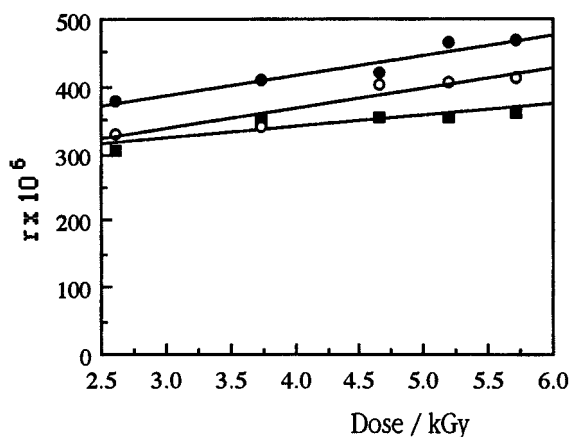


FIGURE 5. The variations of binding ratio of dye – AAm/IA hydrogel (containing 40 mg IA) systems with irradiation dose: ● Basic Violet 1 (6.6 mg BV 1/l); ■ Basic Blue 9 (4 mg BB 9/l); ○ Basic Blue 12 (8 mg BB 12/l).

in the water and hydrogels also have returned to their original colors.

In later experiments, the adsorption of dyes to AAm/IA hydrogels was measured, looking at effects of different contents of IA and irradiation doses. The binding ratio versus IA content in hydrogel and irradiation dose is plotted and shown in Figs 4 and 5.

The amount of adsorbed dyes to AAm/IA hydrogels increased with increasing content of IA in AAm/IA hydrogels and irradiation dose. Increasing carboxyl groups in the hydrogels with increasing of IA contents caused electrostatic interactions between the cationic groups of dyes and the anionic groups of itaconic acid in the hydrogels. On the other hand, the crosslinks of hydrogels increased with the increase of irradiation dose and reduced the size of pores. So, dye molecules in small pores of hydrogel interacted with hydrophilic groups and the amount of adsorbed dye molecules increased.

CONCLUSION

This study has shown that AAm/IA hydrogels adsorb cationic dyes such as Basic Blue 9, Basic Violet 1 and Basic Blue 12, while AAm hydrogels do not.

Type S adsorption isotherms were found and are characteristic of weak solute–solid interactions. The adsorption of the dyes increased with the content of IA in the hydrogels.

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

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